

Exploring Atmospheric Autoxidation of Organic Emission from Volatile Chemical Products

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ABSTRACT

The atmospheric chemistry of organic peroxy radicals (RO_2), which are formed by the gas-phase oxidation of volatile organic compounds (VOCs), governs the chemical fate of VOCs in Earth's atmosphere. Upon formation, RO_2 react through bimolecular or unimolecular pathways to produce functionalized closed-shell products with lower volatility, which can partition into condensed phase and contribute to formation of secondary organic aerosol (SOA). While the major RO_2 bimolecular reactions (e.g. $\text{RO}_2 + \text{NO}$, $\text{RO}_2 + \text{HO}_2$) are well-known, the importance of RO_2 unimolecular chemistry, such as gas-phase autoxidation, is recognized more recently. Gas-phase autoxidation chemistry, which is initiated by a RO_2 intramolecular H-shift reaction, transforms VOCs into highly oxygenated organic molecules (HOMs) that are important SOA precursors. In this thesis, I investigate the atmospheric autoxidation chemistry of several classes of VOCs used as solvents or effective ingredients in consumer and industrial products – also known as volatile chemical products (VCPs) – which represents an emerging source of urban anthropogenic VOCs. Four simple molecules were selected as proxies from various VCP classes to probe the autoxidation chemistry of these compound classes (diethyl ether from simple ethers, 2-ethoxyethanol from glycol ethers, 1,2-diethoxyethane from diethers, and ethyl propionate from esters). Gas-phase oxidation experiments, together with computational analyses, were conducted to examine the H-shift reactions of RO_2 derived from those systems and evaluate how specific functional groups influence RO_2 H-shift rate coefficients. While H-shift processes in ether, glycol ether, and diether-derived RO_2 are accelerated and can compete with their bimolecular reactions with NO_x species under modern urban atmospheric conditions, ester functionalities are found to suppress autoxidation chemistry and formation of HOMs. Overall, this work provides mechanistic insights into the ways in which functional groups modulate RO_2 autoxidation pathways and production of HOMs, thereby improving understanding of how VCP emissions may contribute to urban SOA formation.

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NOMENCLATURE

- °C.** Degrees centigrade.
- HO₂.** Hydroperoxyl radical.
- HO_x.** Hydrogen oxide radicals, including OH and HO₂ radicals.
- K.** Kelvin.
- min.** Minute.
- NO.** Nitric oxide.
- NO₂.** Nitric dioxide.
- NO₃.** Nitrate radical.
- NO_x.** Nitrogen oxides, including NO and NO₂.
- O₃.** Ozone.
- OH.** Hydroxyl radical.
- ppb.** Parts per billion.
- ppm.** Parts per million.
- ppt.** Parts per trillion.
- s.** Second.

Chapter 1

INTRODUCTION

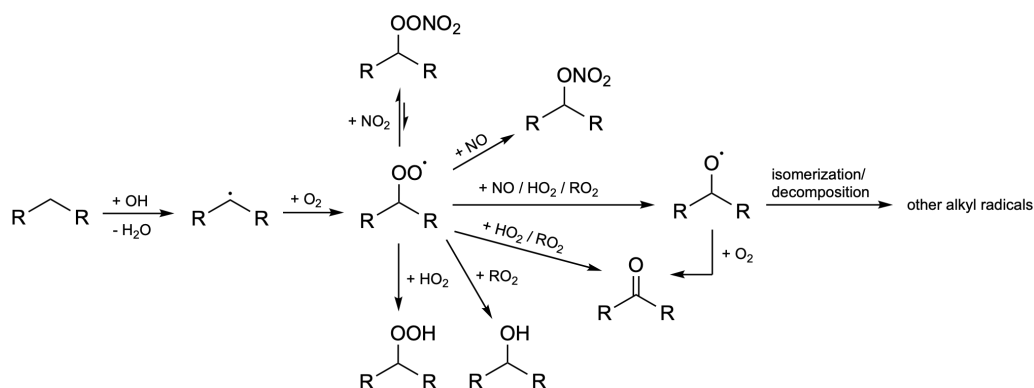
1.1 Background and Motivation

The emission of volatile organic compounds (VOCs) from both natural and anthropogenic sources constantly drives changes in the chemistry of Earth's atmosphere. Those emissions have further impact on air quality, human health, and global climate, both by themselves and through their photochemical transformations. Once emitted into the atmosphere, the VOCs undergo gas-phase oxidation, as their primary chemical transformation pathway in the atmosphere. Gas-phase oxidation of VOCs is usually initiated by reactions with strong oxidants such as OH, NO₃, and O₃. These reactions typically produce alkyl radicals (R·) as the first intermediates. Subsequent rapid addition of molecular oxygen (O₂) to the nascent alkyl radical leads to formation of organic peroxy radicals (RO₂).^{1,2} The chemistry of RO₂ plays a central role in the evolution of VOCs in the atmosphere, as well as the cycling of reactive radicals, and formation of tropospheric ozone and other secondary reaction products.³ Under tropospheric conditions, a given RO₂ may have several competing reaction pathways available, and the fate of the RO₂ will be dependent on the chemical state of the atmosphere and the structure of RO₂.^{3,4} Some RO₂ reactions can lead to the formation of oxidized VOC (OVOC). If reaching low enough vapor pressures, these more oxidized secondary products can condense onto airborne particulate matter or initiate new particle formation, contributing to formation of secondary organic aerosol (SOA) in the atmosphere.²

Organic aerosols (OA) account for a significant fraction of the total sub-micrometer aerosol mass in the atmosphere. SOA, which is the OA formed in the atmosphere by chemical transformation of VOC, is responsible for a dominant fraction of total organic particulate mass.⁵ A detailed understanding of the properties of SOA is therefore essential for fully addressing the health, climate, and visibility effects of atmospheric particulate matter. However, major uncertainties in the sources, composition, and formation pathways of SOA continue to hinder the accurate representation of SOA loading and behavior in climate models.^{2,6}

Addressing the mechanism of gas-phase oxidation of VOC, which is the primary process that drives down the volatilities of organic species in the atmosphere, is

one crucial step in resolving the existing uncertainties in SOA production.^{3,6} Therefore, a rigorous representation of RO₂ chemistry becomes essential. Among the myriads of bimolecular and unimolecular reactions a RO₂ can undergo, it is traditionally believed that bimolecular reactions between RO₂ and NO, HO₂, or other RO₂ dominate the loss of RO₂.² Most of the radical termination channels of RO₂ bimolecular reactions end up adding polar functional groups to the carbon backbone of the VOC. The addition of oxygen-containing functional groups, such as hydroxyl (-OH), hydroperoxyl (-OOH), nitrate (-ONO₂), can lower the vapor pressure of organic species by over two to three orders of magnitude.^{2,7} Thus, the bimolecular reaction pathways of RO₂ have been the focus of research regarding their ability to generate low-volatility organics through single to multiple generations of chemistry.

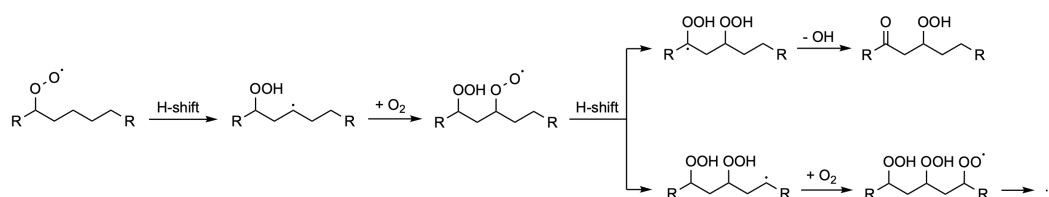


Scheme 1.1: Simplified mechanism for the atmospheric oxidation of an example VOC and subsequent bimolecular reactions of derived RO₂.

However, recent studies raise the question that whether bimolecular reactions alone are able to account for the SOA growth observed in the atmosphere.⁸ There has been long-standing discrepancy between model prediction and field observation regarding both the amount and the level of oxidation of SOA observed in the atmosphere.^{2,6,9} It has been observed that the oxygen-to-carbon ratio (O/C) of the condensed-phase organic matter increases quickly in the atmosphere.⁹ The rapid oxygenation is difficult to attribute solely to consecutive oxidation reactions by OH radical.⁸ Model and laboratory studies also struggles to account for the low volatility of organic matter observed. While SOA was traditionally thought to be produced predominately by semivolatile organic compounds, emerging studies indicates that SOA volatility should be much lower than previously assumed.^{9,10} These discrepancies suggest the potential existence of a reaction mechanism that is capable of rapidly producing organic compounds with high O/C ratio and low

volatility.

The gas-phase autooxidation chemistry has been recognized to be such a pathway that produces highly oxygenated organic molecules (HOMs) with low volatility and high O/C ratio.^{8,11,12} HOMs were first detected from laboratory studies of ozonolysis of biogenic VOC monoterpenes (C₁₀H₁₆),^{11,13} and its formation pathway was later elucidated. Autooxidation is defined as the process in which the RO₂ first undergoes an intramolecular hydrogen shift (H-shift), producing a hydroperoxyalkyl radical (often denoted as QOOH in combustion chemistry), to which O₂ then rapidly attaches, forming a new, now more oxidized, RO₂. The successive isomerization and O₂ addition processes can result in rapid addition of oxygen to VOCs and, thereby, formation of molecules with high O/C ratio and, often, multiple hydroperoxide groups.^{12,14} Those HOMs are shown to have low volatility and readily undergo gas-particle transfer, contributing to secondary organic aerosol (SOA) particle formation and/or growth.^{8,11} The high organic peroxide contents in HOMs also indicate their potential human health impact, as they can decompose to reactive oxygen species (ROS) upon respiratory deposition and cause redox imbalance inside the human body.¹⁵



Scheme 1.2: Key steps in atmospheric autooxidation of an example RO₂.

The autooxidation process was known to take place in the condensed phase as well as at elevated temperatures such as in combustion chemistry and biological systems,^{16,17} and only recently has the reaction been recognized at atmospheric-relevant conditions.^{12,14} The autooxidation pathways become competitive with bimolecular chemistry as the bimolecular lifetime of RO₂ increases, such as in environments with large emissions of VOCs and modest or low NO levels (0.05–1 ppb), where RO₂ can survive for 10–100 s before reacting with NO, HO₂, or other RO₂.¹⁴ Thus, it is unsurprising that autooxidation was first observed and verified in experimental settings as a significant pathway for biogenic VOCs (isoprene, monoterpenes, etc.),^{18–21} which are the dominant emissions in environments of low radical abundances, such as in shaded regions below tree canopies and regions remote from anthropogenic NO_x

emissions. However, as a result of the recent successful reduction of NO_x emission in urban areas (with some urban NO_x levels falling below 500 to 100 ppt),²² autoxidation chemistry is expected to be increasingly favored in the photochemistry of a modern urban atmosphere.¹⁴ Given that autoxidation pathways can generate large amounts of low-volatility vapors that contribute to aerosol formation, it becomes imperative to characterize this low- NO_x chemistry for the array of different VOCs typically found in an urban atmosphere.

Along with the growing interests in autoxidation and HOMs in the atmospheric science community, researchers have extended their investigation to a broader range of VOC precursors, including anthropogenic VOCs (AVOCs) such as aromatics and alkanes.^{23–25} However, similar studies on an emerging class of AVOC – volatile chemical products (VCPs) – have been sparse. VCPs can be found in a range of consumer and industrial products, including personal care products, cleaning agents, coatings, adhesives, pesticides, and printing inks.²⁶ These products contain organic solvents or effective ingredients that are volatile, such as alcohols, glycol ethers, and esters, and upon application, can lead to substantial emissions of VOCs to the atmosphere over an extended period.^{27,28} With VOC emission from combustion sources declining, thanks to successful air pollution control strategies, volatile chemical products (VCPs) have emerged as a new major source of VOC in industrialized cities. VCPs are now considered to account for half or more of volatile organic emissions in some urban atmospheres.^{26,29} They have also been studied for their SOA forming potential under various conditions, demonstrating that VCPs may account for much of the unexplained SOA mass in modern urban environments.^{30–32} Since H-shift chemistry of RO_2 has been shown to be an important process for many organic substrates, it is likely that many VCP compounds also produce HOMs via autoxidation.

One important feature of VCP compounds is that many of them are functionalized, substituted with oxygen-containing functional groups such as hydroxy ($-\text{OH}$), ether ($-\text{OCH}_2-$), carbonyl ($\text{C}=\text{O}$), ester ($-\text{C}(\text{O})\text{O}-$), etc. Descriptions of the chemistry of functionalized organic species have been mainly based on the oxidation mechanism of their hydrocarbon counterparts, and the effects of functional groups are often assumed to limit to changes in kinetics, energetics, and branching ratios associated with known pathways, such as VOC reaction with OH and RO_2 bimolecular reactions.^{33,34} Those effects are often predicted using structure-activity relationships (SARs).^{35–37} However, studies have shown that there can be major dif-

ferences between the chemistry of functionalized VOC and that of unfunctionalized (alkyl-substituted) ones. Presence of certain functional groups in RO₂ can enable their bimolecular and/or unimolecular pathways to proceed much more rapidly than expected or yield unexpected products.^{38,39}

Here, the effect of functional groups on RO₂ H-shift process is discussed as an example. One reason for the impact of autoxidation process to be underestimated in atmospheric conditions is that the H-shift of unfunctionalized RO₂ derived from straight-chain alkanes is too slow to compete with the standard bimolecular reaction pathways of RO₂.¹² However, functional groups at the carbon, from which the hydrogen is subtracted, can greatly accelerate RO₂ H-shift reactions by activating the neighboring C-H bond, stabilizing the reaction transition state (TS), and lowering the energy barrier to H atom transfer.^{12,40,41} While the unsubstituted H-shift typically have rate coefficients below 10⁻³ s⁻¹, substituents such as -OH, -OOH, -OCH₂- groups can enhance the rate to reach 0.05 – 0.1 s⁻¹.^{14,40} H-shift reactions that involve abstracting an aldehydic (C=O) or allylic (-C-C=C) hydrogen can be even more favorable, with rate coefficients potentially reaching ~1 s⁻¹, due to stabilization of the H-shift TSs by resonance.⁴⁰⁻⁴² In an atmosphere with NO levels falling below 1 ppb, a condition now common in urban regions in North America and Europe,^{43,44} where RO₂ can survive for 10–100 s before reacting with other bimolecular reactants (e.g. NO_x species), these H-shift processes can not only compete with, but even dominate over standard RO₂ bimolecular pathways.¹⁴ Therefore, the functionalized VOCs, such as the VCP compounds, likely have a higher potential of producing HOMs than hydrocarbon emissions, which further emphasizes the importance of unraveling their atmospheric autoxidation mechanisms.

This thesis is motivated by the existing knowledge gap in gas-phase oxidation, especially the autoxidation mechanism, of VCP-derived VOCs. Given that VCPs encompass a broad range of chemical classes, this thesis will focus on three specific classes of compounds: glycol ethers, ethers, and esters. These compound classes are commonly used in various products across residential, commercial, and industrial settings.⁴⁵⁻⁴⁸ Studies have shown that many semi- or intermediate compounds from these classes are sufficiently volatile to evaporate and participate in atmospheric photochemical processes.^{30,45} For each of the three classes, one to two simple compounds are selected as proxies for their longer-chain family members, and their autoxidation pathways are investigated.

1.2 Thesis Overview

The work included in this thesis details my investigations of atmospheric autoxidation pathways of various classes of functionalized VOCs commonly used as VCPs. Specifically, I unraveled their autoxidation mechanism by estimating the rate coefficients of major H-shift reactions of RO_2 derived from OH-initiated oxidation of those VOCs. To study the H-shift rate coefficients of RO_2 in those systems, I performed chamber experiments at varied HO_2 concentrations to modulate the competition between bimolecular and autoxidation chemistry. The reaction products were measured by a high-resolution time-of-flight chemical ionization mass spectrometer combined with low-pressure gas chromatography (GC-CIMS),⁴⁹ which provides us isomer-resolved detection of multifunctional organic species. The experimental data were analyzed to evaluate the yields of autoxidation products at varied HO_2 levels, and the autoxidation pathways of various RO_2 are characterized with help from computational investigations,⁵⁰ performed by our Danish colleague Henrik Kjaergaard and his students from University of Copenhagen, and box model simulations.

Chapter 2 examines the autoxidation chemistry of simple short-chain aliphatic ether, with diethyl ether investigated as the model system. Chapter 3 investigates the chemistry of short-chain glycol ether, where 2-ethoxyethanol is studied as the model compound for this class. Chapter 4 focuses on a long-chain ether with two ether linkages: 1,2-diethoxyethane. Chapter 5 studies ethyl propionate as the model compound for the family of saturated alkyl esters. It should be noted that Chapters 2 to 4 were originally written as standalone manuscripts, which were published in or submitted to scientific journals prior to the completion of this thesis. Supplemental information pertaining to the main thesis chapters can be found in Appendices A, B, C, and D respectively.

*Chapter 2*AUTOXIDATION OF SHORT-CHAIN ETHERS: DIETHYL
ETHER

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- (1) Yu, H.; Chen, J.; Crounse, J. D.; Almeida, T. G.; Kjaergaard, H. G.; Wennberg, P. O. Atmospheric Autoxidation Chemistry of Diethyl Ether. *ACS ES&T Air* **2025**, 2, 2566–2576, DOI: 10.1021/ACSESTAIR.5C00204,

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Abstract

We report estimates of the rate coefficients for atmospheric autoxidation chemistry of diethyl ether (DE), a simple aliphatic ether as a representative for the ether family, an important class of volatile chemical products (VCPs). We perform chamber experiments to estimate the rate coefficients of the H-shift reactions of peroxy radicals (RO₂) formed by hydroxyl radical (OH) oxidation of DE relative to the rate coefficients of their reaction with HO₂. We also estimate these rate coefficients for the fully deuterated version, diethyl ether-*d*₁₀ (DE-*d*₁₀). Computational methods based on multi-conformer transition state theory are used to guide our interpretation of these rate coefficients. At ambient temperature (294 ± 1 K), H-shift rate coefficients of DE RO₂ are estimated to be ~0.09 ± 0.06 s⁻¹, while those of DE-*d*₁₀ RO₂ are ~8 to 15 times smaller due primarily to reduction in quantum tunneling. Our estimates agree well with theoretical predictions. The RO₂ autoxidation rate coefficients are sufficiently fast to be competitive with their bimolecular reactions when NO levels are less than ~1 ppb - common urban atmospheric conditions following the controls of NO_x emissions, indicating efficient formation of highly oxygenated organic molecules (HOMs), which can be important secondary organic aerosol (SOA) contributors, from volatile ether compounds.

2.1 Introduction

Aliphatic ethers are an important class of volatile organic compound (VOC) that are widely used as solvents for fats, oils, waxes, resins, dyes, gums, hydrocarbons, etc. They are also good solvents for extractions applied in a wide variety of chemical reactions.^{1,2} Moreover, due to their good ignition properties, low emissions and low soot formation, some ethers are used as fuel additives or even as an alternative to diesel fuel.^{3,4} The use of substantial quantities of these volatile organics as fuel additives and solvents for industrial synthesis and in volatile chemical products (VCPs) will lead to significant emission of these compounds into the atmosphere.^{5,6} The subsequent atmospheric chemistry of these molecules will determine their impact on atmospheric pollutants such as ozone and aerosol formation.

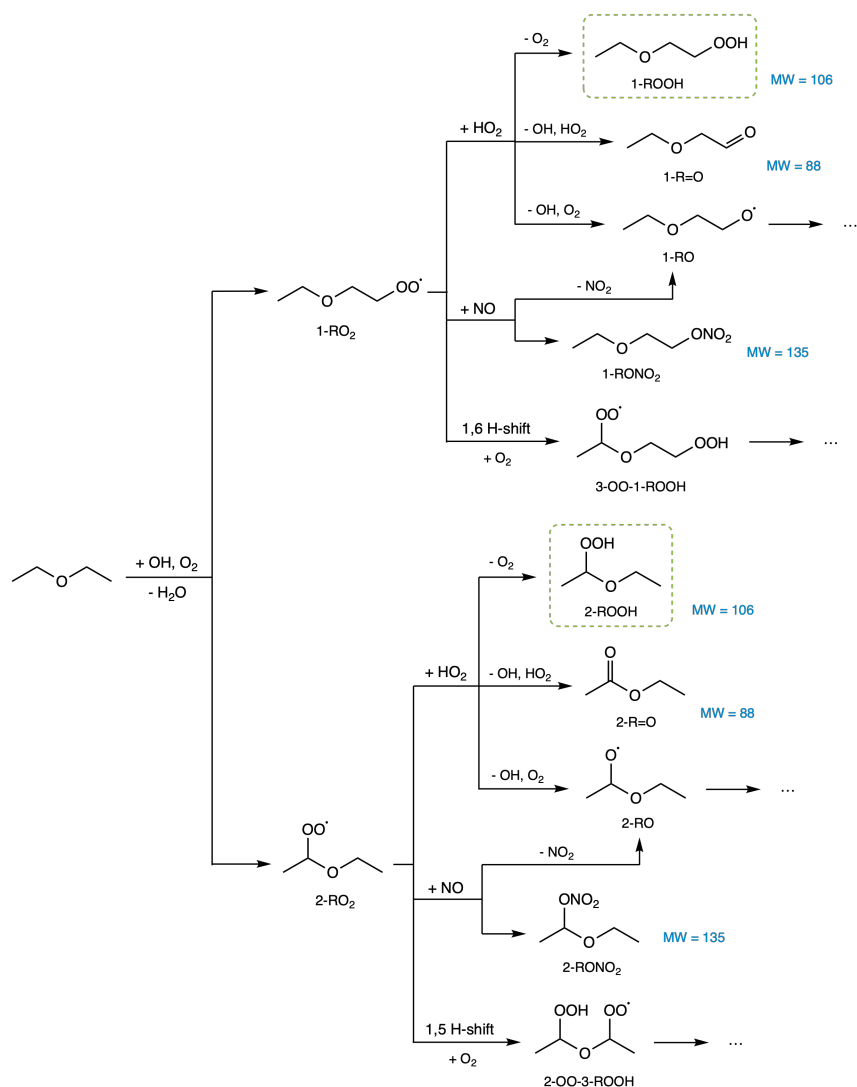
The atmospheric oxidation of saturated aliphatic ethers is generally initiated by hydrogen abstraction by OH radicals, yielding an alkyl radical.^{7,8} The abstraction of hydrogen atoms from carbons adjacent to the ether oxygen is relatively fast - with rate coefficients typically $\sim 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 300 K, which gives the ether compounds an atmospheric lifetime on the order of a few hours to one day.^{9,10} The rapid addition of oxygen (O₂) to the alkyl radical yields organic peroxy radicals (RO₂, first steps in Scheme 2.1).^{11,12} The fate of these RO₂ depends on the ambient condition and their chemical structure.^{13,14} Generally, bimolecular reactions between RO₂ and other radicals, such as NO, HO₂, and RO₂, are believed to dominate the chemical fate of RO₂.¹²

Recent instrumental developments have greatly improved the detection and quantification of oxidation products, both in the field and laboratory, including those that do not form from bimolecular reactions. These tools have demonstrated that oxidation pathways other than bimolecular chemistry can also play a significant role in the evolution of VOCs in the atmosphere.¹⁵⁻¹⁷ Gas-phase autoxidation is such an uncanonical pathway that is known to be important under atmospheric-relevant conditions.^{15,18,19} The key process in autoxidation involves an intramolecular hydrogen shift (H-shift) to the RO₂, producing a hydroperoxide group (-OOH) and an alkyl radical center, to which O₂ then rapidly attaches to form a new, more oxidized RO₂: a hydroperoxy RO₂.^{18,20} Successive isomerization and O₂ addition processes can lead to rapid formation of highly oxygenated organic molecules (HOMs) with high O/C ratio and low volatility, which makes HOMs important contributors to the growth of secondary organic aerosol (SOA).^{15,19,20} Studies have suggested that HOM production from autoxidation may resolve some of the long-standing observation-model

discrepancy in atmospheric SOA budget.^{15,21}

Oxygenated functional groups attached to the carbon from which the hydrogen atom is abstracted, such as -OH, -OCH₂-, C=O etc., can greatly accelerate RO₂ H-shift reactions by reducing the C-H bond strength and thereby lowering the barrier to hydrogen atom transfer.^{18,22} Our recent study on 2-ethoxyethanol (2-EE), for example, demonstrated that the RO₂ H-shifts from carbon atoms alpha to an ether or a hydroxy group can proceed at $\sim 0.05\text{--}0.2\text{ s}^{-1}$ and be competitive with their bimolecular reactions.²³ Autoxidation chemistry of RO₂ from other functionalized substrates, arising from both biogenic and anthropogenic sources, has also been shown to be favorable,^{24–28} especially under conditions where NO and HO₂ levels are sufficiently low that the RO₂ have a long bimolecular lifetime. Such conditions often occur in remote and forested regions,²⁹ as well as in modern urban atmosphere that are becoming less polluted.^{30–32} NO, a major anthropogenic pollutant and key atmospheric reactant, reacts with RO₂ at rate coefficients typically $(8\text{--}10) \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ under ambient temperature.¹⁴ As NO levels consistently fall below 1 ppb in those areas,^{33,34} RO₂ H-shift reactions occurring at rates of $\sim 0.1\text{ s}^{-1}$ can rival their reactions with NO (at an effective rate $<0.2\text{ s}^{-1}$), making HOM formation through RO₂ autoxidation an important contributor to the total organic constituents in the atmosphere.

Here we study the autoxidation chemistry of aliphatic ethers, using diethyl ether (DE, CH₃CH₂OCH₂CH₃) as a representative example. The compound is among the most used simple aliphatic ethers, and its basic photo-oxidation mechanism has been widely studied, including its traditional bimolecular chemistry and high-temperature autoxidation.^{4,7,8,10,35,36} In a study by Orlando,⁸ autoxidation chemistry was suggested as an explanation for certain observations of experiments conducted in absence of NO. However, DE's autoxidation pathways at ambient temperature have not been investigated extensively, with few existing studies providing only computational results.^{1,4,37–39} We perform a series of gas-phase oxidation experiments of DE and fully deuterated DE (DE-d10, CD₃CD₂OCD₂CD₃) by hydroxyl radicals (OH) at varied HO₂ levels to estimate the efficiency of autoxidation pathways of DE RO₂ relative to their bimolecular reaction with HO₂. DE-d10 is included in our analysis to study the kinetic isotope effect in RO₂ H-shift process.^{40,41} Using theoretical calculations and box model simulations, we analyze the experimental results to obtain estimates of the rate coefficients of autoxidation reactions in both DE and DE-d10 system.



Scheme 2.1: Oxidation of DE by OH radical. Subsequent reactions of the peroxy radicals and respective reaction products are also shown, including RO₂ + HO₂/NO bimolecular reactions and unimolecular H-shift reactions. Further pathways from H-shift reactions are shown in Scheme 2.2. The molecular masses of major closed-shell products are denoted in blue. Products that are detected by our instrument are shown in green boxes. Mechanism of DE-d10 oxidation by OH radical is similar and is shown in Scheme A.1. Products from RO₂ + NO pathways are not the focus of this study and are briefly discussed in Section A.8.1.

2.2 Methods

2.2.1 Experimental Method

Experiments are conducted in a ~0.7 m³ FEP Teflon (DuPont) environmental chamber at laboratory temperature of 294 ± 1 K and pressure at ~993 hPa. The chamber is housed within an enclosure covered by UV reflective metal inside and can be equipped with either 350 nm (Sylvania 350 Blacklight) or 254nm (Sankyo Denki

G40T10) UV lamps. DE (>99%, Sigma Aldrich) and/or DE-d10 (D 99%, Cambridge Isotope Laboratories, Inc.) are introduced into the chamber during the experiments. Since the OH reactivity of DE-d10 is significantly lower than that of DE due to kinetic isotope effect,^{42,43} in experiments where both VOCs are introduced into the chamber, the initial concentrations of DE-d10 are increased by a factor of three to four times that of DE, so that similar amount of both VOCs are consumed (see Table A.1 for the detailed list of experimental conditions). Oxidation of both VOCs are initiated by reaction with OH radicals (Scheme 2.1 and A.1), which are produced by photolysis of H₂O₂ (30% by mass, Macron Fine Chemicals) through reaction:



The primary bimolecular reactant in the experiments is the HO₂ radical, which is mainly produced by the reaction between CH₃OH (>99%, Sigma Aldrich) and OH radical:



We conduct experiments at different HO₂ levels to modulate the competition between bimolecular and autoxidation chemistry in the system, which allows us to constrain the rate coefficients of unimolecular H-shift reactions. We use a similar method as in Yu et al.²³ to constrain the HO₂ concentrations in the experiments and a detailed description is given in Section A.9.1. Briefly, the production of HO₂ through reaction R2 is modified by varying the OH production rate (reaction R1) by changing the number and the type of UV lamps in the chamber enclosure. 254 nm UV lights, which photolyze H₂O₂ at a much higher rate than 350 nm lamps, are used for faster chemistry where RO₂ + HO₂ reactions are more favored, while 350 nm UV lights are used to achieve slower chemistry where more autoxidation products are produced. The oxidation rate of CH₃OH is kept much higher than that of DE and DE-d10 to suppress RO₂ + RO₂ chemistry, which results in [HO₂] approximately 25 times higher than total [RO₂] throughout our experiments. The concentrations of HO₂, as well as other radical species, in each experiment can be estimated using the box model described below. The estimated [HO₂] ranges from $\sim 1.5 \times 10^9$ molecules/cm³ (~ 0.06 ppb) with one 350 nm UV light, to $\sim 5.6 \times 10^{10}$ molecules/cm³ (~ 2.3 ppb) with eight 254 nm UV lights. The uncertainty in estimated [HO₂] is

discussed in detail in Section A.9.1, which is an important source of uncertainty in our estimations of various reaction parameters in the following sections. The HO_2 level in our experiments correspond to RO_2 bimolecular lifetimes ($\tau_{\text{RO}_2+\text{HO}_2}$) ranging from around 1 to 40 seconds, which is calculated as:

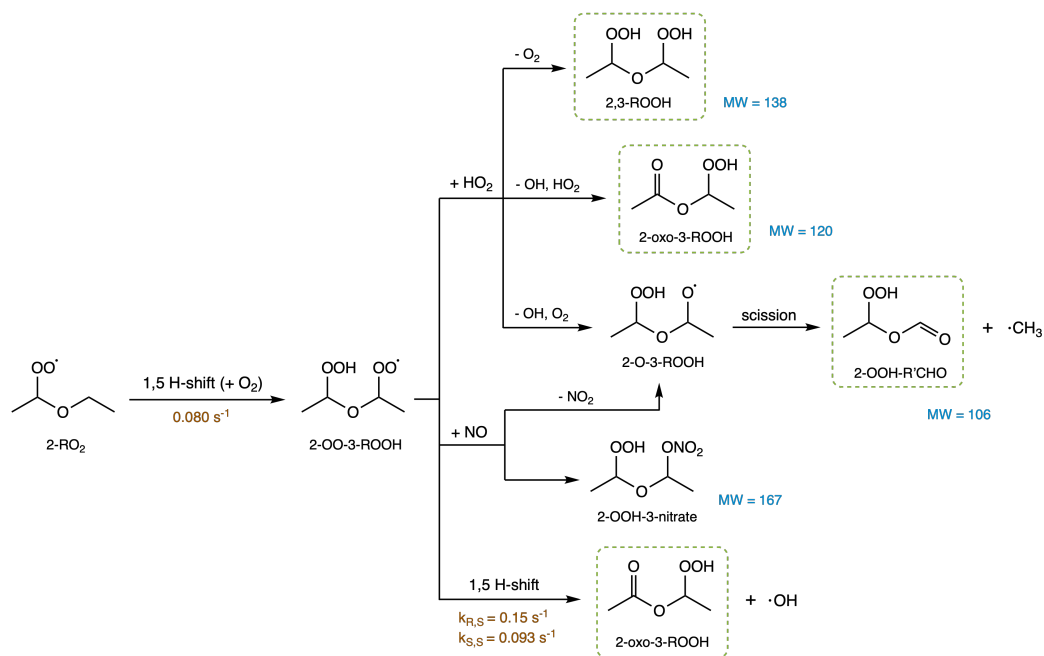
$$\tau_{\text{RO}_2+\text{HO}_2} = \frac{1}{k_{\text{RO}_2+\text{HO}_2} [\text{HO}_2]} \quad (2.1)$$

VOCs (CH_3OH , DE, and DE-d10) are transferred into the chamber through gas-tight 500 cm^3 glass bulbs. The desired mixing ratios were prepared via serial dilution using a vacuum/ N_2 system, with pressure in the bulbs measured by pressure sensors (MKS 1000 and 10 Torr Baratron pressure transducers). H_2O_2 is added by directly evaporating a known amount of the solution into the chamber. Photochemistry is initiated upon illumination of the UV lights. The total oxidation time for each experiment is varied depending on the rate of photochemistry in the chamber to achieve a similar amount of DE oxidation (see Table A.1).

The reaction products are measured by a high-resolution time-of-flight chemical ionization mass spectrometer coupled with low-pressure gas chromatography (GC-CIMS). A summary of the instrumentation is provided here, with more details available in previous publications.^{44,45} The instrument uses CF_3O^- as a reagent ion, which is sensitive to multifunctional oxygenated products, such as hydroperoxides and nitrates.^{44,45} The mass spectrometer (HRTof-CIMS) can either sample directly from the chamber (direct sampling mode) or sample the effluent of the GC (GC mode). In the GC mode, the oxidation products are pulled from the chamber, and then cryotrapped and preconcentrated at the head of a 2m GC column (Restek RTX-1701). After a trapping period, the analytes are separated and elute as the column temperature increases at a ramp rate controlled by an automated temperature program (GC temperature profile used is shown in Table A.2). The analytes, either directly pulled from the chamber or from the effluent of GC, are transferred into the CIMS through a fluorocopolymer-coated glass flow tube, where the sample flow is diluted with N_2 and mixes with the reagent ion flow from the ion source. CF_3O^- ions react with the analytes through ion-molecule clustering and/or fluoride transfer reactions to form product ions observed at $m/z = \text{mass neutral} + 85\text{ amu}$ and $m/z = \text{mass neutral} + 19\text{ amu}$, respectively.⁴⁵ Hydroperoxides can produce a small fraction of characteristic fragmentation ions (1-10%), such as $m/z\ 63\ (\text{FCO}_2^-)$, which facilitates our identification of those compounds.

Due to lack of synthetic standards for most oxidation products in this study, we estimate the CIMS sensitivity of the target compounds using their reagent ion-molecule collision rates. For analytes forming well-bound ion clusters, their sensitivity is proportional to their ion-molecule collision rate with CF_3O^- .⁴⁵ The ion-molecule collision rate is calculated following the methods outlined by Su and Chesnavich,⁴⁶ using calculated dipole moment and polarizability of the molecule.⁴⁷ The resulting estimates of the sensitivities of the compounds, along with further details of the CIMS calibration processes, can be found in Section A.3. The uncertainties in the calculated instrument sensitivities of the oxidation products will be another source of uncertainty in our following analysis of various reaction parameters in the system, which is discussed in detail in Section A.9.2.

2.2.2 Computational Method



Scheme 2.2: Autoxidation Mechanism of 2-RO₂ from DE. The H-shift rate coefficients are calculated by MC-TST at 294 K. Subsequent bimolecular reaction of 2-OO-3-ROOH + HO₂/NO and the products are also shown. The molecular masses of major oxidation products are denoted in blue. Products that are detected by our instrument are shown in green boxes. The autoxidation mechanism of the deuterated 2-RO₂-d₉ is shown in Scheme A.2. Products from 2-OO-3-ROOH+NO reaction are not the focus of this study and are briefly discussed in Section A.8.1.

The rate coefficients of the H/D-shift reactions of key RO₂'s in the system is calculated using multi-conformer transition state theory (MC-TST) outlined by Møller et al.⁴⁸ Quantum chemical methods are first used to calculate the potential energy

surface (PES) of the investigated reaction pathways. Conformational isomers of reactants and transition states (TSs) were sampled with the Merck Molecular Force Field (MMFF94)⁴⁹ method implemented in Spartan '24 software (Wavefunction, Inc.), with the keywords “searchmethod=systematic” and “keepall” to ensure that all conformations found by the program are retained. Each dihedral angle is rotated 3 times (120 degree) for the initial sampling. The conformer sampling for the hydrogenated compounds is also used for the deuterated compounds by simply switching D for H at the B3LYP level. For radical species, the keyword “ffhint=X~~+0”, where X is the label of the atom bearing the formal radical center, is added to let the force field assign a neutral charge to that atom. All conformations then have their geometry optimized at the B3LYP/6-31+G(d) level of theory^{50–54} using Gaussian 16.⁵⁵ Duplicates are identified and removed based on an electronic energy and electric dipole moment similarity threshold ($\Delta E < 10^{-5}$ Hartree and $\Delta\mu < 0.015$ Debye, respectively).⁴⁸ Unique conformers whose zero-point corrected energies are less than 2 kcal/mol relative to the global minimum undergo a further optimization at the ω B97X-D/aug-cc-pVTZ level.^{56–58} The number of unique conformations for RO₂ reactants and H-shift TSs under the cutoff value (2 kcal/mol) ranged from 1 to 16. Frequency calculations are carried out to obtain vibrational frequencies and rotational constants. Calculated vibrational modes are inspected to ensure that the geometry of each reactant conformer corresponds to a potential energy surface (PES) minimum, and each TS conformer corresponds to a PES first-order saddle-point indicated by one imaginary frequency. Intrinsic reaction coordinate (IRC) are calculated at the B3LYP/6-31+G(d) level for all conformers, and further optimized at ω B97X-D/augcc-pVTZ level for the lowest energy conformer of each TS. Finally, single-point restricted open-shell ROCCSD(T)-F12a/cc-pVDZ-F12 calculations^{59,60} are performed by Molpro 2020.2^{61,62} to provide more accurate electronic energies for lowest-energy conformers. As recommended,⁶⁰ a value of 0.9 is assigned to the geminal Slater exponent β .

Thermal rate coefficients $k(T)$ are calculated with Equation 2.2,

$$k = \kappa \frac{k_B T}{h} \frac{\sum_i^{TS} \exp\left(\frac{-\Delta E_i}{k_B T}\right) Q_{TS_i}}{\sum_j^R \exp\left(\frac{-\Delta E_j}{k_B T}\right) Q_{R_j}} \exp\left(-\frac{E_{TS} - E_R}{k_B T}\right) \quad (2.2)$$

where k_B is the Boltzmann constant, h is the Planck constant, and T is the temperature. The sums in the numerator and denominator of the third term of Equation 2.2 sum over the rigid-rotor harmonic oscillator partition functions (Q) of all in-

cluded TS or reactant conformers, each exponentially weighted by their relative zero-point corrected energy (ΔE). The partition functions and relative energies are calculated at the ω B97X-D/aug-cc-pVTZ level. The reaction energy barrier $\Delta^\ddagger E_0$ is the ω B97X-D/aug-cc-pVTZ zero-point corrected F12 electronic energy difference between the lowest-energy TS and reactant conformer. κ is the transmission coefficient, which is estimated with asymmetric Eckart tunneling correction⁶³ based on IRC end-point calculated at F12// ω B97X-D/aug-cc-pVTZ level.

This MC-TST approach has consistently led to rate coefficients of unimolecular H-shift reactions that are within a factor of 5 of the experimental measured values.⁴⁸ The approach is not designed for evaluating D-shift reactions and may have larger uncertainties of about a factor of 10.²⁰ The calculated H/D-shift rate coefficients guide the development of the autoxidation mechanism for DE and DE-d10 illustrated in Scheme 2.2 and A.2. Additional details regarding the calculation of H/D-shift rate coefficients are provided in Section A.4.1.

2.2.3 Box Model

A MATLAB-based gas-phase chemistry box model is used to simulate the experimental results. The model uses the MATLAB ode15s solver to compute time-dependent concentrations of species in the system based on the given initial conditions and a specified chemical mechanism. The reactions and chemical kinetics implemented in the model are initially adopted from the Master Chemical Mechanism (MCM, <https://mcm.york.ac.uk/MCM>), estimations from Jenkin et al.,^{9,14} and the calculated RO₂ H-shift rate coefficients determined in this work. More detailed information regarding the implemented mechanism in the model is given in Section A.5.

The output from the model simulation is compared with the experimental data to help evaluate the kinetics and branching ratios of key reactions in the mechanism. The implemented mechanism is then modified to minimize the difference between the experimental and model results by adjusting the RO₂ H-shift rate coefficients and branching fractions of relevant bimolecular reactions within their estimated uncertainties. Through the optimization of the mechanism, we estimate the reaction kinetics of both autoxidation and bimolecular chemistry.

2.3 Results and Discussion

2.3.1 Identity of Oxidation Products

Figure 2.1 shows the gas chromatograms of major oxidation products from an experiment with relatively high level of HO_2 , ~ 1 ppb ($\tau_{\text{RO}_2+\text{HO}_2} \sim 2.5$ s). Figure 2.1a and b show the reaction products from DE oxidation, and Figure 2.1c and d show the reaction products from DE-d10 oxidation. Oxidation products from DE-d10 elute slightly earlier than these from DE, a phenomenon also observed in previous GC-MS studies.⁶⁴

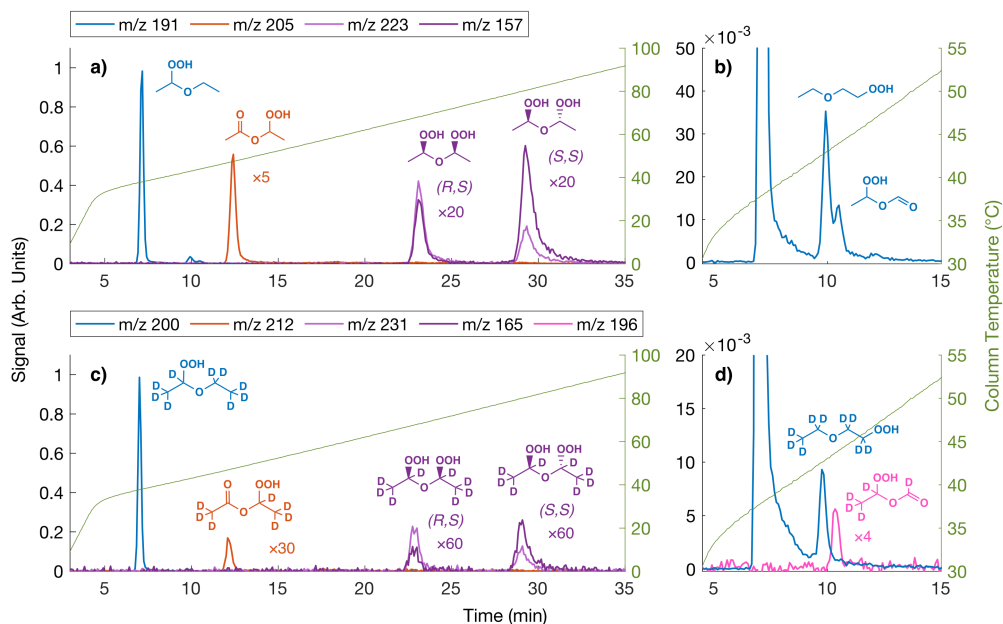


Figure 2.1: Gas chromatograms of major oxidation products. (a) GC traces of DE oxidation products, (b) Zoomed-in view of (a) for products eluting at 5-15 min, (c) GC traces of DE-d10 oxidation products, (d) Zoomed-in view of (c) for products eluting at 5-15 min. Certain signals in the figure are scaled up by a factor denoted in the figure. The peak assignment of the diastereomers of dihydroperoxides (m/z 223 and 231) is tentative.

Oxidation products detected at highest abundance are the alkyl hydroperoxides (ROOHs) as the major first-generation bimolecular products in the system. The ROOHs from DE oxidation are detected at m/z 191, while the ROOH-d9 from DE-d10 oxidation are detected at m/z 200. Smaller amounts of products from 2- RO_2 and 2- RO_2 -d9 autoxidation pathways, i.e. the reaction products from 2-OO-3-ROOH and 2-OO-3-ROOH-d9 (Scheme 2.2 and A.2), are also observed, including the ketohydroperoxides (2-oxo-3-ROOH at m/z 205 and 2-oxo-3-ROOH-d7 at m/z 212), stereoisomers of the dihydroperoxides (2,3-ROOH at m/z 223 and 2,3-ROOH-d8 at m/z 231), and 2-OOH-R'CHO (m/z 191) and 2-OOH-R'CHO-d5 (m/z 196). We do

not detect autoxidation products from 1-RO₂ and 1-RO₂-d₉, likely due to the low yield of primary RO₂, resulting from the very slow OH abstraction of H/D atoms from the methyl group, as well as the low H/D-shift reaction rate of primary RO₂ (Scheme A.3).

Most products are detected as ion clusters with CF₃O⁻ at m/z = mass neutral + 85, except the dihydroperoxides (m/z 223 and 231), which undergoes significant fluoride transfer reactions, producing ions detectable at m/z = mass neutral + 19 (m/z 157 and 165). The dihydroperoxides also produce relatively high yields of fragment ions, such as m/z 63 (FCO₂⁻) and 81 (likely FCO₂⁻·H₂O) - fragment ions characteristic of CF₃O⁻ ionization of hydroperoxides, and 79 (FC₂H₄O₂⁻) - a fluorine transfer product from CF₃O⁻ ionization of acidic organics.⁶⁵ We sum the parent plus all fragments to quantify the yields of the dihydroperoxides (detailed in Section A.6.2). Two chromatographic peaks are observed for dihydroperoxides, which are tentatively assigned to different diastereomers of the compound. While certain diastereomers can be separated with our GC system, enantiomers cannot be separated. In the case of the dihydroperoxide, the presence of a plane of symmetry limits the number of stereoisomers to three: the meso form [(*R,S*) and (*S,R*)], and the enantiomer pair, (*R,R*) and (*S,S*). For convenience, we refer to the stereoisomer with different configuration at both chiral centers (the meso form) as (*R,S*), and those with same configuration [(*R,R*) and (*S,S*)] as (*S,S*). Due to lack of synthetic standards, we tentatively assign the peaks based on our expectation of the strength of the interaction between the analytes and the column. Based on the calculated molecular structures of the stereoisomers (detailed in Section A.4.3), there is intramolecular hydrogen-bonding interaction between the two hydroperoxide groups in the (*R,S*) isomer, which does not exist for the (*S,S*) isomers. The intramolecular H-bond likely weakens the (*R,S*) isomer's interaction with the column, and we thereby assume that the (*R,S*) peak elutes earlier than the (*S,S*) peak from the column. If this assignment is incorrect, it would affect our conclusions regarding the stereoselectivity of the H-shift process as discussed in Section A.8.4.

Although the autoxidation products formed from DE-d₁₀ should initially contain a deuterated hydroperoxide group (-OOD), these products are detected as hydroperoxides at an m/z value 1 unit lower. This is due to the fast D-H exchange of the hydroperoxide deuterium atom with the hydrogen atoms in background H₂O in the chamber and sampling system (Scheme A.2). Such rapid exchange has been observed in previous studies.^{27,41}

2.3.2 H-shift Rate Coefficients

The following sections describe our experimental estimation of the H-shift rate coefficients and branching ratios for relevant reaction pathways of key RO_2 in the system: 2-RO_2 and 2-OO-3-ROOH from DE oxidation, and their equivalents from DE-d10 oxidation. We estimate the reaction rate coefficients by quantifying the oxidation products of relevant reaction channels and analyzing how their yields change as a function of $[\text{HO}_2]$. The hydroperoxides (from bimolecular reactions of simple RO_2), the dihydroperoxides (from bimolecular reactions of hydroperoxy RO_2), and the ketohydroperoxides (from H-shift reactions of hydroperoxy RO_2) are the foci of our analysis.

2.3.2.1 2-RO_2 and $2\text{-RO}_2\text{-d9}$

To estimate the 1,5 H-shift rate coefficient of 2-RO_2 , we compare the yield of 2-ROOH , the major bimolecular product from the reaction of 2-RO_2 with HO_2 (Scheme 2.1), with the yields of products formed from the RO_2 produced following its 1,5 H-shift, 2-OO-3-ROOH . These products include $2,3\text{-ROOH}$, 2-oxo-3-ROOH , and 2-OOH-R'CHO as illustrated in Scheme 2.2. We assume that the ratio of the yields of these compounds is equivalent to the ratio between their formation rates (subsequent losses of the compounds are ignored, see Section A.5 for more details). The formation rate of 2-ROOH can be expressed as $\alpha_{2\text{-ROOH}}k_{2\text{-RO}_2+\text{HO}_2}[2\text{-RO}_2][\text{HO}_2]$, where $\alpha_{2\text{-ROOH}}$ is the branching fraction to 2-ROOH formation from the bimolecular reaction between 2-RO_2 and HO_2 , and $k_{2\text{-RO}_2+\text{HO}_2}$ is the overall rate coefficient of reaction $2\text{-RO}_2 + \text{HO}_2$. The sum of formation rates of all oxidation products from 2-OO-3-ROOH is equal to the loss rate of 2-OO-3-ROOH , which, assuming steady state for $[2\text{-OO-3-ROOH}]$, is equal to the formation rate of 2-OO-3-ROOH : $k_{1,5 \text{ H-shift, } 2\text{-RO}_2}[2\text{-RO}_2]$, where $k_{1,5 \text{ H-shift, } 2\text{-RO}_2}$ is the 1,5 H-shift rate coefficient of 2-RO_2 . Thus, the ratio between the yields of 2-ROOH and oxidation products of 2-OO-3-ROOH can be formulated as:

$$\begin{aligned}
 & \frac{[2\text{-ROOH}]}{[2,3\text{-ROOH}] + [2\text{-oxo-3-ROOH}] + [2\text{-OOH-R'CHO}]} \\
 &= \frac{\alpha_{2\text{-ROOH}}k_{2\text{-RO}_2+\text{HO}_2}[2\text{-RO}_2][\text{HO}_2]}{k_{1,5 \text{ H-shift, } 2\text{-RO}_2}[2\text{-RO}_2]} \\
 &= \frac{\alpha_{2\text{-ROOH}}k_{2\text{-RO}_2+\text{HO}_2}}{k_{1,5 \text{ H-shift, } 2\text{-RO}_2}}[\text{HO}_2]
 \end{aligned} \tag{2.3}$$

Equation 2.3 implies that there should be a linear relationship between the ratio of product yields (left-hand side of the equation) and $[\text{HO}_2]$. Such behavior is observed, as shown in Figure 2.2. According to Equation 2.3, the slope of this relationship is proportional to the ratio of rate coefficients between bimolecular and unimolecular reactions of 2-RO_2 .

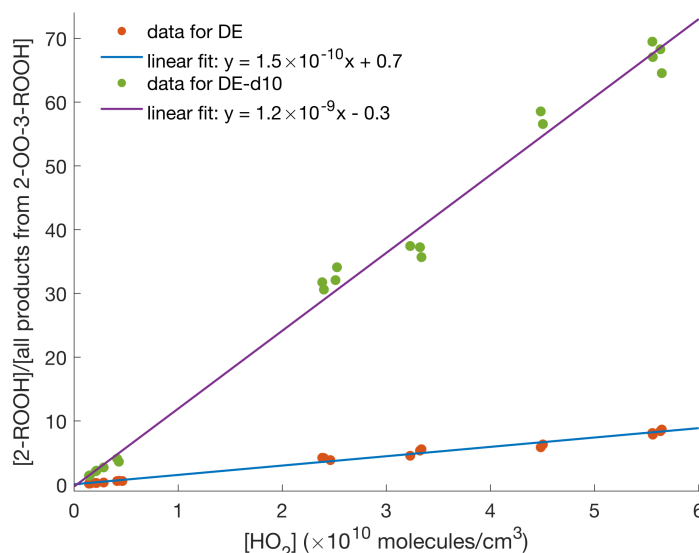


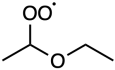
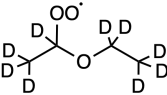
Figure 2.2: $[2\text{-ROOH}]/([2,3\text{-ROOH}] + [2\text{-oxo-3-ROOH}] + [2\text{-OOH-R'CHO}])$ vs. $[\text{HO}_2]$ at ambient temperature for DE and DE-d10 system, and respective unweighted linear regression fits. The uncertainties in the data are dominated by common systematic errors as detailed in Section A.9 ($\sim 28\%$ for concentration ratios and $\sim 16\%$ for $[\text{HO}_2]$). The R^2 values of the linear fits are 0.986 for DE data (blue line) and 0.991 for DE-d10 data (purple line).

Based on Equation 2.3, the 1,5 H-shift rate coefficient of 2-RO_2 can be derived from the expression: $\frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2}}{(\text{slope in Equation 2.3})}$. The bimolecular rate coefficient $k_{2\text{-RO}_2+\text{HO}_2}$ is estimated to be $1.59 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K, using the method proposed by Wennberg et al.⁶⁶ and Jenkin et al.,¹⁴ with a high level of uncertainty at $\sim 52\%$, which is the major source of uncertainty in our following estimation of the H-shift rate coefficients in addition to the uncertainty in CIMS calibration ($\sim 28\%$) and $[\text{HO}_2]$ ($\sim 16\%$). The branching fraction $\alpha_{2\text{-ROOH}}$ can be estimated by analyzing the ratio between $[2\text{-ROOH}]$ and $[1\text{-ROOH}]$ at high $[\text{HO}_2]$, where the effect of H-shift reactions on the yields of ROOHs is small. More detailed analysis of the relationship between $[2\text{-ROOH}]/[1\text{-ROOH}]$ and $[\text{HO}_2]$ is provided in Section C.8.1. Briefly, at high HO_2 concentrations, the yield of the two hydroperoxides is mainly influenced by two parameters: 1). the branching fraction of 1-RO_2 ($\alpha_{1\text{-RO}_2}$) and 2-RO_2 ($\alpha_{2\text{-RO}_2}$) in the initiation step (Scheme 2.1 and A.1), and 2). the branching fraction of $\text{RO}_2 + \text{HO}_2$ reaction to ROOH formation. We use box model simulations to facilitate

our estimation of these two parameters, and the resulting parameters for 2-RO₂ and 2-RO₂-d9 are presented in Table 2.1.

Therefore, based on our estimations and linear regression fitting in Figure 2.2, we can estimate the 1,5 H-shift rate coefficient of 2-RO₂ to be $0.094 \pm 0.068 \text{ s}^{-1}$ and that of 2-RO₂-d9 to be $0.012 \pm 0.009 \text{ s}^{-1}$ at ambient temperature of 294 K (Table 2.1). The H-shift rate coefficient of 2-RO₂ agrees with that calculated with the MC-TST method (0.11 s^{-1} at 298 K³⁹ and 0.080 s^{-1} at 294 K, uncertainty within a factor of 5). It is also close to that of similar RO₂'s from 2-EE system,²³ where H-shift reactions from carbons alpha to an ether group occur at rate of $0.05 - 0.1 \text{ s}^{-1}$ at ambient temperature, as well as on the same order of magnitude as similar H-shifts adjacent to hydroxy and hydroperoxy groups ($0.05 - 0.4 \text{ s}^{-1}$).^{20,67} H-shift processes from those systems are all faster than those from similar alkane RO₂, demonstrating the reduction in energy barrier for hydrogen atom abstraction due to the activation effect by the adjacent oxygen atom.^{18,22} The H-shift reaction rate coefficient of 2-RO₂-d9 is much slower than that of 2-RO₂ ($\sim 8 \pm 6$ times slower) as expected due to the kinetic isotope effect. Previous computational studies suggest that hydrogen transfer is significantly faster for H (¹H) compared to D (²H) nuclei due to a combination of quantum mechanical zero-point energy and tunneling effects.^{40,43} Our estimation yields a D-shift rate coefficient much higher than the computational prediction. The low theoretical rate coefficient likely results from an underestimation in the tunneling factor of the D-shift processes in our computational method. More details regarding the phenomenon are discussed in Section 2.3.2.3.

Table 2.1: Parameters of key reactions involving 2-RO₂ and 2-RO₂-d9. Reaction parameters derived from experimental results shown here are applied in box model simulations. Derivation of uncertainties are detailed in Section A.9. ^a Derived branching fractions for production of respective RO₂'s during initiation of the VOC. ^b Derived branching fractions for production of ROOH from RO₂ + HO₂ reactions for respective RO₂'s.

Peroxyl Radicals	$\alpha_{2\text{-RO}_2}$ ^a	$\alpha_{2\text{-ROOH}}$ ^b	1,5 H/D-shift rate coefficient (s ⁻¹) at 294 K	
			Theory	Experiment
2-RO ₂ 	0.97 ± 0.01	$0.87 + 0.13 / -0.34$	0.080	0.094 ± 0.068
2-RO ₂ -d9 	0.986 ± 0.004	$0.90 + 0.10 / -0.36$	0.0016	0.012 ± 0.009

2.3.2.2 2-OO-3-ROOH and 2-OO-3-ROOH-d9

We estimate the subsequent 1,5 H-shift rate coefficient of 2-OO-3-ROOH using the observed variation with $[\text{HO}_2]$ in the yields of its major unimolecular and bimolecular reaction products, 2-oxo-3-ROOH and 2,3-ROOH (Scheme 2.2). As above, we assume that the ratio of the yields of these compounds is equal to the ratio of their formation rates:

$$\begin{aligned}
 & \frac{[\text{2-oxo-3-ROOH}]}{[\text{2,3-ROOH}]} \\
 &= \frac{\alpha_{\text{2-oxo-3-ROOH}} k_{\text{2-OO-3-ROOH}+\text{HO}_2} [\text{2-OO-3-ROOH}] [\text{HO}_2] + k_{\text{1,5 H-shift, 2-OO-3-ROOH}} [\text{2-OO-3-ROOH}]}{\alpha_{\text{2,3-ROOH}} k_{\text{2-OO-3-ROOH}+\text{HO}_2} [\text{2-OO-3-ROOH}] [\text{HO}_2]} \\
 &= \frac{\alpha_{\text{2-oxo-3-ROOH}}}{\alpha_{\text{2,3-ROOH}}} + \frac{k_{\text{1,5 H-shift, 2-OO-3-ROOH}}}{\alpha_{\text{2,3-ROOH}} k_{\text{2-OO-3-ROOH}+\text{HO}_2}} \times \frac{1}{[\text{HO}_2]}
 \end{aligned} \tag{2.4}$$

$\alpha_{\text{2-oxo-3-ROOH}}$ and $\alpha_{\text{2,3-ROOH}}$ are the branching fractions to 2-oxo-3-ROOH and 2,3-ROOH formation from the bimolecular reaction between 2-OO-3-ROOH and HO_2 , $k_{\text{2-OO-3-ROOH}+\text{HO}_2}$ is the overall rate coefficient of reaction 2-OO-3-ROOH+ HO_2 , and $k_{\text{1,5 H-shift, 2-OO-3-ROOH}}$ is the 1,5 H-shift rate coefficient of 2-OO-3-ROOH.

Equation 2.4 suggests that there is a linear relationship between the ratio of product yields $[\text{2-oxo-3-ROOH}]/[\text{2,3-ROOH}]$ and $1/[\text{HO}_2]$. The trend observed is shown in Figure 2.3. Based on Equation 2.4, the slope of the linear fit equals to the ratio between the H-shift rate coefficient and the bimolecular rate coefficient with the branching ratio to 2,3-ROOH formation ($\frac{k_{\text{1,5 H-shift, 2-OO-3-ROOH}}}{\alpha_{\text{2,3-ROOH}} k_{\text{2-OO-3-ROOH}+\text{HO}_2}}$). Thus, estimation of the 1,5 H-shift rate coefficient requires knowledge of the bimolecular rate coefficient ($k_{\text{2-OO-3-ROOH}+\text{HO}_2}$) and the branching fraction to formation of the dihydroperoxide ($\alpha_{\text{2,3-ROOH}}$). Similar to the previous section, the bimolecular rate coefficient is estimated to be $1.87 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 294 K based on the method in Wennberg et al.⁶⁶ and Jenkin et al.¹⁴ Derivation of the branching fraction is facilitated by the intercept of the linear fit, which equals to the ratio between the branching fractions of two channels of 2-OO-3-ROOH+ HO_2 reaction ($\frac{\alpha_{\text{2-oxo-3-ROOH}}}{\alpha_{\text{2,3-ROOH}}}$). The branching fraction to the third reaction channel ($\alpha_{\text{2-O-3-ROOH}}$, formation of alkoxy radical 2-O-3-ROOH) is derived from the yields of 2-OOH-R'CHO, which is formed by the scission reaction of 2-O-3-ROOH (see Scheme 2.2):

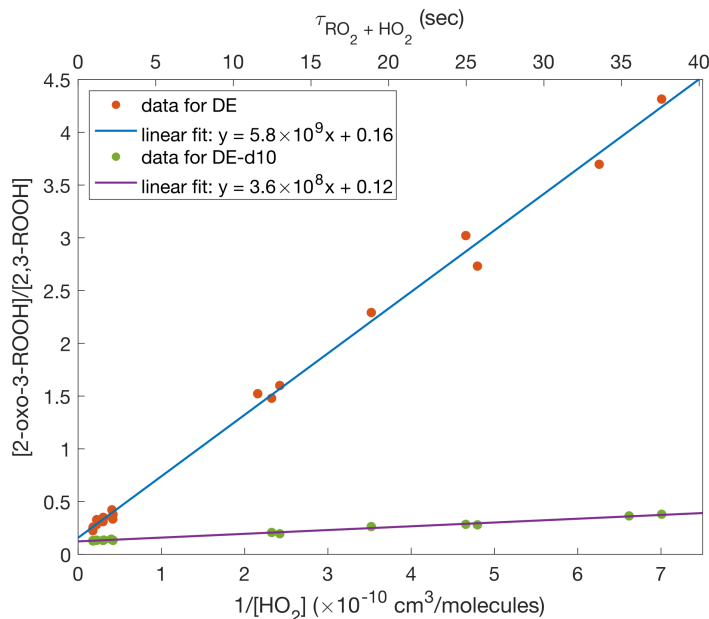


Figure 2.3: $[\text{2-oxo-3-ROOH}]/[\text{2,3-ROOH}]$ vs. $1/[\text{HO}_2]$ at ambient temperature for DE and DE-d10 system, and respective unweighted linear regression fits. Corresponding bimolecular lifetime ($\tau_{\text{RO}_2 + \text{HO}_2}$) of 2-OO-3-ROOH is calculated using Equation 2.1, and is presented on the top axis. The uncertainties in the data are dominated by common systematic errors as detailed in Section A.9 ($\sim 28\%$ for concentration ratios, $\sim 16\%$ for $1/[\text{HO}_2]$). The respective R^2 values of the linear fits are 0.996 for DE data (blue line) and 0.993 for DE-d10 data (purple line).

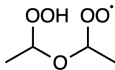
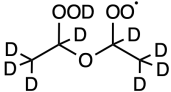
$$\begin{aligned}
 & \frac{[\text{2-OOH-R'CHO}]}{[\text{2,3-ROOH}]} \\
 &= \frac{\alpha_{\text{2-OOH-R'CHO}} k_{\text{2-OO-3-ROOH} + \text{HO}_2} [\text{2-OO-3-ROOH}] [\text{HO}_2]}{\alpha_{\text{2,3-ROOH}} k_{\text{2-OO-3-ROOH} + \text{HO}_2} [\text{2-OO-3-ROOH}] [\text{HO}_2]} \\
 &= \frac{\alpha_{\text{2-OOH-R'CHO}}}{\alpha_{\text{2,3-ROOH}}} \\
 &= \frac{\alpha_{\text{scission}} \alpha_{\text{2-O-3-ROOH}}}{\alpha_{\text{2,3-ROOH}}}
 \end{aligned} \tag{2.5}$$

where α_{scission} indicates the branching fraction to scission reaction from 2-O-3-ROOH. The following analysis is based on the assumption that $\alpha_{\text{scission}} = 1$. More details regarding the fate of 2-O-3-ROOH is discussed in Section A.4.2.

Thus, knowledge of the intercept of the linear relationship and the yield of 2-OOH-R'CHO enables us to estimate the branching fractions of the three channels of 2-OO-3-ROOH+HO₂ reaction and the 1,5 H-shift rate coefficient. More details regarding this derivation are in Section A.8.3. The resulting reaction parameters at 294 K are shown in Table 2.2. The estimated H-shift rate coefficient is within the

factor-of-5 uncertainty of that predicted by MC-TST, while the estimated D-shift rate coefficient, similar to that of 2-RO₂-d9, is faster than predicted. The 1,5 H-shift rate coefficient of 2-OO-3-ROOH is estimated to be $0.090 \pm 0.055 \text{ s}^{-1}$, similar to that of 2-RO₂. The D-shift rate coefficient of the deuterated 2-OO-3-ROOH-d9 is estimated to be about 15 ± 8 times slower than its non-deuterated counterpart (Table 2.2). Somewhat surprisingly, the addition of the hydroperoxide group (-OOH) alpha to the hydrogen abstraction site does not appear to enhance the H-shift rate. Despite the additional weakening of the C-H bond by the hydroperoxide group, the impact of this substitution may be countered by the intramolecular bonding between the -OO and -OOH groups of the RO₂ (discussed in Section A.4.4),⁶⁸ which requires additional energy to break in order for the H-shift process to happen.

Table 2.2: Parameters of key reactions involving 2-OO-3-ROOH and 2-OO-3-ROOH-d9. Reaction parameters derived from experimental results shown here are applied in box model simulations. Derivation of uncertainties are detailed in Section A.9. ^b Derived branching fractions for reaction channels of 2-OO-3-ROOH+HO₂ reactions. ^c The H-shift rate coefficient reported here is an average for (*R,S*) and (*S,S*) diastereomers. Stereoisomer-specific H-shifts are discussed in Section A.8.3.

Peroxy Radicals	$\alpha_{2,3}\text{-ROOH}^b$	$\alpha_{2\text{-oxo-3-ROOH}}^b$	$\alpha_{2\text{-O-3-ROOH}}^b$ ($\alpha_{2\text{-OOH-R'CHO}}$)	1,5 H/D-shift rate coefficient (s ⁻¹) at 294 K	
				Theory	Experiment ^c
2-OO-3-ROOH 	$0.83 + 0.06 / -0.05$	0.14 ± 0.05	0.03 ± 0.01	<i>R,S</i> : 0.15 <i>S,S</i> : 0.093	0.090 ± 0.055
2-OO-3-ROOH-d9 	$0.87 + 0.02 / -0.04$	0.10 ± 0.03	0.03 ± 0.01	<i>R,S</i> : 0.0013 <i>S,S</i> : 0.0010	0.006 ± 0.004

2.3.2.3 Kinetic Isotope Effect

Hydrogen abstraction by RO₂ is faster for H (¹H) compared to D (²H) nuclei mainly due to 1) a lower energy barrier for the hydrogen transfer, and 2) a greatly reduced tunneling of deuterium owing to its larger mass.^{40,41} The quantum chemistry methods employed here predict energy barrier differences between H- and D-shift to be consistently ~1 kcal/mol (see Table A.4), resulting from differences in the zero-point corrected vibrational energy, which is in good agreement with previous calculations on similar H/D-shift reactions.²⁰ This change in barrier height leads to a D-shift that is a factor of 5 slower than the corresponding H-shift at room temperature. In addition, the calculated Eckart tunneling factor κ is 7-23 times smaller for D-shifts

here, due to a heavier tunneled mass and a wider potential energy barrier, which further decreases the rate coefficients (Table A.6). In the previous work on various H/D-shift reactions in hexanols, the Eckart tunneling coefficient of D-shifts was found to be a factor of 4-17 smaller than that of H-shifts.²⁰

The Eckart approach estimates the tunneling effects by assuming the reaction occurs via a one-dimensional potential energy barrier, whose shape is approximated based on the TS imaginary frequency and the height of the barrier on both sides of the reaction coordinate. Although the use of Eckart tunneling correction in a TST framework has been successful in predicting rate coefficients of atmospheric reactions, the use of a one-dimensional potential may be less appropriate in capturing kinetic isotope effects.⁶⁹ Thus, the reaction rate coefficients for D-shifts presented here may be underestimated. However, all experimentally estimated D-shifts here are within a factor of 10 of the theoretically calculated D-shifts. The experimental H/D-shifts rate coefficients in Table 2.1 and 2.2 indicate a drop in rate coefficient of a factor of 8 ± 6 for 2-RO₂ and a factor of 15 ± 8 for 2-OO-3-ROOH (derivation of uncertainties are discussed in Section A.9.3). These numbers are comparable to previous work on H-shifts reactions which find factors of larger than 20 for the alcohols.²⁰

2.4 Conclusions

The autoxidation chemistry of ether compounds is studied through investigating the H-shift reaction of RO₂ formed in the oxidation of the simple ethers DE and DE-d10. We estimate that DE RO₂ undergo H-shift reactions at rates of $\sim 0.09 \text{ s}^{-1}$ at 294 K, which agrees well with the computational results (Table 2.1 and 2.2). At higher temperature, RO₂ H-shift rates will increase due to the high energy barrier along the H-shift reaction coordinate,^{13,19} and thus we expect that the H-shift rate coefficients of DE RO₂ will be $\sim 0.1 \text{ s}^{-1}$ at 298 K (temperature dependence of H-shift rate coefficients in Table A.5). We also examine the kinetic isotope effect involving in RO₂ hydrogen transfer by investigating the chemistry of RO₂ from fully deuterated DE-d10, and show that the chemistry is consistent with H-shift through a substantial barrier. The estimated rate coefficients of the H-shifts are equivalent to the rate of reactions of these RO₂ with NO at [NO] of $\sim 0.4 \text{ ppb}$. Thus, with NO_x levels in areas heavily influenced by urban emission often falling below 1 ppbv, sometimes even below 0.5 ppb,^{33,34} autoxidation chemistry of ether compounds becomes increasingly competitive, leading to higher production of highly oxidized and low-volatility organic products.

Substitution of oxygen-containing functional groups at the carbon from which the hydrogen atom is abstracted enhances the H-shift reaction rate. While the ambient temperature H-shift rates of unsubstituted RO₂ are generally considered to be negligible ($<10^{-3} \text{ s}^{-1}$),^{18,22} substituents such as hydroxy (-OH), hydroperoxy (-OOH), and ether (-OCH₂-) groups (as shown here) enhance the H-shift rate to around 0.05 – 0.1 s⁻¹.^{18,20,23} The effect of multiple functional groups on the hydrogen transfer rate at the hydrogen subtraction site is briefly discussed. The substitution of both -OCH₂- and -OOH groups does not result in an extra enhancement in the H-shift rate, in this particular case, possibly due to intramolecular interactions between these functional groups and the RO₂. As the multigeneration oxidation products of VOCs contain increasingly complex functionalization, unravelling the combined effect of multiple oxygenated groups on autoxidation rates will be crucial for understanding the mechanism of OVOCs formation.

We expect our estimation of the H-shift rates of DE RO₂ to inform the extension of this chemistry to describe the atmospheric oxidation of larger and more complex volatile ethers. Large ether and glycol ether compounds are commonly used in various products across residential, commercial, and industrial settings,^{70–73} including such compounds as Carbitol, or 2-(2-ethoxyethoxy)ethanol, an organic solvent with broad applications. Investigating their autoxidation chemistry pathways is crucial for understanding their full fate in the atmosphere and their air quality implication. The long carbon chain in these compounds likely enables consecutive H-shifts and oxygen addition. If the fast H-shift chemistry observed here also extends to larger compounds with ether moieties, it could drive rapid formation of HOMs bearing multiple hydroperoxide and carbonyl groups, producing substantial amount of SOA precursors.

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Chapter 3

AUTOXIDATION OF GLYCOL ETHERS: 2-ETHOXYETHANOL

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Abstract

We investigate the gas-phase photo-oxidation of 2-ethoxyethanol (2-EE) initiated by OH radical, with a focus on its autoxidation pathways. Gas-phase autoxidation - intramolecular H-shifts followed by O₂ addition - has recently been recognized as a major atmospheric chemical pathway that leads to formation of highly oxygenated organic molecules (HOMs), which are important precursors for secondary organic aerosols (SOA). Here, we examine the gas-phase oxidation pathways of 2-EE, a model compound for glycol ethers, an important class of volatile organic compounds (VOC) used in volatile consumer products (VCPs). Both experimental and computational techniques are applied to analyze the photochemistry of the compound. We identify oxidation products from both bimolecular and autoxidation reactions from chamber experiments at varied HO₂ levels, as well as provide estimations of rate coefficients and products branching ratios for key reaction pathways. The H-shift processes of 2-EE peroxy radicals (RO₂) are found to be sufficiently fast to compete with bimolecular reactions under modest NO/HO₂ conditions. More than 30% of produced RO₂ are expected to undergo at least one H-shift for conditions typical of modern summer urban atmosphere, where RO₂ bimolecular lifetime is becoming > 10 s, which implies the potential for glycol ether oxidation to produce considerable amounts of HOMs at reduced NO_x levels and elevated temperature. Understanding the gas-phase autoxidation of glycol ethers can help fill the knowledge gap in the formation of SOA derived from oxygenated VOCs emitted from VCP sources.

3.1 Introduction

The gas-phase oxidation of volatile organic compounds (VOCs) in the atmosphere is usually initiated by reactions with oxidative species such as OH, NO₃, and O₃. Subsequent addition of molecular oxygen (O₂) to the nascent alkyl radical leads to formation of organic peroxy radicals (RO₂). The fate of RO₂ depends on the chemical state of the atmosphere, and traditionally, bimolecular reactions with NO, HO₂, or other RO₂ are considered to dominate their loss.^{1,2} Recently, gas-phase autoxidation chemistry has been recognized to be another important pathway.³⁻⁵ Autoxidation is generally defined as the process in which the RO₂ first undergoes an intramolecular hydrogen shift (H-shift), producing a hydroperoxyalkyl radical (often denoted QOOH in combustion chemistry), to which O₂ then rapidly attaches, forming a new, now more oxidized, RO₂. The successive isomerization and O₂ addition processes can result in rapid addition of oxygen to VOCs and thereby formation of highly oxygenated organic molecules (HOMs). HOMs have low volatility and thereby readily undergo gas-particle transfer, contributing to secondary organic aerosol (SOA) particle formation and/or growth.^{3,6,7}

The autoxidation pathways become competitive with bimolecular chemistry as the bimolecular lifetime of RO₂ increases,^{3,4,6,7} such as in environments with large emissions of VOCs and modest or low NO levels (0.1–1 ppb), where RO₂ can survive for 10-100 sec before reacting with NO, HO₂, or other RO₂.^{3,4} As a result of the recent successful reduction of NO_x emission in urban areas (some urban NO_x levels falling below 500 to 100 ppt^{3,8}), autoxidation chemistry is expected to be increasingly favored in the photochemistry of modern urban atmosphere. Given that autoxidation pathways can generate large amounts of low-volatility vapors that contribute to aerosol formation, it is imperative to characterize this low-NO_x chemistry for the array of different VOCs typically found in urban atmosphere.

Success in air pollution control strategies can shift not only the major photochemical pathway of reactive organics in urban air, but also the characteristics of these organic emissions. With VOC emission from combustion sources declining, volatile chemical products (VCPs) - including solvents, personal care products, cleaning agents, coatings, etc. - have emerged as a new major source of VOC in industrialized cities.⁹⁻¹¹ VCPs are now considered to account for half or more of volatile organic emissions in some urban atmospheres, and have been studied for their SOA forming potential under various conditions,⁹⁻¹⁵ demonstrating that VCPs may account for much of the unexplained SOA mass in modern urban environments.^{9,12} Since H-

shift chemistry of RO_2 has been shown to be an important process for many organic substrates,^{16–20} it is likely that many VCP compounds also produce HOMs via autoxidation.

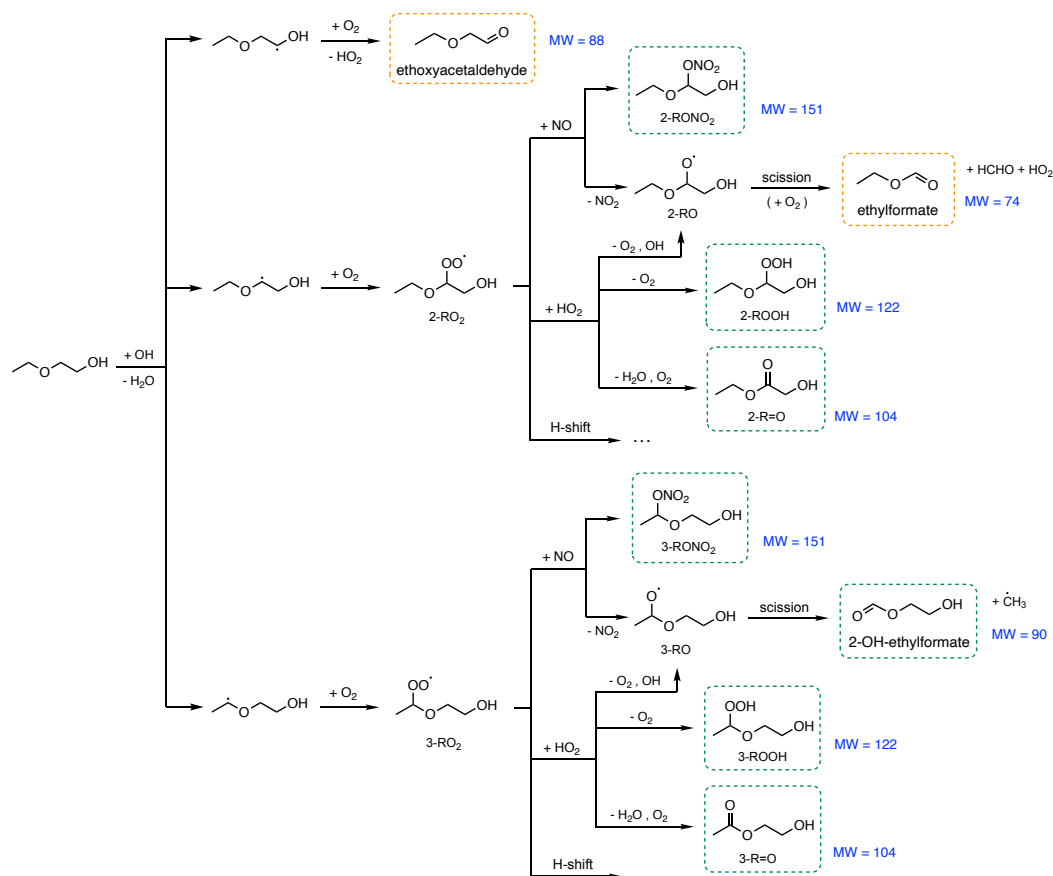
In this study, we explore the gas-phase oxidation of 2-ethoxyethanol (2-EE, Scheme 3.1) as a model system for the diverse family of glycol ethers. Glycol ethers are compounds with formula of $\text{R}-(\text{OCH}_2\text{CH}_2)_n-\text{OR}'$ ($n = 1, 2, 3$). They are a class of VCPs widely used as solvents in products such as architecture coatings, cleaning products, and adhesives.^{21–23} Studies have shown that many semi- or intermediate volatile glycol ether compounds are sufficiently volatile to evaporate and participate in atmospheric photochemical processes.^{12,24} However, studies on photo-oxidation of glycol ethers remain sparse, and most still focus on traditional bimolecular pathways.^{12,25,26} Here, we study 2-EE, the simplest glycol ether, as a model molecule of this class of compound. 2-EE is often used as a component or solvent for inks, paints, resins, dyes, and varnishes.²⁵ It is also detected in emission from diesel/biodiesel blends used in vehicles.²⁷ We conduct a series of photo-oxidation experiments of 2-EE by OH radicals with differing HO_2 concentrations to explore the competition between bimolecular and autoxidation chemistry of 2-EE RO_2 . Then, guided by computational techniques, we analyze the system to identify oxidation products and estimate autoxidation rate coefficients.

3.2 Methods

3.2.1 Experimental Design

We conduct a suite of oxidation experiments of 2-ethoxyethanol (Sigma Aldrich, >99%) initiated by reaction with the OH radical at different HO_2 mixing ratios in a $\sim 0.7 \text{ m}^3$ Teflon environmental chamber. The chamber is housed inside an enclosure with UV reflective metal and can be equipped with either 350 nm (Sylvania 350 Blacklight) or 254 nm (Sankyo Denki G40T10) UV lamps. Experiments are conducted under laboratory temperature at $294 \pm 1 \text{ K}$ and pressure at $\sim 993 \text{ hPa}$, and under high temperature at $309.5 \pm 2 \text{ K}$ with a heater (Finlandia FIN-45) being used to warm up the chamber enclosure. The mechanism of 2-EE oxidation by OH radical is shown in Scheme 3.1. Two major peroxy radicals (2- RO_2 and 3- RO_2 , Scheme 3.1) are produced through the initiation step.

To constrain the H-shift rate coefficients of the RO_2 in the system, we study the competition between the $\text{RO}_2 + \text{HO}_2$ bimolecular channel and autoxidation chemistry by comparing the yields of hydroperoxides, the major products from the $\text{RO}_2 + \text{HO}_2$



Scheme 3.1: Oxidation of 2-EE by OH radical. H-abstraction from the methyl or hydroxy groups is assumed to be negligible and is thus not shown. Subsequent reaction pathways of the peroxy radicals and some of the products are also shown, including RO₂+NO reaction forming organonitrates (RONO₂) and alkoxy radicals (RO), RO₂+HO₂ reaction forming hydroperoxides (ROOH), alkoxy radicals (RO), carbonyls (R=O), and unimolecular H-shifts. Major oxidation products are shown in boxes, with their molecular masses indicated in blue. Those that are detectable by our instrument are shown in green boxes, while those not detectable are in orange boxes.

channel, and autoxidation products as HO₂ concentrations are varied. The RO₂ in the system are prepared by oxidation of 2-EE via OH radicals, which are produced from photolysis of H₂O₂ (30% by mass, Macron Fine Chemicals) through reaction:



Most of the HO₂ is formed in the chamber by addition of CH₃OH (Sigma Aldrich, > 99.9%) resulting in:



A small additional amount of HO_2 is produced via the reaction of OH with H_2O_2 , via the reactions following alkoxy formation, and in several of the autoxidation channels.

To study the rate of unimolecular chemistry, we perform experiments at variable concentrations of HO_2 . We vary HO_2 concentrations across different experiments by changing the number and the type of UV lamp in the chamber enclosure thereby modifying the production rate of OH (Reaction R1) and subsequently the production of HO_2 (Reaction R2). We keep the oxidation rate of CH_3OH much higher than that of 2-EE, to not only ensure that the production rate of HO_2 greatly exceeds that of RO_2 so that $\text{RO}_2 + \text{RO}_2$ chemistry is minimized, but also help constrain the HO_2 concentrations in the chamber. A detailed description about the method determining $[\text{HO}_2]$ in our system is in Section B.6.1. In our experiments, the CH_3OH concentrations are ~ 46 ppm ($\sim 1.1 \times 10^{15}$ molecules/ cm^3) and 2-EE concentrations are ~ 600 ppb ($\sim 1.5 \times 10^{13}$ molecules/ cm^3) (see Table B.1 for a list of experimental conditions). The resulting $[\text{HO}_2]$ ranges from $\sim 1.7 \times 10^9$ molecules/ cm^3 (~ 0.07 ppb) with one 350 nm UV light, to $\sim 6.2 \times 10^{10}$ molecules/ cm^3 (~ 2.5 ppb) with eight 254 nm UV lights. Estimates of the concentration of $[\text{HO}_2]$ in each experiment is determined using the box model described below and are listed in Section B.5.

In most experiments, we infer the amount of 2-EE oxidized ($\Delta[2\text{-EE}]$) during the experiment by addition of ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$, Sigma Aldrich, 99.8%), measuring its decay and the growth of its major oxidation product glycoaldehyde (HOCH_2CHO , formed through the reaction: $\text{HOCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{O}_2} \text{HOCH}_2\text{CHO} + \text{H}_2\text{O} + \text{HO}_2$). The rate coefficient for the reaction of OH with EG at room temperature is measured by Aschmann and Atkinson²⁸ to be $(1.47 \pm 0.26) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A more detailed description on determining $\Delta[2\text{-EE}]$ is given in Section B.6.3.

3.2.2 Instrumentation

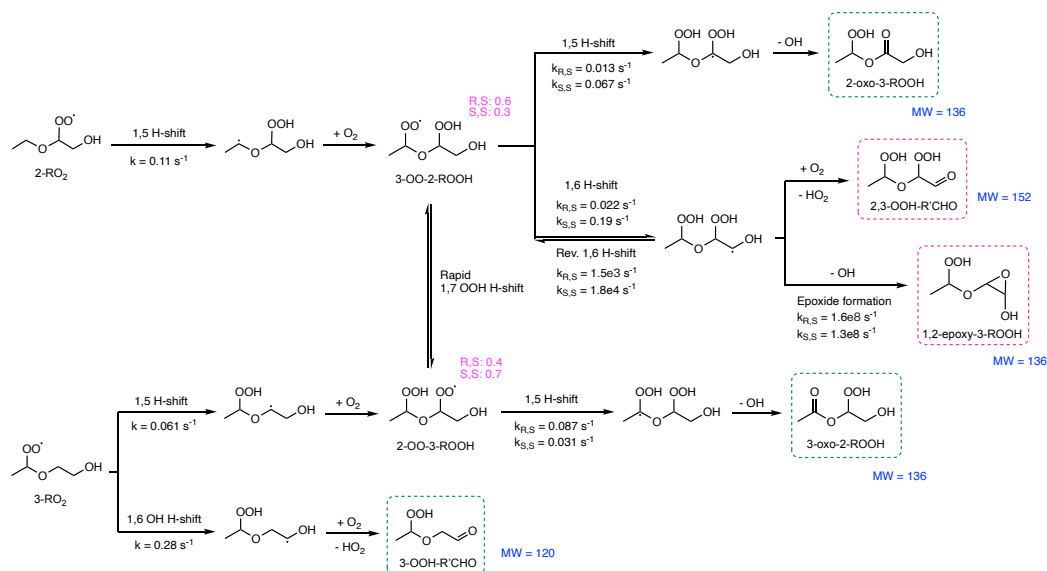
The oxidation products are measured by a low-pressure gas chromatography technique combined with high-resolution time-of-flight chemical ionization mass spectrometer (GC-CIMS) using CF_3O^- as reagent ion. The configuration of the instrument is described in detailed elsewhere,^{3,29,30} and a brief summary is provided here. The GC-CIMS technique was developed to provide isomeric-resolved detection of gas-phase oxygenated organic compounds, including many species that are traditionally deemed difficult to measure, e.g., organic hydroperoxides and nitrates. However,

products with low volatility that would readily partition into condensed phase may fail to be detected in our experiments despite being sensitive to the instrument. The GC consists of a 1-meter fused silica column (Restek RTX-1701), which is cooled through evaporation and expansion of liquid CO₂ and warmed up by an electrical heating system, with nitrogen served as the carrier gas. The mass spectrometer (HRTof-CIMS) can sample either from the output of GC (GC mode), or directly from the chamber (direct sampling mode). In the GC mode, the oxidation products are first cryotrapped and preconcentrated at the head of the GC column, and then separated as column temperature increases at a predetermined ramp rate controlled by an automated temperature program. After eluting from the GC column, the analytes are transferred to the CIMS and react with CF₃O⁻ through simple clustering chemistry and are observed as CF₃O⁻ cluster ions at m/z neutral mass + 85 amu.²⁹ Quantification of the analytes requires knowledge of CIMS sensitivity of the target compound, which for well-bound clusters is proportional to their ion-molecule collision rate with CF₃O⁻. The ion-molecule collision rate is determined by methods in Su and Chesnavich³¹ using the calculated dipole moment and polarizability of the molecule.³² We estimated instrumental sensitivity for major products observed in the system based on the ion-molecule collision rate and measured sensitivity for ethylene glycol.³³ The resulting sensitivities are shown in Table B.5, along with a more detailed description of the CIMS calibration processes and the calculated dipole moments, polarizabilities, and ion-molecule collision rates of the oxidation products.

3.2.3 Computational Method

We calculate the rate coefficients of the H-shift reactions of key radicals in the system using multi-conformer transition state theory (MC-TST)³⁴ following the approach detailed by Møller et al.³⁵ This approach has continually yielded unimolecular RO₂ reaction rate coefficients within a factor of 5 of experimentally-available values and has recently been extended to alkoxy radical unimolecular reactions.^{35–38} The computational results guide the development of the autoxidation mechanism for 2-EE illustrated in Scheme 3.2 and subsequent reaction schemes. We calculate the rate coefficients of all potentially competitive H-shifts of the peroxy radicals, but only include those with appreciable rates ($> 10^{-4} \text{ s}^{-1}$) in our figures and following analysis.

Conformers of the reactant and transition state (TS) are sampled systematically using MMFF³⁹ in Spartan'14 (Wavefunction, Inc.) with constraints on selected



Scheme 3.2: Autoxidation mechanism of the peroxy radicals in the 2-EE system based on calculated H-shift rate coefficients at 298.15K. Rate coefficients for different diastereomers of radicals are indicated separately. Here we refer to the diastereomers with the same configuration at both chiral centers as (S,S) (including (R,R) and (S,S) isomers) and those with different configuration as (R,S) (including (S,R) and (R,S) isomers). The fast 1,7 OOH H-shift between peroxy radicals 3-OO-2-ROOH and 2-OO-3-ROOH establishes an equilibrium between the two radicals. The calculated relative abundance of diastereomers of 3-OO-2-ROOH and 2-OO-3-ROOH at equilibrium are indicated in pink. The products that are detectable by our instrument are shown in green boxes. The products that are not detected in our experiments are in pink boxes.

bond lengths in the TS geometry and forcing a neutral charge on the radical center. The resulting structures are optimized at the B3LYP/6-31+G(d) level in Gaussian 16, Revision C.01 (Gaussian, Inc.) with an optimization with the selected bond lengths constrained preceding the free TS optimization for the TSs.^{40,41} Unique conformers with electronic energies within 2 kcal/mol of the lowest-energy conformer further undergo an optimization and frequency calculation at the ω B97X-D/aug-cc-pVTZ level.⁴² For the lowest-energy conformer of reactant and TS, a CCSD(T)-F12a/VDZ-F12 single-point energy calculation is done in MOLPRO 2012.1 for more accurate barrier heights.^{43,44} This final single-point calculation is omitted for the alkoxy radicals. Tunneling coefficients are calculated using the 1D Eckart approach based on IRC end-point calculated at the same theoretical level as the barrier heights.⁴⁵

MC-TST reaction rate coefficients, k , are then calculated as:

$$k = \kappa \frac{k_B T}{h} \frac{\sum_i^{TS} \exp\left(\frac{-\Delta E_i}{k_B T}\right) Q_{TS_i}}{\sum_j^R \exp\left(\frac{-\Delta E_j}{k_B T}\right) Q_{R_j}} \exp\left(-\frac{E_{TS} - E_R}{k_B T}\right) \quad (3.1)$$

where κ is the Eckart tunneling coefficient, k_B is the Boltzmann constant, T is the absolute temperature and h is Planck's constant. The sum in the numerator sums the rigid-rotor, harmonic oscillator partition functions of all included TS conformers, each exponentially weighted by their relative ZPVE-corrected energy. The sum in the denominator is the same for the reactant conformers. The partition functions and relative energies are calculated at the ω B97X-D/aug-cc-pVTZ level. The final exponential term is the energy difference between the lowest-energy reactant and TS conformers with electronic energies at the CCSD(T)-F12a/VDZ-F12 level and ZPVE at the ω B97X-D/aug-cc-pVTZ. For the alkoxy reactions, the electronic energy is also calculated at the ω B97X-D/aug-cc-pVTZ level.

3.2.4 Box Model

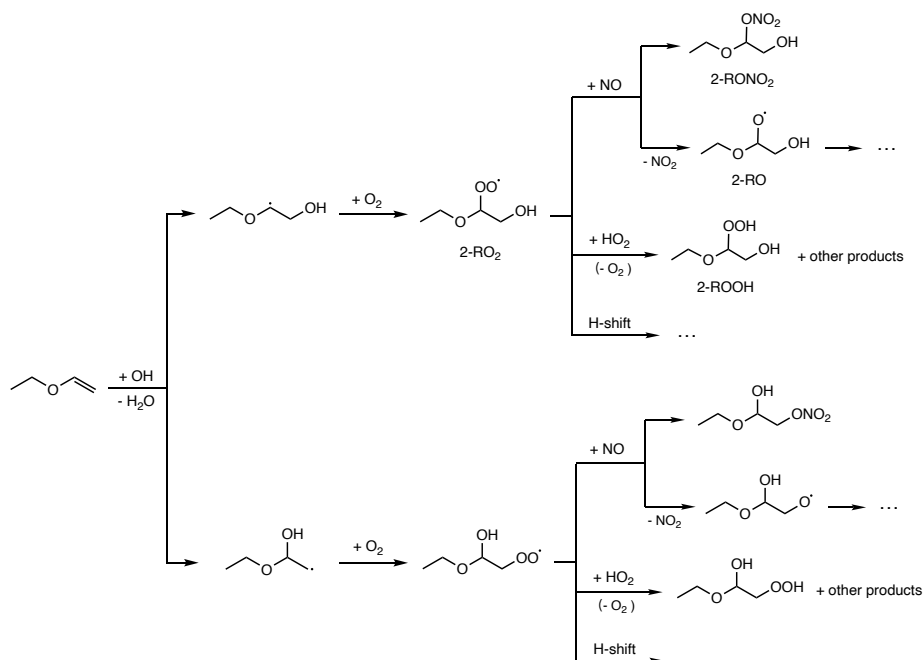
We use a MATLAB-based gas-phase chemistry box model to simulate our experiments and, by comparison with the experimental results, evaluate the kinetics and branching ratios of the chemistry. The model uses a MATLAB ode15s solver to calculate time-dependent concentrations of species in the system based on given initial conditions and a given chemical mechanism. Initially, the reactions and kinetic data implemented in the model are adopted from the Master Chemical Mechanism (MCM, mcm.york.ac.uk/home.htm), estimation from Jenkin et al.⁴⁶ and the calculated H-shift rates. Further details regarding the oxidation mechanism and reaction kinetics we used in the model is in Section B.1. We then minimize the difference between the chamber data and the simulations by adjusting the RO₂ H-shift rates and branching fractions of bimolecular reactions in the mechanism within their calculated uncertainties. The rate coefficients of RO₂ bimolecular reactions, calculated rate coefficients of alkoxy radical unimolecular reactions, and the rapid equilibrium between 3-OO-2-ROOH and 2-OO-3-ROOH (see Scheme 3.2) are not altered.

3.3 Results and Discussion

In our analysis, we seek to generate a nearly complete chemical mechanism for the oxidation of 2-EE by OH to the first generation closed-shell products. We use the bimolecular chemistry reported in literature and MCM as our prior,^{46–49} along with the H-shift chemistry from our calculations. We then modify the mechanism by

adjusting the branching ratios of relevant reactions and H-shift rates to best match the observed dependence of the closed shell products on the abundance of $[\text{HO}_2]$. Optimization of the mechanism is achieved through the following steps: 1). Using prior information and gas-phase synthesis of standards to assign the observed signals in the gas chromatogram (based on their molecular weight and elution temperature) to the expected products in the 2-EE oxidation mechanism (Section 3.3.1); 2). Using the observed ratio between major products from $\text{RO}_2 + \text{HO}_2$ reactions to infer the branching ratios for the bimolecular pathway (Section 3.3.2.1) and the location of hydrogen abstraction from 2-EE (Section 3.3.2.3); 3). Estimating H-shift rates for various RO_2 in the mechanism based on the variation in the measured yields of relevant oxidation products at different $[\text{HO}_2]$ (Section 3.3.2.2 – 3.3.2.5).

3.3.1 Identity of Oxidation Products from Experiments with HO_2



Scheme 3.3: Oxidation of ethyl vinyl ether (EVE) by OH radical. The branching ratio of OH addition at primary carbon to secondary carbon for 1-alkene is estimated to be 0.65:0.35.⁵⁰

Figure 3.1 shows the gas chromatograms of major 2-EE oxidation products formed in an experiment under high $[\text{HO}_2]$ (3.4×10^{10} molecules/cm³) and an experiment under low $[\text{HO}_2]$ (5.1×10^9 molecules/cm³), corresponding to RO_2 lifetimes of approximately 2 and 12 s, respectively. Figure 3.1(c) also shows the products formed in the OH-initiated oxidation of ethyl vinyl ether (EVE, Sigma Aldrich, $\geq 99\%$) to assist in identifying the structural isomers. Scheme 3.3 shows the mechanism of EVE oxidation by OH. The major pathway for OH addition to 1-alkene compounds⁵⁰

produces the same 2-RO₂ as in 2-EE oxidation, allowing us to confirm the identification of products from 2- and 3-RO₂ channels in 2-EE oxidation. The oxidation experiments of EVE are conducted in the same manner as the 2-EE experiments, except that we increase the amount of CH₃OH used to keep the ratio of HO₂ to RO₂ production rates similar.

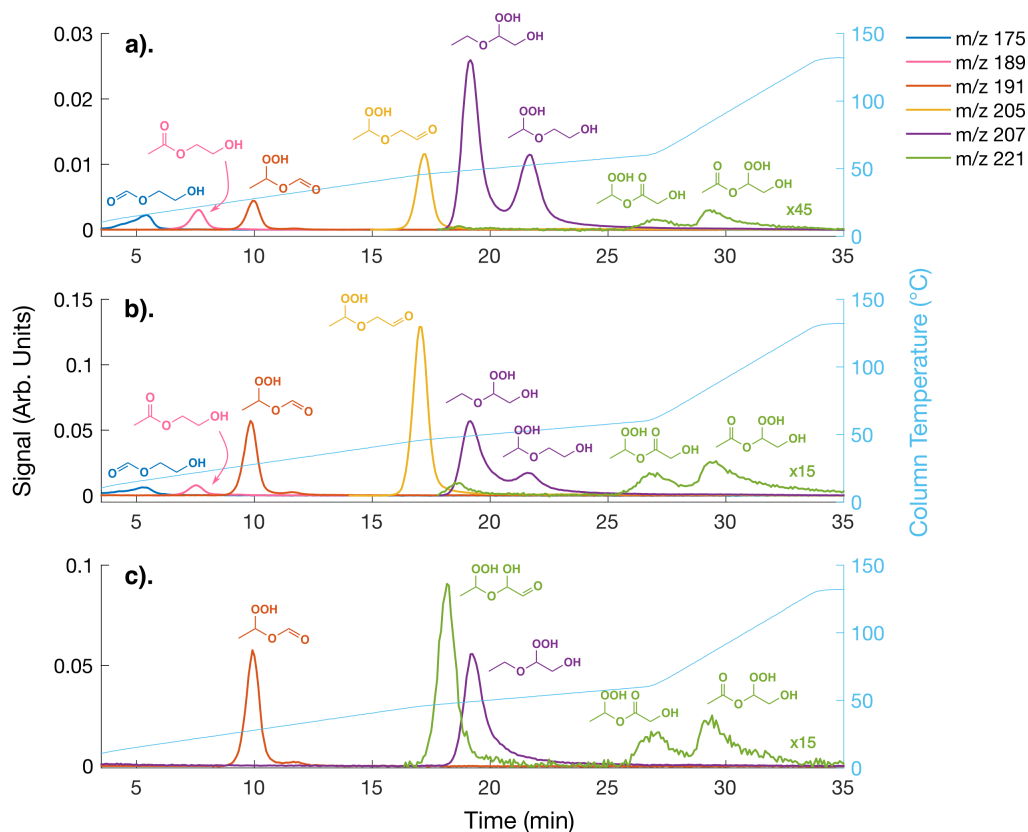
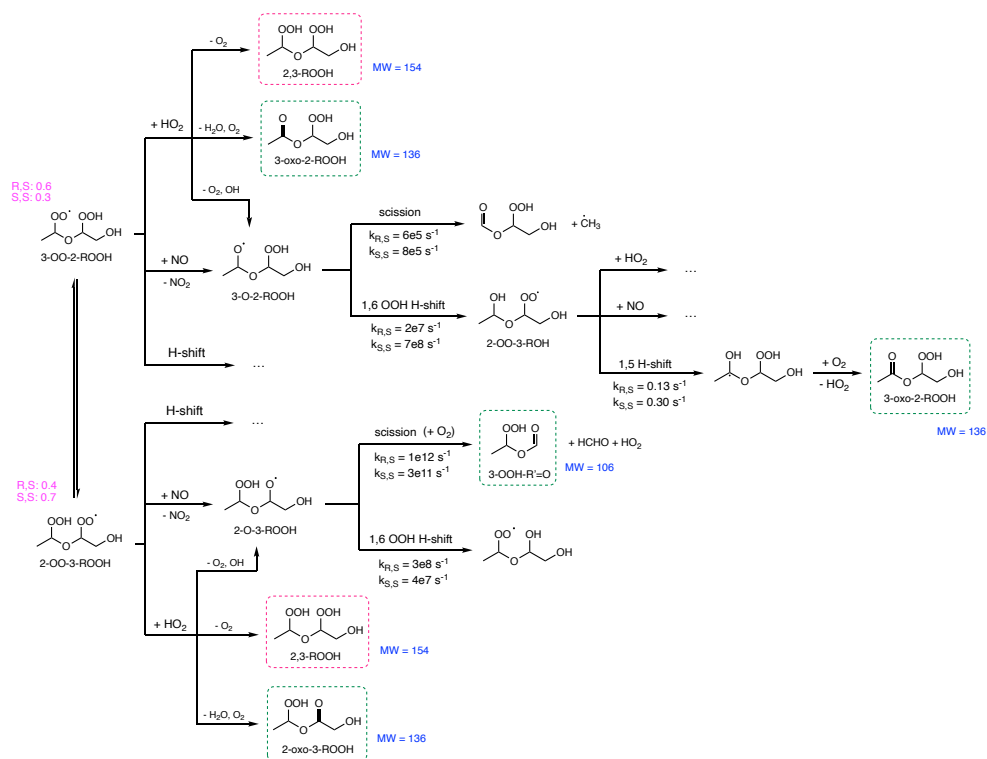


Figure 3.1: Gas chromatograms of major oxidation products from HO₂ experiments, including: 2-OH-ethylformate (*m/z* 175), 3-R=O (*m/z* 189), 3-OOH-R'=O (*m/z* 191), 3-OOH-R'CHO (*m/z* 205), ROOH's (2-ROOH and 3-ROOH, *m/z* 207), and oxo-ROOH's (2-OH-3-OOH-R'CHO, 2-oxo-3-ROOH, 3-oxo-2-ROOH, *m/z* 221). **a).** A 2-EE high HO₂ experiment with [HO₂] = 3.4×10^{10} molecules/cm³ (1.38 ppb), **b).** A 2-EE low HO₂ experiment with [HO₂] = 5.1×10^9 molecules/cm³ (0.21 ppb), **c).** An experiment with ethyl vinyl ether. The *m/z* 221 signals are scaled up by a factor denoted in the figure.

Oxidation products of interest in Figure 3.1 include: 2-OH-ethylformate (*m/z* 175), 3-R=O (*m/z* 189), and the hydroperoxides (ROOHs, *m/z* 207), which are products from bimolecular RO₂+HO₂ channel with higher yields at higher HO₂ condition; 3-OOH-R'CHO (*m/z* 205) produced via H-shift chemistry from 3-RO₂, and the ketohydroperoxides (oxo-ROOH's, *m/z* 221) produced from both 2- and 3-RO₂ H-shift chemistry, both of which have higher yields at lower HO₂ condition.

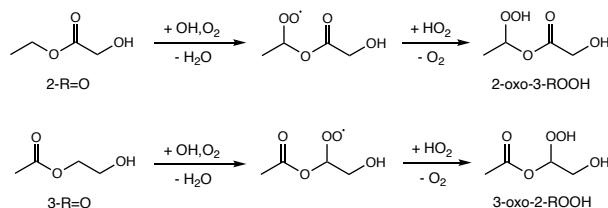
We identify the m/z 191 peak eluting at ~ 10 min as 3-OOH-R'=O (m/z 191) through deuterium exchange experiments to eliminate from consideration the exact mass isomers, e.g., the diols (2-ROH and 3-ROH) produced from self-reactions of 2- and 3-RO₂ (Scheme B.2). Details about the deuteration experiment are described in Section B.7.1. 3-OOH-R'=O is formed following an alkoxy bond scission in the bimolecular chemistry of the 2-OO-3-ROOH peroxy radical, as shown in Scheme 3.4. The high yield of this product under elevated HO₂ levels suggests that the reaction of 2-OO-3-ROOH with HO₂ has a large yield of the 2-O-3-ROOH alkoxy radical, similar to the reactions of other highly functionalized RO₂.^{51,52} The compound is also observed in EVE experiments (Figure 3.1(c)), which demonstrates the production of 2-OO-3-ROOH from 2-RO₂, likely through the rapid equilibrium between 3-OO-ROOH and 2-OO-3-ROOH radicals (Scheme 3.2 and 3.4). Such rapid H-shift between ROOH and RO₂ is also observed in other aliphatic and acyl peroxy radicals.^{53–55}



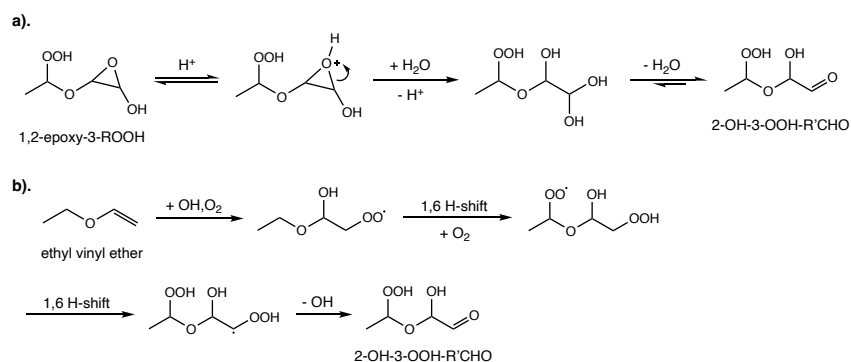
Scheme 3.4: Bimolecular pathways of peroxy radicals 3-OO-2-ROOH and 2-OO-3-ROOH based on calculated rate coefficients at 298.15K. The products that are detectable by our instrument are in green boxes, and those not detected in our experiments are in pink boxes.

To assign the GC signals at m/z 221, we oxidized ethyl glycolate (2-R=O in Scheme 3.1, Sigma Aldrich, 98%) and 2-hydroxyethyl acetate (3-R=O in Scheme 3.1, TCI,

>60%) under high HO_2 condition to produce 2-oxo-3-ROOH and 3-oxo-2-ROOH in the system (oxidation mechanism in Scheme 3.5). The resulting gas chromatograms at m/z 189 and m/z 221 from the experiments are shown in Figure B.2 in Section B.7.1. Comparing with the peaks at the same m/z from a 2-EE and an EVE experiment, we identify the two m/z 221 peaks eluting at higher temperature. We speculate that the first GC peak at m/z 221 corresponds to the compound we denote as 2-OH-3-OOH-R'CHO (Figure 3.1). We propose a formation mechanism of this compound in Scheme 3.6. In the EVE system, it is likely formed through consecutive H-shift processes. In the 2-EE system, we speculate that it is produced from heterogeneous chemistry of the 1,2-epoxy-3-ROOH. We hypothesize that the epoxide undergoes acid-catalyzed ring-opening reactions on the chamber walls or in the CIMS instrument.^{56,57} The observation of 2-OH-3-OOH-R'CHO likely indicate the formation of 1,2-epoxy-3-ROOH as predicted by theory (Scheme 3.2). The possibility for glycol ethers to form gas-phase epoxides suggests a route to formation of SOA, as such epoxides are known to be SOA precursors.^{58,59} The reactive uptake and ring-opening of gas-phase hydroxy-substituted epoxides on surfaces has been demonstrated to be a major pathway that leads to SOA formation under low NO_x conditions.^{56,58–60}



Scheme 3.5: Oxidation of ethyl glycolate (2-R=O) and 2-hydroxyethyl acetate (3-R=O) by OH under high HO_2 condition.

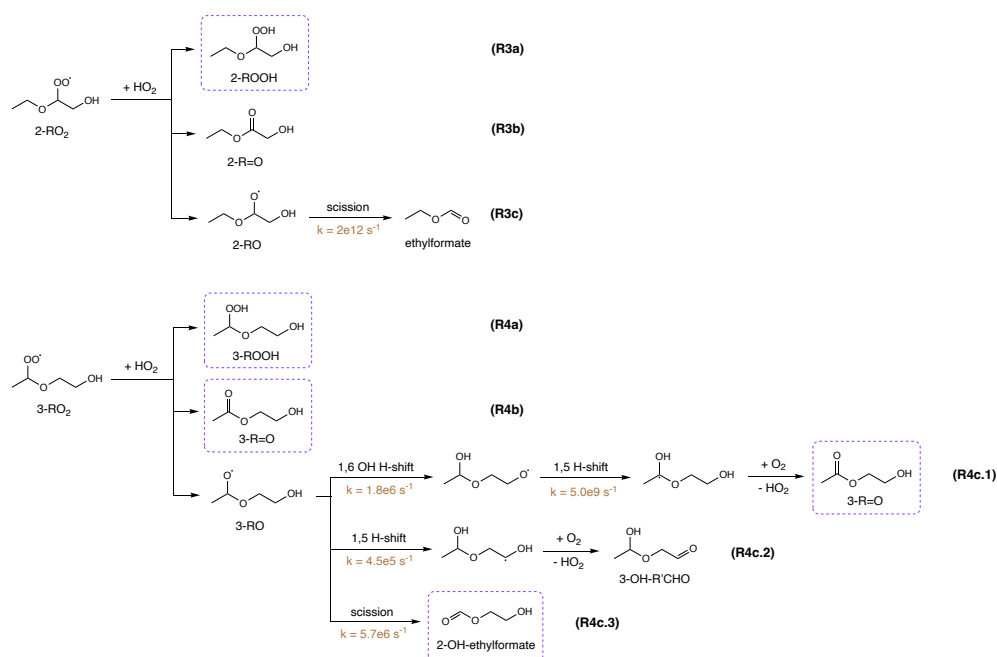


Scheme 3.6: Speculative formation pathways of 2-OH-3-OOH-R'CHO from a). 2-EE, and b). EVE. The mechanism for 2-EE may occur heterogeneously on the chamber walls or in the CIMS instrument.

3.3.2 Products Branching Ratios and H-shift Rate Coefficients

The following sections describe our estimation of the branching ratios of several reaction pathways and the RO₂ H-shift rate coefficients in 2-EE photo-oxidation mechanism. For each of these parameters, we also evaluate their variation with temperature by performing experiments under similar initial conditions at higher temperature of 309.5 ± 2 K. At elevated temperature, H-shift rates of RO₂ increase due to the high energy barrier along the H-shift reaction coordinate,^{3,6,52} while the bimolecular rate coefficients between RO₂ and HO₂ are expected to be slightly slower.

3.3.2.1 Branching Ratios for RO₂+HO₂ Reaction



Scheme 3.7: Mechanism of 2-RO₂+HO₂ (3a-3c) and 3-RO₂+HO₂ (4a-4c) reactions. Products quantifiable are highlighted in purple boxes. Rate coefficients for isomerization and decomposition of alkoxy radicals are calculated at 298.15K using the MC-TST method.³⁸ Calculated MC-TST alkoxy rate coefficients have uncertainties likely within a factor of 10. For the co-products and reagents in each pathway, refer to Scheme 3.1 and B.1.

We estimate the product branching ratios of reaction channels for reactions of 2-EE peroxy radicals with HO₂ by quantifying the closed-shell products of the bimolecular pathways. Reactions between HO₂ and peroxy radicals 2-RO₂ and 3-RO₂ are expected to form hydroperoxides (2-ROOH and 3-ROOH), carbonyls (2-R=O and 3-R=O), alkoxy radicals (2-RO and 3-RO) and their subsequent products (pathways a, b, and c for Reactions 3 and 4 in Scheme 3.7). Most products from the

$3\text{-RO}_2 + \text{HO}_2$ reaction form stable clusters with CF_3O^- , while from the $2\text{-RO}_2 + \text{HO}_2$ reaction, 2-ROOH is the only product that can be quantifiable (detection of 2-R=O is discussed in Section B.7.1). Thus, we use the measured yields of major $3\text{-RO}_2 + \text{HO}_2$ reaction products, i.e., 3-ROOH , 3-R=O , and 2-OH-ethylformate , to infer products branching ratios of $\text{RO}_2 + \text{HO}_2$ reactions in the 2-EE system. In the absence of secondary chemistry, the ratio of yields of the products should be equivalent to the ratio of their production. To derive a more accurate ratio of product yields, concentrations of the products (used in the analysis in following sections) are corrected by accounting for their secondary losses. The detailed procedure of data correction and potential biases in the procedure are described in Section B.4.

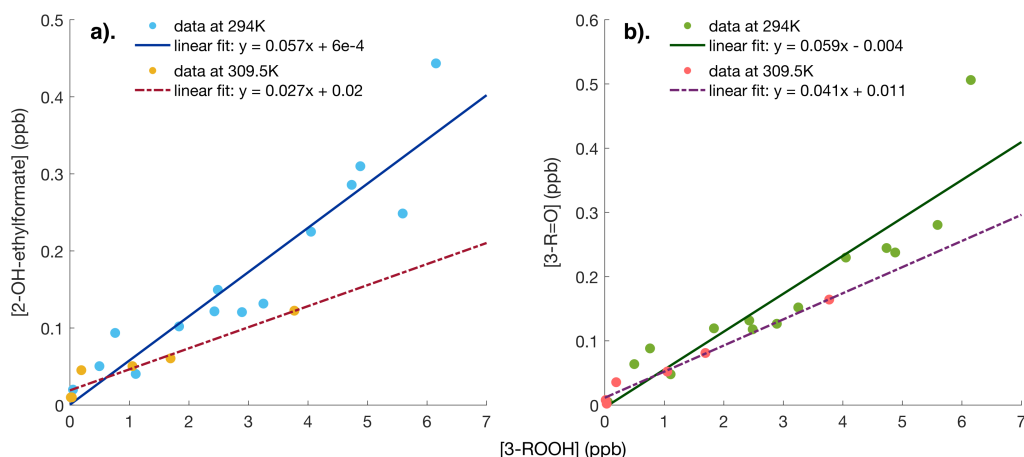


Figure 3.2: a). [2-OH-ethylformate] vs. [3-ROOH], and b). [3-R=O] vs. [3-ROOH] at ambient temperature (294K) and high temperature (309.5K). Solid lines are unweighted linear regression fits to ambient temperature data, and dashed lines are unweighted linear regression fits to high temperature data. The uncertainties in the data are mainly systematic ($\sim 21\%$) due to knowledge of the instrumental calibration detailed in Section B.6. Respective R^2 values of the linear fits are 0.87 (blue solid line), 0.92 (red dashed line), 0.83 (green solid line), and 0.97 (purple dashed line).

Figure 3.2 shows the concentrations of 3-R=O and 2-OH-ethylformate as a function of the concentration of 3-ROOH . At 294 K, the yield of 3-R=O relative to that of 3-ROOH is measured to be 0.059 ± 0.017 , and the yield of 2-OH-ethylformate relative to that of 3-ROOH is 0.057 ± 0.016 . At 309.5 K, the yield of 3-R=O relative to that of 3-ROOH is 0.041 ± 0.011 , and the yield of 2-OH-ethylformate relative to that of 3-ROOH is 0.027 ± 0.008 .

Since 3-R=O is produced both directly from $3\text{-RO}_2 + \text{HO}_2$ (Reaction 4b) and from isomerization of the 3-RO radical (Reaction 4c.1), deriving products branching ratios of $3\text{-RO}_2 + \text{HO}_2$ reaction also requires knowledge of branching fractions of 3-RO

unimolecular pathways. We investigate 3-RO chemistry by conducting a few experiments of 2-EE with NO, in which the production and reaction of alkoxy radicals are dominant. In these experiments, H₂O₂ still serves as source of OH radicals, and NO (sourced from cylinder containing 1993 ± 20 ppm in N₂, Matheson) is added instead of CH₃OH as the source of bimolecular reactants. The gas chromatograms and analysis of the results from NO experiments are in Section B.7.2. As shown in the chromatograms in Figure B.3(a), we observe high yields of decomposition products 2-OH-ethylformate (m/z 175), smaller yields of 3-R=O (m/z 189) from isomerization pathway R4c.1, and probably minimal amounts of 3-OH-R'CHO (m/z 189) from isomerization pathway R4c.2. The measured concentrations of 3-R=O (possibly together with 3-OH-R'CHO) and 2-OH-ethylformate suggest that the ratio of their production to be around 0.095 ± 0.024 (Figure B.5). Thus, we suggest the ratio between isomerization and decomposition channels ($(k_{4c.1} + k_{4c.2})/k_{4c.3}$) of 3-RO is $\sim 1/10$. Our finding that 2-OH-ethylformate is the dominant product of the unimolecular reactions of this alkoxy radical agrees with our MC-TST calculations, and this inferred branching ratio is well within the uncertainty of the computational prediction for alkoxy radical unimolecular reactions.³⁸

Given that there are still uncertainties in our understanding of the effect of chemical activation and temperature on the ratio between isomerization and decomposition channels of alkoxy radicals,^{61,62} here we assume that the 1:10 ratio of $(k_{4c.1} + k_{4c.2}) : k_{4c.3}$ also applies to 3-RO produced from HO₂ experiments and at elevated temperature. With this assumption, the branching fractions for 3-RO₂+HO₂ reaction pathways are listed in Table 3.1. We apply the resulting branching ratios in the box model for both 3-RO₂+HO₂ and 2-RO₂+HO₂ reactions.

Table 3.1: Branching ratios for reaction channels (4a)-(4c) for 3-RO₂+HO₂ reaction estimated from the observed product yields. Derivation of the uncertainties is detailed in Section B.6.

Reaction Channels	Branching ratios at 294 K	Branching ratios at 309.5 K
$k_{4a}k_4$	0.896 ± 0.026	0.936 ± 0.016
$k_{4b}k_4$	0.048 ± 0.013	0.035 ± 0.009
$k_{4c.1} \ k_{4c.2}k_4$	0.005 ± 0.002	0.003 ± 0.001
$k_{4c.3}k_4$	0.051 ± 0.014	0.026 ± 0.008

3.3.2.2 1,6 H-shift rate of 3-RO₂

We estimate the 1,6 H-shift rate of 3-RO₂ (which leads to formation of the hydroperoxyl aldehyde, 3-OOH-R'CHO, Scheme 3.2) from the variation in the yields of 3-ROOH and 3-OOH-R'CHO at different [HO₂]. The ratio of the yields of the two products is equivalent to the ratio between their formation rates:

$$\frac{[3\text{-ROOH}]}{[3\text{-OOH-R'CHO}]} = \frac{\alpha_{4a} k_{RO_2+HO_2} [3\text{-RO}_2] [HO_2]}{k_{1,6 \text{ H-shift}, 3\text{-RO}_2} [3\text{-RO}_2]} = \frac{\alpha_{4a} k_{RO_2+HO_2}}{k_{1,6 \text{ H-shift}, 3\text{-RO}_2}} [HO_2] \quad (3.2)$$

where α_{4a} indicates the branching fraction to ROOH formation derived in the previous section. Thus, the ratio between the yields of 3-ROOH and 3-OOH-R'CHO is expected to be proportional to [HO₂]. As illustrated in Figure 3.3, we observe a linear relationship between the ratio of product yields and [HO₂] at both ambient and elevated temperature. The slope is equal to the ratio between the bimolecular rate coefficient (with the branching to hydroperoxides α_{4a}) and the unimolecular H-shift rate coefficient ($\frac{\alpha_{4a} k_{RO_2+HO_2}}{k_{1,6 \text{ H-shift}, 3\text{-RO}_2}}$).

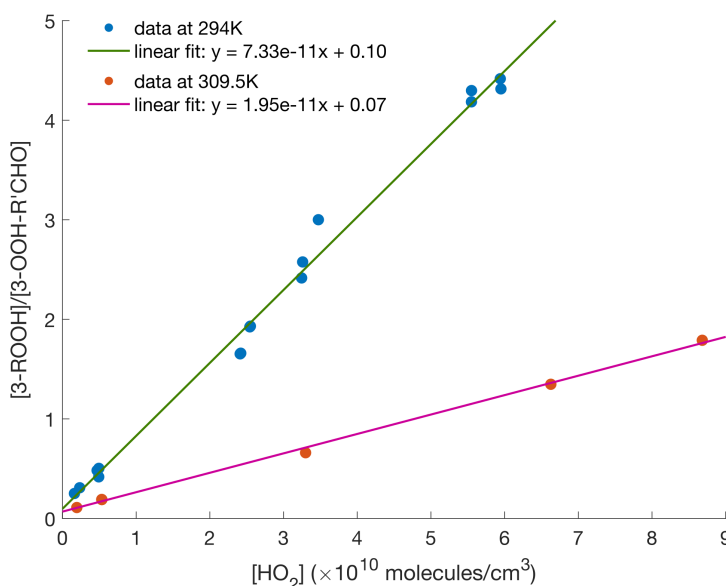


Figure 3.3: $[3\text{-ROOH}]/[3\text{-OOH-R'CHO}]$ vs. $[HO_2]$ at ambient temperature (294 K) and high temperature (309.5 K), and respective unweighted linear regression fits. The uncertainties in the data are mainly systematic and are detailed in Section B.6 ($\sim 25\%$ for concentration ratios and $\sim 17\%$ for $[HO_2]$). The respective R^2 values of the linear fits are 0.992 for ambient temperature data (green solid line), and 0.998 for high temperature data (pink solid line).

As shown in Figure 3.3, the slope is nearly 4 times smaller at high temperature, consistent with a much higher H-shift rate and higher yield of the autoxidation product

at elevated temperature. From the linear regression fitting, we derive the ratio of $\frac{\alpha_{4a}k_{RO_2+HO_2}}{k_{1,6 \text{ H-shift}, 3-RO_2}}$ at ambient temperature to be $(7.33 \pm 2.21) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1}$, and at high temperature to be $(1.95 \pm 0.59) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1}$. We evaluate the bimolecular rate coefficient of RO_2+HO_2 reaction based on derivations from Wennberg et al.¹⁹ and Jenkin et al.⁴⁶ Along with our derivation of the branching fractions of ROOH formation from the previous section, we estimate the 1,6 H-shift rate coefficient of 3- RO_2 to be $0.21 \pm 0.13 \text{ s}^{-1}$ at 294 K, and $0.67 \pm 0.42 \text{ s}^{-1}$ at 309.5 K. Both values agree well with computational prediction of the rate coefficient (0.21 s^{-1} and 0.57 s^{-1} respectively, uncertainty within a factor of 5). This estimated H-shift rate increases by approximately a factor of 3 when the temperature increases by $\sim 15 \text{ K}$.

3.3.2.3 1,5 H-shift rates of 2- and 3- RO_2

1,5 H-shifts of 2- and 3- RO_2 lead to formation of peroxy radicals 3-OO-2-ROOH and 2-OO-3-ROOH (Scheme 3.2), and are in competition with the reaction of 2- and 3- RO_2 with HO_2 leading to the formation of the corresponding hydroperoxides, 2-ROOH and 3-ROOH. In order to estimate the 1,5 H-shift rates, we compare $[2\text{-ROOH}]$ and $[3\text{-ROOH}]$ at varied $[HO_2]$. Assuming the rate coefficient for the reaction of HO_2 with 2- and 3- RO_2 are the same, the ratio of the yields of 2-ROOH and 3-ROOH is equal to the ratio of the steady-state concentrations of the two RO_2 :

$$\frac{[2\text{-ROOH}]}{[3\text{-ROOH}]} = \frac{\alpha_{4a}k_{RO_2+HO_2}[2\text{-}RO_2]_{ss}[HO_2]}{\alpha_{4a}k_{RO_2+HO_2}[3\text{-}RO_2]_{ss}[HO_2]} = \frac{[2\text{-}RO_2]_{ss}}{[3\text{-}RO_2]_{ss}} \quad (3.3)$$

where α_{4a} indicates the branching fraction to ROOH formation, and the subscript “ss” indicates steady state. To derive the expression for $[2\text{-}RO_2]_{ss}$ and $[3\text{-}RO_2]_{ss}$, we start with the rate equations for $[2\text{-}RO_2]$ and $[3\text{-}RO_2]$ in the mechanism:

$$\begin{aligned} \frac{d[2\text{-}RO_2]}{dt} = & \alpha_{2\text{-}RO_2}k_{OH+2EE}[2\text{-}EE][OH] - k_{RO_2+HO_2}[2\text{-}RO_2][HO_2] \\ & - k_{1,5 \text{ H-shift}, 2\text{-}RO_2}[2\text{-}RO_2] \end{aligned} \quad (3.4)$$

$$\begin{aligned} \frac{d[3\text{-}RO_2]}{dt} = & \alpha_{3\text{-}RO_2}k_{OH+2EE}[2\text{-}EE][OH] - k_{RO_2+HO_2}[3\text{-}RO_2][HO_2] \\ & - k_{1,5 \text{ H-shift}, 3\text{-}RO_2}[3\text{-}RO_2] - k_{1,6 \text{ H-shift}, 3\text{-}RO_2}[3\text{-}RO_2] \end{aligned} \quad (3.5)$$

where $\alpha_{2\text{-RO}_2}$ and $\alpha_{3\text{-RO}_2}$ are the branching fractions of 2-RO₂ and 3-RO₂ formation in the initiation step (Scheme 3.1). Assuming steady state for [2-RO₂] and [3-RO₂] will then yields:

$$[2\text{-RO}_2]_{ss} = \frac{\alpha_{2\text{-RO}_2} k_{OH+2EE} [2\text{-EE}] [\text{OH}]}{k_{RO_2+HO_2} [\text{HO}_2] + k_{1,5 \text{ H-shift}, 2\text{-RO}_2}} \quad (3.6)$$

$$[3\text{-RO}_2]_{ss} = \frac{\alpha_{3\text{-RO}_2} k_{OH+2EE} [2\text{-EE}] [\text{OH}]}{k_{RO_2+HO_2} [\text{HO}_2] + k_{1,5 \text{ H-shift}, 3\text{-RO}_2} + k_{1,6 \text{ H-shift}, 3\text{-RO}_2}} \quad (3.7)$$

and the ratio between [2-RO₂]_{ss} and [3-RO₂]_{ss} equals:

$$\frac{[2\text{-RO}_2]_{ss}}{[3\text{-RO}_2]_{ss}} = \frac{\alpha_{2\text{-RO}_2}}{\alpha_{3\text{-RO}_2}} \frac{k_{RO_2+HO_2} [\text{HO}_2] + k_{1,5 \text{ H-shift}, 3\text{-RO}_2} + k_{1,6 \text{ H-shift}, 3\text{-RO}_2}}{k_{RO_2+HO_2} [\text{HO}_2] + k_{1,5 \text{ H-shift}, 2\text{-RO}_2}} \quad (3.8)$$

Therefore, in the limit where [HO₂] is sufficiently high that the rate of bimolecular reactions vastly exceeds that of unimolecular H-shifts, the ratio of the yields of 2-ROOH and 3-ROOH is equal to the ratio of the branching fractions of 2-RO₂ and 3-RO₂ formation pathways, $\alpha_{2\text{-RO}_2}/\alpha_{3\text{-RO}_2}$. At lower HO₂ levels, the H-shift rates become significant in alternating the [2-ROOH]/[3-ROOH] ratio. Higher 3-RO₂ H-shift rates lead to a higher ratio, while higher 2-RO₂ H-shift rates result in a lower ratio.

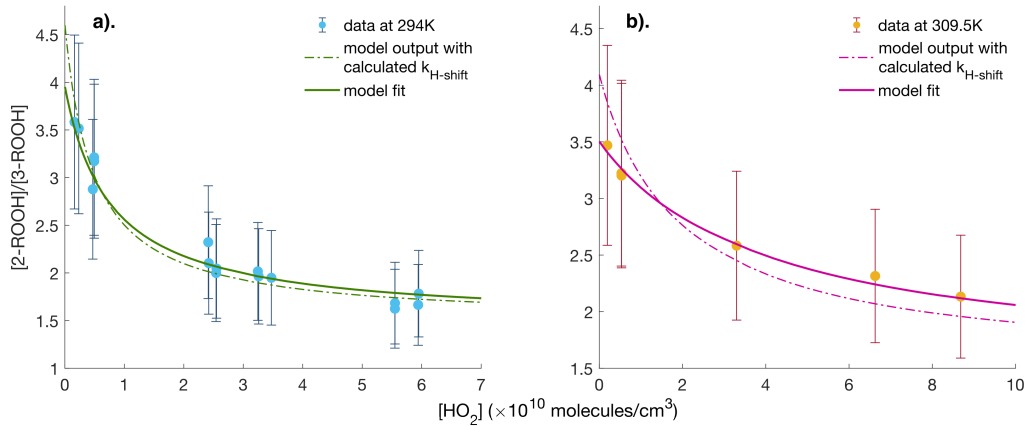
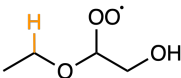
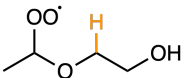
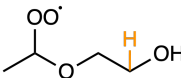


Figure 3.4: [2-ROOH]/[3-ROOH] vs. [HO₂] at **a).** ambient temperature (294 K) and **b).** high temperature (309.5 K). The solid lines represent the optimized model fit to the data. The dashed lines represent the model output based on calculated H-shift rate coefficients. The uncertainties in the data are dominated by common systematic errors as detailed in Section B.6 (~25% for concentration ratios and ~17% for [HO₂]).

Based on Equation 3.8, we adjust $\alpha_{2\text{-RO}_2}/\alpha_{3\text{-RO}_2}$ and the RO₂ 1,5 H-shift rate coefficients in the box model to minimize the difference between the simulation and the observations of [2-ROOH]/[3-ROOH] as shown in Figure 3.4. We applied our derivations of branching ratios and rate coefficients described in previous sections (RO₂+HO₂ branching ratios and $k_{1,6\text{ H-shift},3\text{-RO}_2}$) in the simulations. This analysis suggest that the ratio between 2-RO₂ and 3-RO₂ formation from the OH + 2-EE reaction is 1.5 ± 0.4 , which is in good agreement with the structure-activity relationship (SAR) predictions (~ 1.3).^{47,63,64} From the best fit of the box model to the experimental observations, we estimate 1,5 H-shift rate coefficient of 2-RO₂ to be $0.13 \pm 0.10\text{ s}^{-1}$ at 294 K and $0.54 \pm 0.42\text{ s}^{-1}$ at 309.5 K, while that of 3-RO₂ to be $0.13 \pm 0.10\text{ s}^{-1}$ at 294 K and $0.59 \pm 0.46\text{ s}^{-1}$ at 309.5 K. These values are well within the factor-of-5 uncertainty of the MC-TST H-shift rate coefficients (see Table 3.2). The 1,5 H-shift rates are estimated to increase by approximately a factor of 4 with a temperature increase of $\sim 15\text{ K}$.

Table 3.2: H-shift rate coefficients (in s^{-1}) of simple 2-EE peroxy radicals from calculations and experiments. Rate coefficients derived from experimental results shown here are applied in subsequent box model simulations described in following sections. The hydrogen shown explicitly (in orange) is the one being abstracted during the specified H-shift reaction. Derivation of uncertainties is detailed in Section B.6.

Temperature	Method	Peroxy Radicals		
		2-RO ₂	3-RO ₂	
		 1,5 H-shift	 1,5 H-shift	 1,6 H-shift
294K	Theory	0.083	0.045	0.21
	Experiment	0.13 ± 0.10	0.13 ± 0.10	0.21 ± 0.13
309.5K	Theory	0.26	0.14	0.57
	Experiment	0.54 ± 0.42	0.59 ± 0.46	0.67 ± 0.42

The estimated H-shift rates of 2- and 3-RO₂ are listed in Table 3.2. The 1,5 H-shifts of 2-EE RO₂ are faster than the similar 1,5 H-shift process of RO₂ from alkane and ketone compounds likely due to a reduction in the barrier for hydrogen abstraction alpha to the ether.^{4,6,65} Similarly, due to presence of -OH group, the 1,6 H-shift of 3-RO₂ is faster than its 1,5 H-shift despite a less favorable transition state geometry (seven vs. six-membered ring). The higher reaction barrier for the 1,5 H-shifts also increases its temperature sensitivity compared to the 1,6 H-shift (4 times vs. 3 times

increase at high temperature).^{6,52}

3.3.2.4 H-shift rates of Peroxy Radicals 2-OO-3-ROOH and 3-OO-2-ROOH

The change in the yields of 3-OOH-R'=O at different HO₂ concentrations is sensitive to the H-shift rates of the 2nd-generation peroxy radicals 2-OO-3-ROOH and 3-OO-2-ROOH. Recall that the compound 3-OOH-R'=O is formed through bimolecular chemistry of 2-OO-3-ROOH (Scheme 3.4). The reaction with NO/HO₂ produces the alkoxy radical 2-O-3-ROOH, which then decomposes to form 3-OOH-R'=O. The yield of 3-OOH-R'=O is directly constrained by the competition between H-shifts and bimolecular pathways of 2-OO-3-ROOH. It is also constrained by the competition between H-shifts and bimolecular reactions of 2-RO₂ and 3-RO₂, as well as the H-shift rates of 3-OO-2-ROOH, all of which control the yields of and the equilibrium between the two hydroperoxy RO₂. Thus, 3-OOH-R'=O is expected to have low yield at both extremely high and low [HO₂]. At high [HO₂], less 2-OO-3-ROOH is formed through H-shift processes due to competition with the HO₂ reaction, while at low HO₂ level, 2-OO-3-ROOH preferentially undergoes H-shift rather than forming the intermediate alkoxy radical.

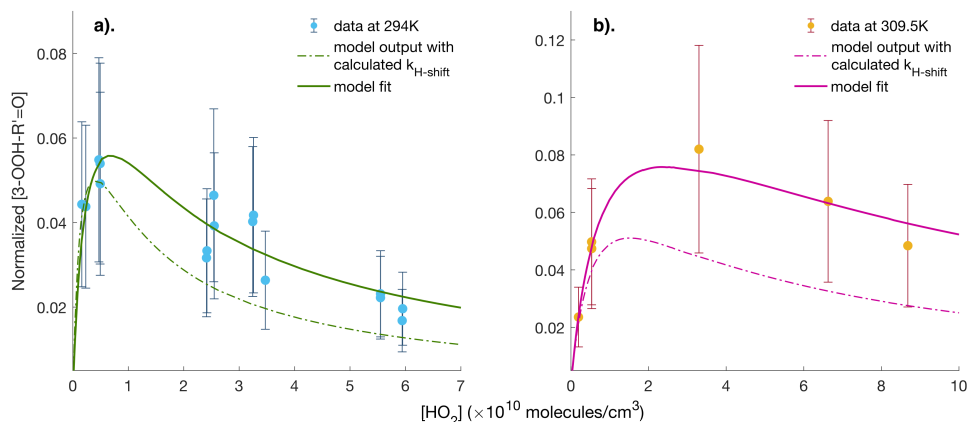


Figure 3.5: [3-OOH-R'=O] normalized by $\Delta[2\text{-EE}]$ vs. [HO₂] at **a).** 294 K and **b).** 309.5 K. The solid lines represent the optimized model results. The dashed lines represent the model output based on calculated H-shift rate coefficients. The uncertainties in the data are dominated by common systematic errors as detailed in Section B.6 (~45% for normalized concentrations and ~17% for [HO₂]).

Shown in Figure 3.5 is [3-OOH-R'=O] normalized by the amount of 2-EE oxidized ($\Delta[2\text{-EE}]$) as a function of [HO₂]. With knowledge of 2-RO₂ and 3-RO₂ reaction rates and product branching ratios from previous sections, we optimize the H-shift rate coefficients for the two hydroperoxy RO₂ in the box model (Scheme 3.2) by

minimizing the difference between the measured and simulated 3-OOH-R'=O yield as a function of $[\text{HO}_2]$. For the bimolecular reaction 2-OO-3-ROOH/3-OO-2-ROOH + HO_2 , we evaluate the rate coefficients based on Wennberg et al.¹⁹ and Jenkin et al.,⁴⁶ and adopt the products branching ratios from the study on methyl vinyl ether RO_2 , a similarly multifunctional oxygenated RO_2 , by Praske et al.⁵¹ We provide our estimates (using the box model) for the H-shift rate coefficients for the two RO_2 in Table 3.3. We estimate that the H-shift rates increase by around a factor of 2 between 294 K and 309.5 K. However, given the large uncertainties underlying our measurements (see Section B.6 for detailed description of uncertainty analysis), this estimate is highly uncertain.

Given the experimental constraints, we are unable to determine stereoisomer-specific H-shift rates for the hydroperoxy RO_2 (like those in Scheme 3.2), as all our detectable products only possess one chiral center and cannot be separated on the column. Our MC-TST calculations shows that there can be major difference in the H-shift rates for different diastereomers of the same peroxy and alkoxy structural radicals, as shown in Schemes 3.2 and 3.4. In some cases, such differences can be attributed to the differences in the hydrogen bonding stabilization of reactants and transition states, but such clear reasons are not always available.^{3,16,37} The variation in the H-shift rates of different stereoisomers of the same radical may lead to enhancement of specific diastereomers of certain SOA precursors, such as the epoxide in 2-EE system, which may subsequently influence their transformation in the atmosphere and the properties of formed SOA.³⁷

3.3.2.5 Formation of 3-oxo-2-ROOH and 2-oxo-3-ROOH

We partially constrain the formation pathways of major autoxidation products, the ketohydroperoxides 3-oxo-2-ROOH and 2-oxo-3-ROOH (Scheme 3.2), from the ratio in their yields, $[\text{3-oxo-2-ROOH}]/[\text{2-oxo-3-ROOH}]$. Measuring the yields of 3-oxo-2-ROOH and 2-oxo-3-ROOH are challenging, however, due to their low volatilities. The vapor pressure of the two compounds estimated by the EVAPORATION method⁶⁶ is on the order of 10^{-7} atm at room temperature. As a result of the low volatility, these compounds are expected to deposit significantly onto surfaces of the chamber and the instrument. In addition to vapor-wall loss, since they eluted from the column at the highest temperature, the ketohydroperoxides are also more susceptible to losses in the column, as they may undergo thermolysis at the elevated temperature required to transmit them.^{67,68} As a result, we observe a

low GC transmission rate of ~25-30% for the m/z 221 compounds. We are also unable to isolate the fractional losses of the individual isomers from our data.

Despite the difficulties in quantifying the two hydroperoxides, we do observe a trend in the ratio of their detected yields ($[3\text{-oxo-2-ROOH}]/[2\text{-oxo-3-ROOH}]$) as the function of $[\text{HO}_2]$. We estimate the ratio by calculating the ratio between the heights of GC peaks for the two compounds. The ratio determined from GC peak integration is likely biased low, since according to our GC peak assignment, 3-oxo-2-ROOH elutes later than 2-oxo-3-ROOH and is thereby likely subject to more losses due to surface contact and potential chemical conversions in the column. In Figure 3.6, we show the relationship between $[3\text{-oxo-2-ROOH}]/[2\text{-oxo-3-ROOH}]$ and $[\text{HO}_2]$, where the green markers represent the ratio estimated from experimental data. The ratio is higher at moderate HO_2 levels and decreases at both high and low HO_2 levels. This feature may arise due to another pathway that produces 3-oxo-2-ROOH in addition to the reactions of 2-OO-3-ROOH and 3-OO-2-ROOH: the 1,5 H-shift of 2-OO-3-ROH peroxy radical (see Scheme 3.4). The radical 2-OO-3-ROH is formed by isomerization of alkoxy radical 3-O-2-ROOH, which is produced from bimolecular reactions of 3-OO-2-ROOH.

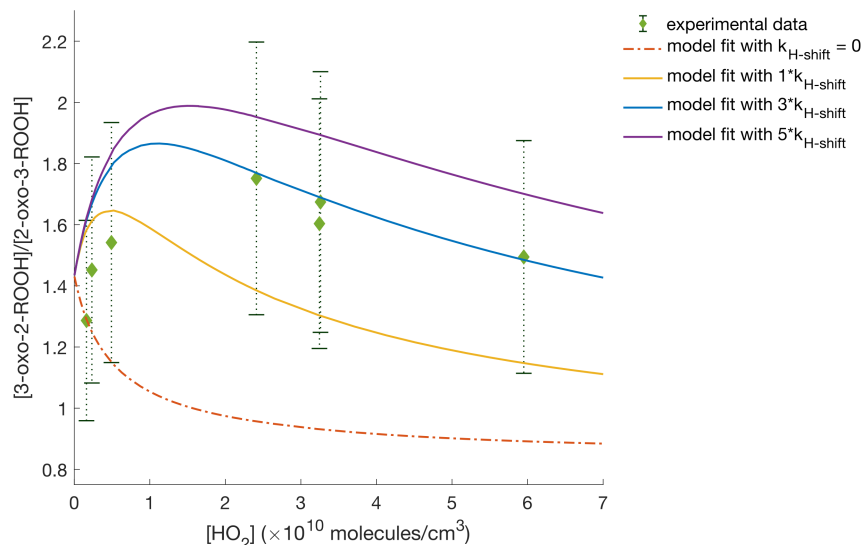


Figure 3.6: $[3\text{-oxo-2-ROOH}]/[2\text{-oxo-3-ROOH}]$ vs. $[\text{HO}_2]$ at ambient temperature (294 K). The results at high temperature (309.5 K) is in Figure B.6. The data (in green markers) are from experiments at 294 K. The orange dashed line is the result from model run without the 1,5 H-shift reaction of 2-OO-3-ROH radical, and the solid lines are results from model run with the 1,5 H-shift rate coefficient of 2-OO-3-ROH scaled by 1 (yellow), 3 (blue), and 5 (purple) times the MC-TST calculated rate coefficient. The uncertainties in the data are dominated by common systematic errors as detailed in Section B.6 (~25% for concentration ratios and ~17% for $[\text{HO}_2]$).

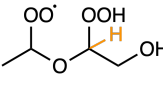
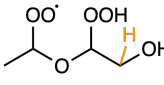
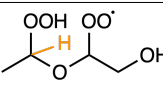
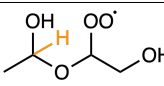
We also show in Figure 3.6 the ratio of [3-oxo-2-ROOH]/[2-oxo-3-ROOH] from model results with the 1,5 H-shift rate coefficient of 2-OO-3-ROH being set to 0, the calculated value, triple the calculated value, and five times of the calculated value. Without the H-shift reaction, the ratio of product yields at high $[\text{HO}_2]$ remains low and close to [3-OO-2-ROOH]/[2-OO-3-ROOH] at equilibrium since the bimolecular reactions of the two hydroperoxy RO_2 are the major source of the compounds. As HO_2 level decreases, the ratio increases as the source of 3-oxo-2-ROOH shifts to the more abundant 2-OO-3-ROOH radical. When we turn on the H-shift reaction of 2-OO-3-ROH radical, we observe an increase in [3-oxo-2-ROOH]/[2-oxo-3-ROOH]. This pathway provides an extra source for 3-oxo-2-ROOH, and, similar to 3-OOH- $\text{R}'=\text{O}$, produces larger amounts of 3-oxo-2-ROOH at moderate $[\text{HO}_2]$ and smaller amounts at high and low $[\text{HO}_2]$. We notice that the ratio modeled from various H-shift rates converge to the same value (~ 1.43) at low $[\text{HO}_2]$, where the production of the two ketohydroperoxides is dominated by the H-shift reactions of 2-OO-3-ROOH and 3-OO-2-ROOH. It also demonstrates that the additional formation of 3-oxo-2-ROOH arising from the 1,5 H-shift of 2-OO-3-ROH being assessed here requires a bimolecular reaction with HO_2 , which does not occur at very low $[\text{HO}_2]$. The ratio between the two products at low $[\text{HO}_2]$ is mainly determined by the equilibrium between and the H-shift rates of the two hydroperoxy RO_2 . Thus, we expect that a better measurement of this ratio can provide another constraint for the unimolecular pathways of the two RO_2 .

As we increase the 1,5 H-shift rate coefficient of 2-OO-3-ROH in the model, the yield of 3-oxo-2-ROOH relative to that of 2-oxo-3-ROOH peaks at greater $[\text{HO}_2]$, and the modeled trend of the ratio between the two products becomes more consistent with the experimental results. The best simulation, though by no means perfect given the bias and large uncertainties in relevant parameters, occurs for H-shift rates ~ 3 times faster than calculated (Table 3.3).

3.4 Conclusions

The RO_2 formed in the oxidation of 2-ethoxyethanol (2-EE) undergo efficient autoxidation through intramolecular H-shift processes to produce low-volatility products and potential SOA precursors. Based on our calculations and estimations of the H-shift rate coefficients of 2-EE RO_2 (Table 3.2 and 3.3), many of the H-shift reactions may occur at rates of 0.1 s^{-1} or faster, corresponding to a RO_2 bimolecular lifetime at 10 s or shorter. We may expect that the H-shift reactions of the substrate outrun its biomolecular chemistry when NO concentrations are ~ 0.5 ppb or lower on warm

Table 3.3: H-shift rate coefficients (in s^{-1}) of multifunctional 2-EE peroxy radicals from calculations and experiments. Rate coefficients derived from experimental results are applied in box model simulations. The hydrogen shown explicitly (in orange) is the one being abstracted during the specified H-shift reaction. Derivation of uncertainties is detailed in Section B.6. ^a We refrain from providing an estimate for the 1,5 H-shift rate coefficient of 2-OO-3-ROH at high temperature as there is major divergence between the model simulation and experimental observations. See Section B.7.3 for more details.

Temperature	Method	Stereoisomer	Peroxy Radicals	
			3-OO-2-ROOH	
			 1,5 H-shift	 1,6 H-shift
294 K	Theory	R, S	0.0095	0.015
		S, S	0.049	0.15
	Experiment		0.047 + 0.059/−0.043	0.12 + 0.15/−0.11
309.5 K	Theory	R, S	0.034	0.055
		S, S	0.15	0.38
	Experiment		0.091 + 0.12/−0.084	0.23 + 0.29/−0.21
	Method	Stereoisomer	Peroxy Radicals	
			2-OO-3-ROOH	2-OO-3-ROH
			 1,5 H-shift	 1,5 H-shift
294 K	Theory	R, S	0.064	0.090
		S, S	0.022	0.22
	Experiment		0.050 + 0.064/−0.046	~ 0.57
309.5 K	Theory	R, S	0.19	0.30
		S, S	0.082	0.66
	Experiment		0.11 + 0.14/−0.10	— ^a

summer afternoons.

It is likely that other glycol ether compounds will also generate substantial yields of hydroperoxide and carbonyl-rich low-volatility autoxidation products under similar atmospheric conditions. The more carbon and oxygen rich glycol ether substrates are likely to produce autoxidation products with extremely low vapor pressure, which readily contributes to SOA formation. The glycol ethers with longer carbon chains, (such as 2-(2-ethoxyethoxy)ethanol, also known as Carbitol) may undergo consecutive H-shifts, creating new QOOH centers on the carbon backbone and

increasingly oxygenated RO₂ to produce HOMs. This chemistry may explain the higher SOA yields observed for several glycol ether and ether compounds under NO_x-free conditions compared to NO_x-present conditions.^{12,21,69}

As a result of successful policies to reduce emissions of NO_x and fossil fuel VOCs in urban areas, both the chemical state and major VOC source of the modern urban atmosphere has been changing.^{3,9,11} As VCPs becomes a major source of urban VOC emission, it is increasingly important to understand the autoxidation chemistry of those compounds to fill our knowledge gap regarding SOA growth and new particle formation in the low NO_x environment. Since many VCPs such as glycol ethers are more oxygenated and functionalized than fossil fuel hydrocarbons, H-shift rates of VCP RO₂ are likely higher due to activation of the C-H bonds by the substituents, which lowers the barrier height for the H-shift.^{6,53} Further investigations on photochemical pathways of VCP compounds, especially their autoxidation chemistry, are essential for understanding the impact of these emissions on air quality.

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*Chapter 4*AUTOXIDATION OF LONG-CHAIN DIETHERS:
1,2-DIETHOXYETHANE

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- (1) Yu, H.; Almeida, T. G.; Rezgui, S. P.; Salo, V.-T.; Crounse, J. D.; Stoltz, B. M.; Kjaergaard, H. G.; Wennberg, P. O. Stealing from a distant neighbor: an unexpectedly fast long-span peroxy radical hydrogen-shift reaction in a long-chain diether. *Chemical Science* **2026**, DOI: 10.1039/D5SC10150F,

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Abstract

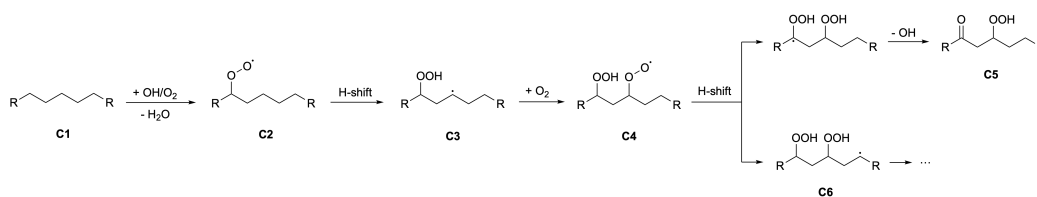
Gas-phase autoxidation is an atmospheric chemistry reaction mechanism capable of transforming volatile organic compounds (VOCs) into highly oxygenated organic molecules (HOMs) that contribute to secondary organic aerosol (SOA) formation and growth. The key steps in this mechanism are intramolecular hydrogen shift (H-shift) reactions in organic peroxy radicals (RO_2). For acyclic saturated molecules, these H-shift reactions are generally sufficiently slow that they cannot compete with atmospheric bimolecular reactions with NO_x species, except for the 1,5 and 1,6 H-shifts, occurring via transition states (TS) of six- and seven-membered rings. Here, we report a surprisingly fast long-range H-shift reaction in a RO_2 formed in the photo-oxidation of a volatile diether. In 1,2-diethoxyethane (1,2-DEE), we observe experimentally a 1,8 H-shift reaction that occurs with a rate coefficient on the order of $\sim 1 \text{ s}^{-1}$ at 294 K – a rate that outcompetes all other RO_2 unimolecular chemistry in the system and will, under most atmospheric conditions, outcompete bimolecular processes as well. Theoretical calculations indicate that activation of the C-H bond by an α -oxyl substituent and weaker transannular strain in the 1,8 H-shift transition state, combined with inductive deactivation of C-H bonds by a β -oxyl group at the abstraction site of competing 1,5 and 1,6 H-shifts, enable the longer-span 1,8 H-shift to be competitive. Our findings broaden the recognized reactivity of functionalized RO_2 and highlight the potential for structurally diverse VOCs to undergo unexpected autoxidation pathways, producing HOMs at greater yield and with higher molecular complexity than previously anticipated.

4.1 Introduction

Volatile organic compounds (VOCs) are emitted to the atmosphere in large quantities by both anthropogenic and biogenic sources and play an important role in the chemical composition of Earth's troposphere.¹ The gas-phase oxidation of VOCs, as the primary chemical transformation pathway of VOCs in the atmosphere, alters their chemical properties, as well as their impact on air quality, human health, and global climate.² The oxidation process is usually initiated by VOC reactions with strong oxidants (most importantly OH radicals but also O₃ and NO₃ radicals) that leads to formation of alkyl radicals (R·), followed by the rapid addition of oxygen (O₂) yielding peroxy radicals (RO₂). The subsequent chemistry of RO₂, which governs the chemical fate of the VOC, is diverse, ranging from unimolecular isomerization reactions to bimolecular reactions with other radicals such as NO, HO₂, and other RO₂.^{3,4} The molecular structure of the RO₂ and the atmospheric conditions determine which reaction pathways will be competitive.^{5,6} The pathways that lead to formation of low-volatility organic species, as potential precursors to formation of secondary organic aerosol (SOA), a major component of atmospheric fine particulate matter, are particularly of interest to atmospheric scientists. For example, the terminating channel of RO₂ bimolecular reactions, which add an oxygen-containing functional group, such as a nitrate (–ONO₂) or hydroperoxy (–OOH) group, to the carbon backbone of VOC, are considered an important pathway that lowers the volatility of organic species in the atmosphere.^{7,8}

Gas-phase autoxidation, which is initiated by a RO₂ unimolecular reaction pathway, is also capable of producing low-volatility organic products (Scheme 4.1).^{9,10} The key step in atmospheric autoxidation is an intramolecular RO₂ hydrogen shift (H-shift) reaction, where the peroxy group abstracts an H atom from the carbon backbone of the radical to produce a hydroperoxyalkyl radical (often denoted as QOOH). An O₂ molecule then quickly adds to the QOOH to form a more oxidized hydroperoxy RO₂.¹¹ These second-generation RO₂ can undergo subsequent rounds of isomerization and O₂ addition, leading to rapid formation of highly oxygenated oxidation products, potentially with multiple hydroperoxide groups and very low volatility. These highly oxygenated organic molecules (HOMs) have been shown to play a role in the formation of new particles and readily undergo gas-particle transfer to existing aerosol.^{10,12}

With the recent successful reduction in urban NO_x emissions, a major contributor of RO₂ bimolecular loss, the formation of HOMs through RO₂ autoxidation is



Scheme 4.1: Key steps in autoxidation of an example VOC. The compound C1 first reacts with OH radical and O₂ to form a peroxy radical (C2), which undergoes an H-shift forming a hydroperoxide functionality and a radical center on the carbon from which the H atom was abstracted, also known as a hydroperoxyalkyl radical or QOOH (C3). Subsequent addition of O₂ forms a hydroperoxy RO₂ (C4), which can undergo further H-shifts. The reaction sequence can either be terminated by abstracting the H atom α to the hydroperoxide group and losing a OH radical to form a ketohydroperoxide (C5), or continue by abstracting a H atom from an unsubstituted carbon to form a new, more oxidized QOOH (C6).

becoming increasingly important in urban atmospheres. In regions where NO levels become sufficiently low (0.05 to 1 ppb), a condition common in nowadays North America and Europe,^{13–15} RO₂ can survive for 10 – 100 s before reacting with other bimolecular reactants (Table 4.1), allowing RO₂ H-shift chemistry even with rate coefficients as low as $\sim 0.05 \text{ s}^{-1}$ to compete with RO₂ bimolecular pathways.¹¹ Evaluating the H-shift rate coefficients for RO₂ from different classes of VOCs thus becomes essential for accurately assessing their atmospheric oxidation potential and addressing current uncertainties in SOA production.

Table 4.1: Typical atmospheric concentrations of RO₂ bimolecular reactants and associated RO₂ lifetimes in urban and suburban environments. Concentrations of bimolecular reactants are adopted from Ren et al.,¹⁶ Praske et al.,¹¹ and Ma et al.¹⁷ Rate coefficients for RO₂ bimolecular reactions are adopted from Jenkin et al.,⁴ and corresponding rate constants and RO₂ lifetimes are calculated at ambient temperature of 298 K and sea level pressure of 10⁵ Pa.

[NO]	$k_{\text{RO}_2+\text{NO}}[\text{NO}]$	$\tau_{\text{RO}_2+\text{NO}}$
0.05 – 0.5 ppb	0.01 – 0.10 s ⁻¹	10 – 100 s
[HO ₂]	$k_{\text{RO}_2+\text{HO}_2}[\text{HO}_2]$	$\tau_{\text{RO}_2+\text{HO}_2}$
20 ppt	0.008 s ⁻¹	125.0 s
[RO ₂]	$k_{\text{RO}_2+\text{RO}_2}[\text{RO}_2]$	$\tau_{\text{RO}_2+\text{RO}_2}$
20 ppt	$8 \times 10^{-4} \text{ s}^{-1}$	1250 s

Previous studies have identified various general trends in H-shift reactivity that provide qualitative information about the potential for different RO₂ H-shifts. Studies have shown that the rate of H-shift process is affected by the molecular structure of the involved RO₂.^{9,18,19} At ambient temperature, the H-shift rate coefficients of RO₂ from straight-chain alkanes are found to be negligible ($< 10^{-3} \text{ s}^{-1}$), while certain

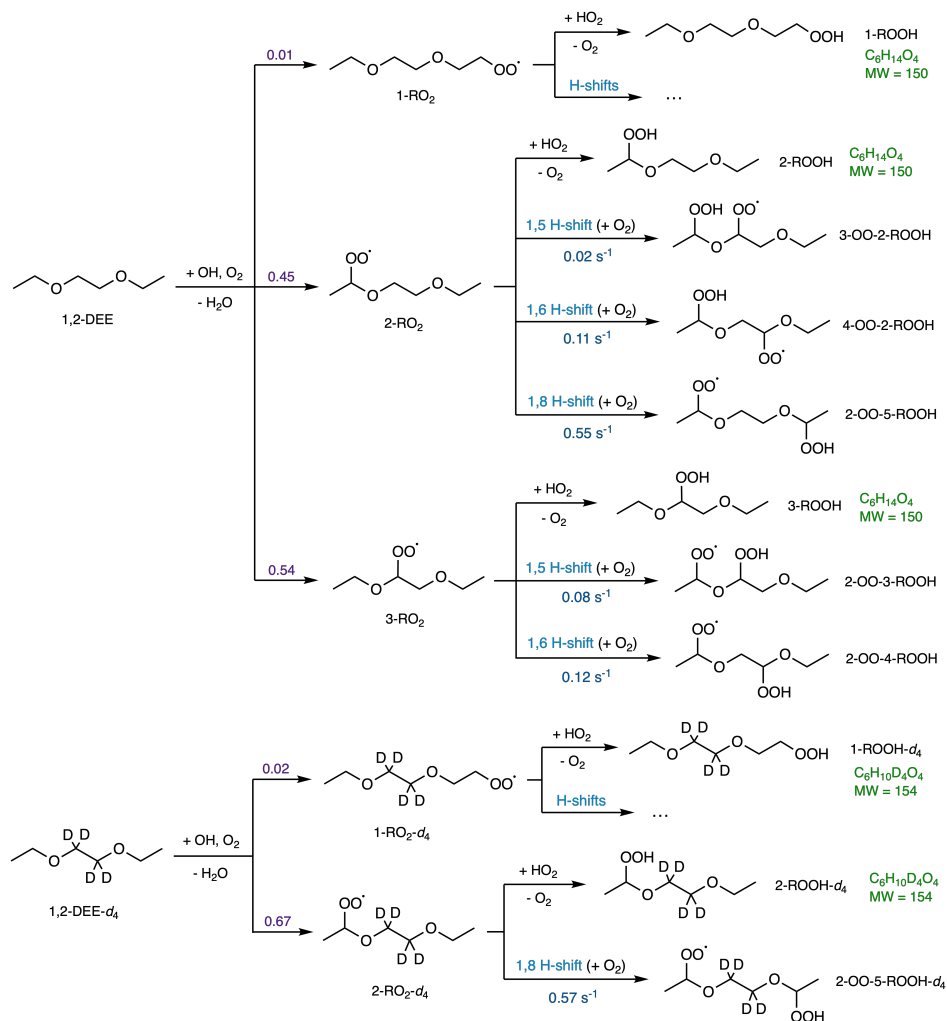
functional groups at the carbon center from which the hydrogen is abstracted increase the lability of C-H bonds and thereby lower the barrier to H atom transfer.^{18,20} For example, in our recent studies on simple ether and glycol ether compounds, we demonstrate that H-shifts where the abstraction site is α to a hydroxyl group (-OH) or ether oxygen (-COC-) can proceed at rate of $\sim 0.1 \text{ s}^{-1}$ at laboratory temperature of 294 K.^{21–23} H-shift reactions that involve abstraction of an aldehydic (C=O) or allylic (-C-C=C) hydrogen can have reaction rate coefficients reaching $\sim 1 \text{ s}^{-1}$ due to stabilization of the transition state by resonance.^{18,19,24,25} Another factor that affects the H-shift rates is the geometry of the ring-like H-shift transition state (TS).^{12,18,19,26} One important feature is the number of atoms in the ring-like structure of the TS. In general, a 1,5 and 1,6 H-shift, with a TS of six and seven-membered ring, is favorable for RO₂ H-shift, while TS with a smaller ring (e.g. 1,4 H-shift) is restricted due to high barriers, and formation of a larger ring (e.g. 1,8 H-shift and beyond) is considered entropically unfavorable.^{12,18,19} Thus, both short- and long-range H-shifts are regarded kinetically uncompetitive and often excluded in evaluations of RO₂ autoxidation chemistry.

In this study, we report the discovery of an unexpected fast 1,8 H-shift reaction at $\sim 1 \text{ s}^{-1}$ in a RO₂ derived from a long-chain diether compound: 1,2-diethoxyethane (1,2-DEE, also known as ethylene glycol diethyl ether). The compound is chosen as a model system to investigate the autoxidation chemistry of long-chain ethers and glycol ethers with multiple ether linkages – a structural motif common in compounds used as organic solvents in industrial and consumer products.^{27–29}

The general reaction mechanism for 1,2-DEE oxidation is shown in Scheme 4.2. To isolate the 2-RO₂ 1,8 H-shift from other H-shift pathways, we synthesize a selectively deuterated 1,2-DEE (1,2-DEE-*d*₄ in Scheme 4.2), where hydrogen atoms on the interior carbon centers are replaced by deuterium (D) atoms. Due to changes in zero-point vibrational energy and the much lower quantum tunneling of deuterium compared to hydrogen,^{30–32} the fraction of 2-RO₂ among all initial deuterated RO₂ is enhanced, and the rates of 1,5 and 1,6 H-shifts to this peroxy radical are expected to decrease by more than an order of magnitude.^{11,33} Thus, in 1,2-DEE-*d*₄, most autoxidation products from the deuterated precursor arise only from the 1,8 H-shift.

To estimate the rate coefficients of major H-shift reactions in 1,2-DEE, we perform a series of chamber experiments on OH-initiated photo-oxidation of 1,2-DEE where competition between RO₂ bimolecular and unimolecular chemistry are modulated by varying the HO₂ concentrations, and the experimental results are analyzed with

help from theoretical calculations and box model simulations. We demonstrate that the 1,8 H-shift outcompetes the 1,5 and 1,6 shifts in 1,2-DEE RO₂, challenging our expectation of how autoxidation proceeds in the atmospheric degradation of ethers and likely other compounds containing heteroatoms on their chain.



Scheme 4.2: A simplified mechanism of autoxidation chemistry of 1,2-DEE and the deuterated 1,2-DEE-*d*₄. The branching fractions of the initial steps are denoted in purple (derived in Section C.8.1). A suite of hydroperoxy RO₂ can be produced from various H-shift reactions (denoted in blue) of simple RO₂. Here we exclude the hetero-atoms when numbering the carbons on the main chain of the compound. The H-shift rate coefficients are calculated by MC-TST method at 294 K. Production of certain RO₂ from 1,2-DEE-*d*₄ are suppressed due to kinetic isotope effect. Those pathways are not shown here. The competing RO₂ + HO₂ reactions and the resulting hydroperoxides are also shown. The molecular formula and molecular masses of closed-shell products are shown in green. Detailed oxidation mechanisms of 1,2-DEE and 1,2-DEE-*d*₄ are in Section C.1.

4.2 Methods

4.2.1 Experimental Details

The photo-oxidation reactions of 1,2-DEE (> 98%, TCI) and 1,2-DEE- d_4 by OH radicals are investigated in a $\sim 0.7 \text{ m}^3$ Teflon environmental chamber. All experiments are performed at laboratory temperature of $294 \pm 1 \text{ K}$ and pressure of $\sim 993 \text{ hPa}$. OH radicals are produced by photolysis of H_2O_2 (30% by mass, Macron Fine Chemicals), which is initiated by illumination of 350 nm (Sylvania 350 Blacklight) or 254 nm (Sankyo Denki G40T10) UV lamps housed within the chamber enclosure:



HO_2 radicals are the primary bimolecular reactant in our experiments. To study the H-shift rate coefficients of RO_2 in the system, we vary the HO_2 concentration across experiments to modulate the competition between bimolecular and autoxidation chemistry. HO_2 is mainly produced thorough reaction between CH_3OH (Sigma Aldrich, > 99%) and OH radical:



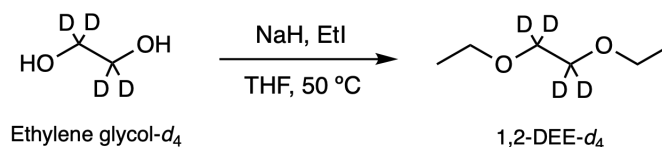
The HO_2 concentrations in the chamber are varied by changing the number and wavelength of UV lamps in the chamber enclosure to modulate OH production rates from Reaction R1, which in turn governs HO_2 formation rates through Reaction R2. The 254 nm UV lights, which provide a high H_2O_2 photolysis rate, are used for experiments with high $[\text{HO}_2]$ where $\text{RO}_2 + \text{HO}_2$ bimolecular reactions are dominant, while the 350 nm UV lights produce low $[\text{HO}_2]$ where autoxidation chemistry becomes favorable. RO_2 self-reactions ($\text{RO}_2 + \text{RO}_2$) are suppressed by ensuring that the concentrations of HO_2 is much higher than those of RO_2 , which is achieved by using much larger concentrations of CH_3OH than the VOCs so that most of OH reacts with CH_3OH in the experiments. A detailed list of experimental conditions is provided in Table C.1. With these conditions, the concentrations of HO_2 in our experiments are estimated by box model simulation (described later) to vary from $\sim 1.7 \times 10^9 \text{ molecules cm}^{-3}$ ($\sim 0.07 \text{ ppb}$) with one 350 nm UV light, to $\sim 5.8 \times 10^{10} \text{ molecules cm}^{-3}$ ($\sim 2.4 \text{ ppb}$) with eight 254 nm UV lights, and are kept ~ 20 times higher than total $[\text{RO}_2]$ throughout the experiments.

The reaction products are measured by a high-resolution time-of-flight chemical ionization mass spectrometer combined with low-pressure gas chromatography (GC-CIMS). Details regarding the instrument has been described elsewhere,³⁴ and only

a summary is provided here. The instrument uses CF_3O^- ($m/z = 85$) as the reagent ion, which is sensitive to multifunctional organic compounds such as hydroperoxides and nitrates.³⁵ During GC operation, the analytes are first cryotrapped at the head of the 2m column (Restek RTX-1701) and then separated and elute as column temperature increases. The sample flow is diluted with N_2 and transferred to the CIMS where it passes through a fluorocopolymer-coated ion-molecule reaction zone. Product ions that result from ion-molecule clustering reactions between the analytes and CF_3O^- ions are detected at $m/z = \text{mass neutral} + 85$ amu, and those result from fluoride transfer reactions are detected at $m/z = \text{mass neutral} + 19$ amu.³⁵ In addition to forming ion clusters, certain compounds generate characteristic fragmentation ions, such as hydroperoxides producing a small fraction (a few %) of ions at m/z 63 (FCO_2^-), which assists in our identification of those analytes. Since we lack authentic standards for the oxidation products, the CIMS sensitivities of most analytes are estimated based on their ion-molecule collision rates with CF_3O^- ,³⁵ which is calculated following the method by Su and Chesnavich³⁶ using dipole moments and polarizabilities calculated *ab initio*.³⁷ The resulting estimated sensitivities, along with more details of the CIMS calibration process, are described in Section C.4. Secondary losses of reaction products in the sampling system are also accounted for when quantifying the product yields, which is discussed in Section C.7.

4.2.2 Synthesis

We synthesized via an $\text{S}_{\text{N}}2$ reaction in Scheme 4.3 the selectively deuterated 1,2-DEE- d_4 using deuterated ethylene glycol (ethylene glycol- d_4) and excess ethyl iodide (EtI). Reagents were purchased from commercial sources and used as received. Synthetic details are provided in Section C.2. The identity of the compound is confirmed by GC-MS analysis (Hewlett Packard 5972 with INNOWAX column).



Scheme 4.3: Synthetic route to 1,2-DEE- d_4

4.2.3 Computational Details

We calculate the theoretical H-shift rate coefficients of key 1,2-DEE RO_2 by multi-conformer transition state theory (MC-TST),^{38,39} using the approach detailed else-

where.^{40,41} The theoretical routine is briefly discussed. First, conformational isomers of reactants, transition states and products are sampled with the Merck Molecular Force Field method (MMFF94)⁴² implemented in Spartan’24 (Wavefunction, Inc.). Each dihedral angle is rotated 3 times (120°) for the initial sampling. The keyword “FFHINT=X~~ +0” was used with open-shell species, to assign a charge of 0 to the radical center X. Once conformer lists were obtained, all structures were optimized at the B3LYP/6-31+G(d) level of theory^{43–47} with the Gaussian’16 software. (Gaussian, Inc.) Unique conformations, filtered based on an electronic energy and electric dipole moment similarity threshold (10^{-5} Hartree and 0.015 Debye respectively), with zero-point corrected energies within 2 kcal/mol of the global minimum were re-optimized at the ω B97X-D/aug-cc-pVTZ level of theory.^{48–50} Calculations done under the Rigid-Rotor Harmonic-Oscillator (RRHO) approximation provided zero-point vibrational energies and partition functions, as well as served to ensure that each optimized structure corresponds to an appropriate potential energy surface stationary point. Intrinsic reaction coordinate (IRC) calculations, followed by geometry optimization of end-points, were done to the lowest conformer of each transition state to verify whether it is connected to the assumed reactants and products. Finally, single-point calculations at the RO-CCSD(T)-F12a/cc-pVDZ-F12 (gem_beta = 0.9)^{51,52} were done with Molpro 2025^{53,54} to the lowest conformer of each stationary point and each conformer obtained from IRC calculations, to obtain more accurate electronic energies. The RO-CCSD(T)-F12a/cc-pVDZ-F12 level-of-theory is hereinafter abbreviated as F12.

Once the reaction pathway energetics were obtained, thermal rate coefficients $k(T)$ were calculated with Equation 4.1:

$$k(T) = \kappa \frac{k_B T}{h} \frac{\sum_i^{TS} \exp\left(\frac{-\Delta E_i}{k_B T}\right) Q_{TS_i}}{\sum_j^R \exp\left(\frac{-\Delta E_j}{k_B T}\right) Q_{R_j}} \exp\left(\frac{-\Delta^\ddagger E_0}{k_B T}\right) \quad (4.1)$$

where k_B is the Boltzmann constant, h is the Planck constant, and T is the temperature. The multi-conformer approach employed here expands the total partition functions of the transition state and reactant in the Eyring equation as sums over Boltzmann-weighted conformer contributions. Q_{TS_i} and Q_{R_j} are the RRHO partition functions of the i th TS conformer and the j th reactant conformer respectively, and ΔE_i and ΔE_j are the zero-point corrected energies of the i th TS conformer and the j th reactant conformer respectively, taken relative to their respective lowest conformation, calculated at the ω B97X-D/aug-cc-pVTZ level. The reaction energy barrier $\Delta^\ddagger E_0$ is defined as the difference in zero-point corrected energy be-

tween the lowest-conformers of the transition state and reactant, calculated at the F12// ω B97X-D/aug-cc-pVTZ level. The transmission coefficient κ was calculated with the Eckart tunneling correction,⁵⁵ using asymmetric potentials based on IRC end-points calculated at the F12// ω B97X-D/aug-cc-pVTZ level. For reactions leading to spontaneous elimination of OH radical in the product side of the reaction coordinate, a symmetric potential was used instead, where the reactant-side barrier height is used for both the forward and backward directions. Intramolecular H-shift rate coefficients predicted with the MC-TST approach employed here have consistently shown good agreement with experimentally measurements, within a factor of 5.^{12,40} The calculated H-shift rate coefficients are shown in Scheme 4.4, Table 4.4, and Section C.5.

To understand the observed selectivity trend in terms of molecular structures, we performed an additional set of calculations to assess the impact of inductive, stereoelectronic, and steric effects on reaction energy barriers. Inductive effects were probed with a local electrophilicity index ω^+ ,⁵⁶ whose calculation is based on the global electrophilicity index ω as defined by Parr et al.⁵⁷ and the Fukui function for nucleophilic attack $f^+(X)$ ^{58,59} condensed onto the radical-center X:

$$\omega^+ = \omega f^+(X) \quad (4.2)$$

$$\omega = \frac{(I + A)^2}{8(I - A)} \quad (4.3)$$

where I and A are the vertical ionization potential and electron affinity, respectively,^{60,61} obtained with single-point calculations done with the optimized structure of the neutral molecule. The condensed Fukui functions $f^+(X)$ were calculated from partial charge differences between the anion and the neutral species, calculated with Natural Population Analysis (NPA),⁶² using the Natural Bond Orbital (NBO7.0) software.⁶³ Further details can be found in the Section C.5.4. Stereoelectronic effects were analyzed with second-order perturbation theory analysis of NBO donor-acceptor interactions.⁶⁴

Steric effects were probed with Natural Steric Analysis,^{65,66} done with NBO7.0, and by analysis of non-covalent interactions (NCI) based on reduced density gradient plots⁶⁷ and electron density (ρ) integrals over NCI domains,⁶⁸ done with the Multiwfn 3.8 software.^{69,70} The quantitative NCI analysis employed here is based on the q_{bind} index as a measure of interaction strength,⁶⁸ where a positive or negative value indicate an overall repulsive or attractive interaction respectively, and is calculated

as:

$$q_{bind} = q_{rep} - q_{att} = \int_{\Omega(\lambda_2 > 0)} \rho^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r} - \int_{\Omega(\lambda_2 < 0)} \rho^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r} \quad (4.4)$$

where the repulsive term q_{rep} is obtained by integration over regions where the second-largest eigenvalue of the electron density Hessian (λ_2) is positive, and the attractive term q_{att} is obtained from integration over regions where λ_2 is negative. Further details are in Section C.5.5 and C.5.6.

4.2.4 Box Model

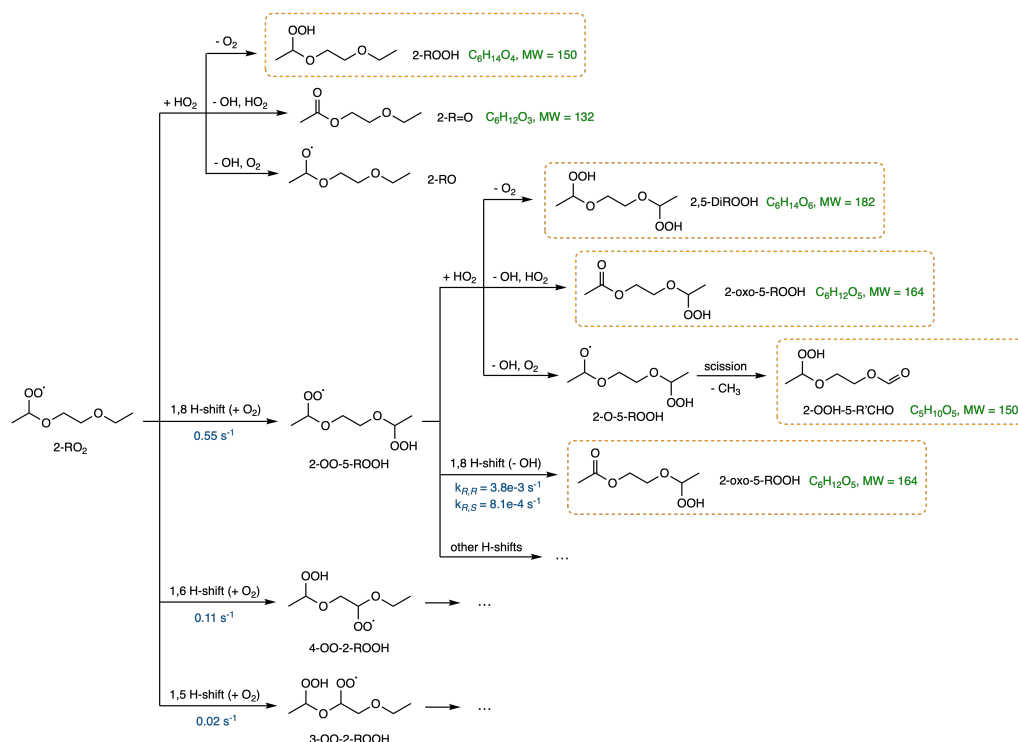
We use a MATLAB-based gas-phase chemistry box model to simulate the experimental results and evaluate the kinetics and branching ratios of key oxidation reactions. The model uses the MATLAB ode15s solver to calculate time-dependent concentrations of chemical species based on given initial conditions and a specified chemical mechanism. The reactions and kinetic data implemented in the model are initially adopted from the Master Chemical Mechanism (MCM),⁷¹ estimations from literatures,^{4,72} and calculated RO₂ H-shift rate coefficients. We minimize the difference between the experimental and model results by adjusting reaction parameters of key reactions in the mechanism, including the RO₂ H-shift rate coefficients and branching fractions of bimolecular reactions. Details regarding the oxidation mechanism and reaction kinetics implemented in the model is provided in Section C.6.

4.3 Results and Discussion

4.3.1 Experimental Results

4.3.1.1 Identity of Oxidation Products

Shown in Scheme 4.4 is the mechanism of 1,2-DEE 2-RO₂'s bimolecular reaction with HO₂ and H-shift reactions. We focus our analysis on the major first-generation reaction products: the hydroperoxide (2-ROOH) formed by reaction between initial RO₂ and HO₂, and the ketohydroperoxides (2-oxo-5-ROOH and 2-OOH-5-R'CHO) and the dihydroperoxide (2,5-DiROOH), both produced from subsequent chemistry of the hydroperoxy RO₂. The formation of 2-RO₂ reaction products through bimolecular chemistry or 1,8 H-shift (Scheme 4.4) does not involve abstracting H atoms from the two central carbons. Thus, 1,2-DEE-*d*₄ oxidation products formed via these pathways (Scheme C.2 and C.7) retain 4 deuterium atoms and have molecular mass 4 Da higher than their non-deuterated counterparts. The 1,2-DEE-*d*₄ oxidation products from pathways that involves abstracting D atoms by OH or RO₂



Scheme 4.4: Mechanism of 1,2-DEE 2-RO₂ bimolecular reaction with HO₂^{3,73,74} and H-shift reactions. The H-shift rate coefficients are calculated by MC-TST method at 294 K and denoted in blue. Subsequent bimolecular reaction of 2-OO-5-ROOH + HO₂ and products are also shown. Further reactions from 4-OO-2-ROOH and 3-OO-2-ROOH are shown in Scheme C.3-C.4. The molecular formula and molecular masses of major oxidation products are denoted in green. Products that are detected by our instrument are shown in orange boxes. More detailed oxidation mechanisms of 2-RO₂ and deuterated 2-RO₂-d₄ are in Section C.1.

radicals (see Scheme C.5-C.6), however, will have a lower molecular mass (and a lower yield due to the kinetic isotope effect).^{30,32} As one C–D bond is broken during autoxidation of the deuterated precursor, a mass shift by 1 Da occurs because the shifted deuterium on the hydroperoxide group (–OOD) undergo rapid D/H exchange with the hydrogen in background H₂O in the chamber.³² Such feature enables us to identify 1,2-DEE oxidation products from different reaction pathways in the mass spectra.

Shown in Figure 4.1 are the gas chromatograms of major reaction products from a 1,2-DEE and a 1,2-DEE-d₄ oxidation experiment under similar conditions at HO₂ level of ~1 ppb. The deuterated oxidation products elute slightly earlier than the non-deuterated products.⁷⁵ As mentioned above, we observe 2-ROOH-d₄ and deuterated oxo-ROOH and DiROOH from 1,8 H-shift reaction of 2-RO₂-d₄ at 4 *m/z* units higher than their non-deuterated counterparts (e.g. *m/z* 239 vs. *m/z* 235

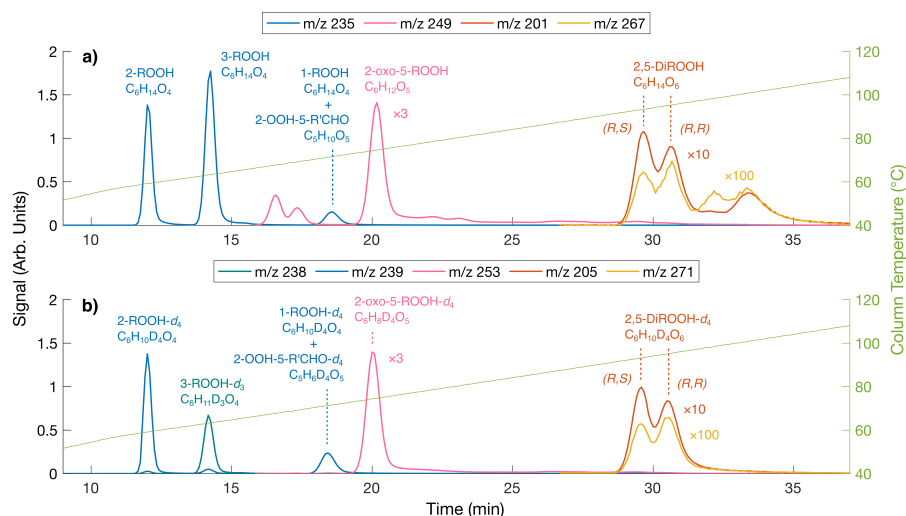


Figure 4.1: Gas chromatograms of major reaction products from 1,2-DEE and 1,2-DEE- d_4 oxidation and tentative peak assignments. **a)** 1,2-DEE oxidation products, **b)** 1,2-DEE- d_4 oxidation products. Certain signals are scaled up by a factor denoted in the figure. Most reaction products are detected at m/z = mass neutral + 85, except the DiROOHs which are detected at m/z = mass neutral + 85 and + 19, and as other fragment ions (not shown here, see Figure S5). Tentative assignment of different stereoisomers of DiROOHs are also denoted (discussed in Section C.1.1). In this work, we refer to the stereoisomer with different configurations at both chiral centers, i.e. the meso form (R,S) and (S,R), as (R,S), and those with same configuration, i.e. (R,R) and (S,S), as (R,R).

for 2-ROOH). Other oxidation products that result from abstraction of 1 or 2 D atoms between the ether oxygens, however, appear at only 3 or 2 m/z units higher, such as the deuterated 3-ROOH (3-ROOH- d_3 at m/z 238 in Figure 4.1b, Scheme C.2). More detailed chromatographic analysis of 1,2-DEE oxidation products can be found in Section C.1.1. From these chromatograms, we can distinguish the 1,2-DEE autoxidation products from the 1,8 H-shift reaction of 2-RO₂, including 2-oxo-5-ROOH, 2-OOH-5-R'CHO, and 2,5-DiROOH, from those formed via other H-shift pathways (discussed in Section C.1.1). Detection of these products at high yields confirms the occurrence of the 1,8 H-shift, and their higher yields relative to products from other autoxidation pathways suggests that the reaction outcompetes other H-shift pathways in the system.

4.3.1.2 H-shift Rate Coefficients

We estimate the H-shift rate coefficients experimentally by examining the yields of major 1,2-DEE oxidation products as a function of $[\text{HO}_2]$. Here, we focus on the rate coefficients of 1,8 H-shift of 2-RO₂ and 2-OO-5-ROOH (Scheme 4.4). For other H-shift reactions in the system, we are only able to provide rough estimates of

their rate coefficients, mainly due to uncertainties in isomer-specific yields of certain products from those pathways and in estimations of relevant reaction parameters. A discussion of other H-shift processes is provided in Section C.8.

2-RO₂ 1,8 H-shift The rate coefficient of the 1,8 H-shift reaction in 2-RO₂ is estimated by comparing the yields of its major product from the first-generation bimolecular reaction, 2-ROOH, with the sum of the yields of autoxidation products formed following the 1,8 H-shift, including 2-oxo-5-ROOH, 2-OOH-5-R'CHO, and 2,5-DiROOH.

In absence of secondary chemistry, we assume that the ratio between the product yields is equivalent to the ratio between their production rates. By assuming steady state for the radical species, we can formulate the production rates of those compounds as:

$$P_{2\text{-ROOH}} = \alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [2\text{-RO}_2] [\text{HO}_2] \quad (4.5)$$

$$P_{2\text{-oxo-5-ROOH} + 2\text{-OOH-5-R'CHO} + 2,5\text{-DiROOH}} = P_{2\text{-OO-5-ROOH}} = k_{1,8 \text{ H-shift, } 2\text{-RO}_2} [2\text{-RO}_2] \quad (4.6)$$

where P indicates the production rate of certain species, $\alpha_{2\text{-ROOH}}$ is the branching fraction to 2-ROOH from the bimolecular reaction $2\text{-RO}_2 + \text{HO}_2$, $k_{2\text{-RO}_2+\text{HO}_2}$ is the overall rate coefficient of the reaction $2\text{-RO}_2 + \text{HO}_2$, and $k_{1,8 \text{ H-shift, } 2\text{-RO}_2}$ is the rate coefficient of the 1,8 H-shift reaction of 2-RO₂. Thus, the ratio between the yields of 2-ROOH and products from 2-OO-5-ROOH can be expressed by combining Equation 4.5 and 4.6:

$$\begin{aligned} & \frac{[2\text{-ROOH}]}{[2\text{-oxo-5-ROOH}] + [2\text{-OOH-5-R'CHO}] + [2,5\text{-DiROOH}]} \\ &= \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [2\text{-RO}_2] [\text{HO}_2]}{k_{1,8 \text{ H-shift, } 2\text{-RO}_2} [2\text{-RO}_2]} \\ &= \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2}}{k_{1,8 \text{ H-shift, } 2\text{-RO}_2}} [\text{HO}_2] \end{aligned} \quad (4.7)$$

Consistent with Equation 4.7, we observe a linear relationship between the ratio of product yields and estimated $[\text{HO}_2]$ (Figure 4.2). The 1,8 H-shift rate coefficient of 2-RO₂ can thus be derived from the slope of the linear relationship by:

$$k_{1,8 \text{ H-shift, } 2\text{-RO}_2} = \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2}}{(\text{slope in Fig. 4.2})} \quad (4.8)$$

From linear regression fitting, we find the slope in Figure 4.2 to be $(1.32 \pm 0.43) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$. The rate coefficient $k_{2\text{-RO}_2+\text{HO}_2}$ can be estimated based on

method in Jenkin et al.⁴ and Wennberg et al.⁷⁶ to be $1.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K. We estimate the branching ratio $\alpha_{2\text{-ROOH}}$ by comparing the concentrations of simple hydroperoxides (ROOH) at high $[\text{HO}_2]$, where their yields are less affected by autoxidation chemistry and are mainly controlled by the branching fractions of respective simple RO_2 (α_{RO_2}) during the initiation step (Scheme 4.2) and the branching fractions to the formation of ROOH (α_{ROOH}) from bimolecular reaction $\text{RO}_2 + \text{HO}_2$. We estimate those parameters using box model simulations, and more details about this analysis is provided in Section C.8.1.

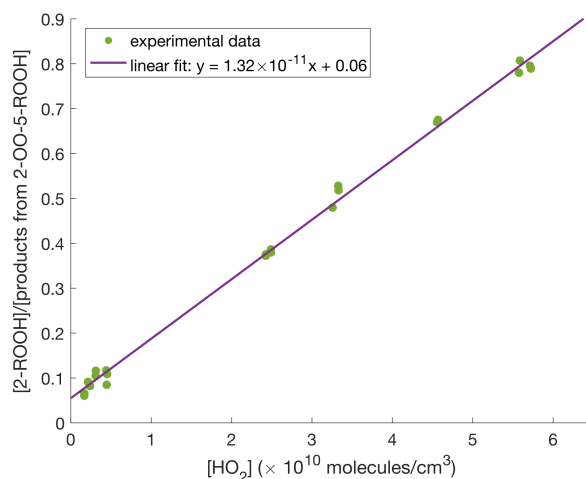


Figure 4.2: $[2\text{-ROOH}]/([2\text{-oxo-5-ROOH}] + [2\text{-OOH-5-R'CHO}] + [2,5\text{-DiROOH}])$ vs. $[\text{HO}_2]$ at ambient temperature (294 K), and the result from linear regression fit ($R^2 = 0.997$). $[\text{HO}_2]$ is calculated using the box model described in section above.

Based on our evaluations of relevant reaction parameters listed in Table 4.2, we estimate the 1,8 H-shift rate coefficient of 2- RO_2 to be $1.17 \pm 0.85 \text{ s}^{-1}$. The estimated H-shift rate coefficient agrees well with that calculated using the computational method (0.55 s^{-1}). The source of uncertainties in the derived parameters is discussed below. We also estimate the rate coefficients of other 2- RO_2 and 3- RO_2 H-shift reactions (1,5 and 1,6 H-shifts) using similar measure based on the yields of other autoxidation products. More details of the estimation process are provided in Section S8.3. The average of the experimental rate coefficients of 2- RO_2 and 3- RO_2 1,6 H-shift reactions are estimated to be $\sim 0.18 \text{ s}^{-1}$, and the average of those of the 1,5 H-shifts are estimated to be $\sim 0.06 \text{ s}^{-1}$. These values also agree well with theoretical predictions, with calculated 1,6 H-shift rate coefficients of 0.11 and 0.12 s^{-1} for 2- RO_2 and 3- RO_2 , respectively, and 1,5 H-shift rate coefficients of 0.02 and 0.08 s^{-1} (Table 4.4). In contrast to intuition, the entropically unfavorable 1,8 H-shift proceeds much faster than the 1,5 and 1,6 H-shifts. The rates of 1,5 and 1,6 H-shift reactions of

simple 1,2-DEE RO₂'s are similar to those of 1,5 and 1,6 H-shifts in other organic substrates adjacent to an oxygen-containing functional group, such as hydroxy, hydroperoxy, and ether groups (generally at $\sim 0.05 - 0.2 \text{ s}^{-1}$).^{11,20,22,23} These H-shifts are facilitated by the electron-donating α -oxygen atoms, which stabilize the H-shift TSs.^{25,77} The rate of the 1,8 H-shift is notably higher, approaching values reported for rapid H-shifts in aldehyde, isoprene, and terpene-derived RO₂.^{18,76,78–80} The high 2-RO₂ 1,8 H-shift rate coefficient likely results from a combination of factors, which is further discussed in the theoretical section below.

Table 4.2: Estimations of key reaction parameters in evaluating 1,8 H-shift rate coefficient of 1,2-DEE 2-RO₂. ^a Branching fraction to formation of 2-ROOH from 2-RO₂ + HO₂ reactions. ^b Calculated by MC-TST method with an uncertainty about a factor of 5.

$\alpha_{2\text{-ROOH}}^a$	1,8 H-shift rate coefficient (s^{-1}) at 294 K	
	Theory ^b	Experiment
$0.79 + 0.21 / -0.31$	0.55	1.17 ± 0.85

2-OO-5-ROOH 1,8 H-shift The rate coefficient of the subsequent 1,8 H-shift reaction of the hydroperoxy RO₂ 2-OO-5-ROOH can be estimated by analyzing the variations in the yields of two of its major reaction products, 2-oxo-5-ROOH and 2,5-DiROOH (Scheme 4.4), as a function of [HO₂]. The ratio between the yields of the two compounds, which is assumed to be equal to their production rates as above, can be formulated as:

$$\begin{aligned}
 & \frac{[2\text{-oxo-5-ROOH}]}{[2,5\text{-DiROOH}]} \\
 &= \frac{\alpha_{2\text{-oxo-5-ROOH}} k_{2\text{-OO-5-ROOH}+\text{HO}_2} [2\text{-OO-5-ROOH}] [\text{HO}_2] + k_{1,8 \text{ H-shift, } 2\text{-OO-5-ROOH}} [2\text{-OO-5-ROOH}]}{\alpha_{2,5\text{-DiROOH}} k_{2\text{-OO-5-ROOH}+\text{HO}_2} [2\text{-OO-5-ROOH}] [\text{HO}_2]} \\
 &= \frac{\alpha_{2\text{-oxo-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}} + \frac{k_{1,8 \text{ H-shift, } 2\text{-OO-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}} k_{2\text{-OO-5-ROOH}+\text{HO}_2}} \times \frac{1}{[\text{HO}_2]}
 \end{aligned} \tag{4.9}$$

where $\alpha_{2\text{-oxo-5-ROOH}}$ and $\alpha_{2,5\text{-DiROOH}}$ indicate the branching fractions to formation of the two compounds from the reaction between 2-OO-5-ROOH and HO₂, and $k_{2\text{-OO-5-ROOH}+\text{HO}_2}$ indicates the overall rate coefficient of the bimolecular reaction. Notice that here we refer [2,5-DiROOH] to the total concentrations of both diastereomers, (*R,R*) and (*R,S*), of 2,5-DiROOH (Figure 4.1), and our following analysis of 2-OO-5-ROOH reaction parameters, unless otherwise specified, refers to the average behavior of (*R,R*) and (*R,S*) diastereoisomers of the peroxy radical.

Consistent with Equation 4.9, there is a linear relationship between the ratio of the yields of the two compounds and $1/[\text{HO}_2]$ (Figure 4.3). We derive the H-shift rate

coefficient from the slope of the linear fit in Figure 4.3, with knowledge of the bimolecular rate coefficient ($k_{2\text{-OO-5-ROOH}+\text{HO}_2}$) and the branching ratio to formation of the dihydroperoxide ($\alpha_{2,5\text{-DiROOH}}$):

$$k_{1,8 \text{ H-shift, } 2\text{-OO-5-ROOH}} = \alpha_{2,5\text{-DiROOH}} k_{2\text{-OO-5-ROOH}+\text{HO}_2} \cdot (\text{slope in Fig. 4.3}) \quad (4.10)$$

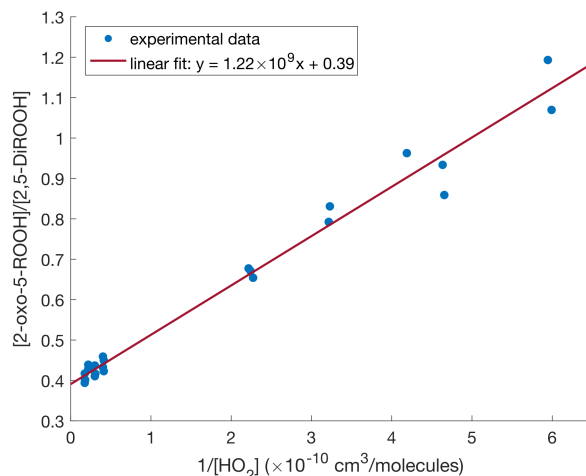


Figure 4.3: $[2\text{-oxo-5-ROOH}]/[2,5\text{-DiROOH}]$ vs. $1/[\text{HO}_2]$ at ambient temperature (294 K), and the result from linear regression fit ($R^2 = 0.979$).

The slope of the linear relationship is $(1.22 \pm 0.40) \times 10^9 \text{ molecule cm}^{-3}$. As above, the bimolecular rate coefficient is estimated using the method in Jenkin et al.⁴ and Wennberg et al.⁷⁶ to be $2.10 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K. The branching fractions of the three channels of $2\text{-OO-5-ROOH} + \text{HO}_2$ reaction is derived from: 1) the intercept of the linear fit, which equals to the ratio between the branching fractions of reaction channels to formation of 2-oxo-5-ROOH and 2,5-DiROOH, and 2) the yields of 2-OOH-5-R'CHO (Scheme 4.4), which is formed from the reaction channel to formation of alkoxy radical 2-O-5-ROOH ($\alpha_{2\text{-O-5-ROOH}}$). The resulting reaction parameters are in Table 4.3, with more details regarding this derivation provided in Section C.8.2.

With these constraints, the 1,8 H-shift rate coefficient of 2-OO-5-ROOH is estimated to be $0.017 \pm 0.011 \text{ s}^{-1}$. We estimate stereoisomer-specific rate coefficients of this H-shift by comparing the yields of (*R,S*) and (*R,R*)-2,5-DiROOH (Figure 4.1) as a function of HO_2 concentrations (detailed in Section S8.2). The 1,8 H-shift rate coefficient of (*R,R*)-2-OO-5-ROOH is estimated to be $0.027 \pm 0.017 \text{ s}^{-1}$, and that of the (*R,S*) isomer to be $0.007 \pm 0.004 \text{ s}^{-1}$, which agree less closely with theoretical predictions (0.0038 s^{-1} and $8.1 \times 10^{-4} \text{ s}^{-1}$ for (*R,R*) and (*R,S*) stereoisomers respectively). This second-generation 1,8 H-shift is estimated to be much slower than the

first-generation 1,8 H-shift process, despite the presence of an α -hydroperoxyl substituent, which should be C–H bond activating in hydrocarbon-derived systems.^{9,18} Similar behavior is also reported in previous studies, where α -hydroperoxyl substitution to an abstraction site that is already α -oxyl substituted decreases the RO₂ H-shift rate coefficient.^{23,81} Theoretical evaluation of this phenomenon is also provided in section below.

Table 4.3: Estimations of key reaction parameters in evaluating 1,8 H-shift rate coefficient of 2-OO-5-ROOH. ^a Branching fractions for reaction channels of 2-OO-5-ROOH + HO₂ reaction. ^b Calculated by MC-TST method with an uncertainty about a factor of 5.

$\alpha_{2,5\text{-DiROOH}}^{\text{a}}$	$\alpha_{2\text{-oxo-5-ROOH}}^{\text{a}}$	1,8 H-shift rate coefficient (s ⁻¹) at 294 K	
		Theory ^b	Experiment
0.65 ± 0.09	0.26 ± 0.07	0.0038 (<i>R,R</i>)	0.017 ± 0.011 (average)
		8.1 × 10 ⁻⁴ (<i>R,S</i>)	0.027 ± 0.017 (<i>R,R</i>)
			0.007 ± 0.004 (<i>R,S</i>)

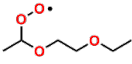
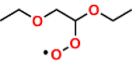
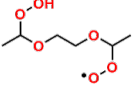
4.3.1.3 Sources of Experimental Uncertainties

The major source of the large uncertainty in our estimated H-shift rate coefficients is the uncertainty in the estimated rate coefficients of relevant RO₂ + HO₂ bimolecular reactions, i.e. $k_{2\text{-RO}_2+\text{HO}_2}$ and $k_{2\text{-OO-5-ROOH}+\text{HO}_2}$. Based on recommendations in JPL⁸² and IUPAC⁸³ documentations, we estimate the uncertainties in the bimolecular rate coefficients to be ~52%. Since the H-shift rate coefficients are evaluated relative to the bimolecular rate coefficients (Equation 4.8 and 4.10), our estimates are highly sensitive to the errors in those bimolecular rates. A better constrained $k_{\text{RO}_2+\text{HO}_2}$ shall thereby grant us more confidence in our estimation of the H-shift rates. Other contributors to the uncertainty in our estimates include errors in the measured concentrations of relevant reaction products and the linear regression fit. The major source of those errors comes from the uncertainties in our knowledge of the CIMS sensitivity of those compounds (~25%) and the estimated experimental [HO₂] (~16%). A more detailed uncertainty analysis is provided in Section C.9.

4.3.2 Computational Results

H-shift reaction energy barriers and rate coefficients calculated for major first-generation peroxy radicals, 2-RO₂ and 3-RO₂, and the major second generation peroxy radical, 2-OO-5-ROOH, are shown in Table 4.4.

Table 4.4: Reaction energy barriers ($\Delta^\ddagger E_0$) calculated as the zero-point corrected energy difference between the lowest-conformer of the TS and reactant, multi-conformer TST rate coefficients (k_{MC}), multi-conformer ratio of partition functions ($Q_{TS/R}$, third term in Equation 4.1), and Eckart tunneling factor (κ), calculated at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory and 294 K, for H-shift reactions of 1,2-DEE-derived RO₂.

Reactant	Reaction	$\Delta^\ddagger E_0$ [kcal mol ⁻¹]	k_{MC} [s ⁻¹]	$Q_{TS/R}$	κ
 2-RO ₂	1,5 H-shift	20.50	2.3×10^{-2}	0.0949	67.4
	1,6 H-shift	18.76	1.1×10^{-1}	0.0226	71.5
	1,8 H-shift	16.85	5.5×10^{-1}	0.0054	56.1
 3-RO ₂	1,5 H-shift	19.87	7.8×10^{-2}	0.1130	66.1
	1,6 H-shift (α -OR)	18.55	1.2×10^{-1}	0.0130	88.6
 2-OO-5-ROOH	(R,R) 1,5 H-shift (δ -OOH)	21.03	5.1×10^{-3}	0.0959	37.1
	(R,R) 1,6 H-shift (γ -OOH)	20.30	1.1×10^{-2}	0.0565	38.4
	(R,R) 1,8 H-shift (α -OOH)	20.09	3.8×10^{-3}	0.0173	30.7
	(R,S) 1,5 H-shift (δ -OOH)	20.57	1.1×10^{-2}	0.0523	63.6
	(R,S) 1,6 H-shift (γ -OOH)	19.49	4.8×10^{-2}	0.0283	84.4
	(R,S) 1,8 H-shift (α -OOH)	20.80	8.1×10^{-4}	0.0118	32.3

Consistent with the experimental findings, the *ab initio* calculations indicate that the 1,8 H-shift reaction in 1,2-DEE 2-RO₂ is faster than the competing shorter-span pathways, 1,5 and 1,6 H-shifts. This is an unexpected finding given that longer-span H-shifts, such as 1,7 or 1,8 H-shifts, are typically observed to be less competitive due to the larger entropic penalty that accompanies the loss of many internal rotors during the formation of an eight- or nine-membered ring-like TS.^{18,19} While this entropic penalty is indeed larger for the 2-RO₂ 1,8 H-shift reaction than it is for its shorter-span counterparts, as seen from the smaller calculated ratio of partition functions $Q_{TS/R}$ (third term in Equation 4.1) in Table 4.4, its reaction energy barrier $\Delta^\ddagger E_0$ is also much lower, by about ~ 2 and ~ 4 kcal mol⁻¹. It is known that π -donating substituents, such as oxyl (-OR) or amino (-NRR') groups, can increase the lability of C-H bonds in α positions substantially,⁷² stabilizing H-shift TSs via $n_O \rightarrow \sigma_{CH}^*$ hyperconjugation.^{25,77} However, all three abstraction sites in the investigated 2-RO₂ H-shifts are both secondary and α -oxyl substituted, so that, in principle, this C-H bond activating effect is present regardless of the H-shift span. It is therefore clear that some other effect impacting the relative stability of H-shift TSs must be driving the observed selectivity.

Recent work done on similar reactions^{81,84} show that the presence of different

heteroatoms in a radical substrate alters the selectivity of intramolecular H-shift reactions, such that the optimum span is different from what would be expected in a hydrocarbon-derived analogue. It is also shown that these differences are due, in part, to the inductive deactivation of C-H bonds by σ -withdrawing heteroatoms. While π -donation affects only the α position (in a saturated chain), the effect of electron withdrawal by electronegative atoms can propagate further along the σ -framework, polarizing the C-H bonds in β and γ positions.^{81,84,85} As a result, these polarized C-H bonds are less nucleophilic, and thus less susceptible to attack by an electrophilic radical center (such as a peroxy group). In the case of 1,2-DEE 2-RO₂, the abstraction sites in the 1,5 and 1,6 H-shift reactions are β -oxyl substituted, whereas the site in the 1,8 H-shift is not. Reaction assistance provided by an α -oxyl group via hyperconjugation to the shorter-span H-shifts is then likely partly offset by induction from a β -oxyl group.

We tested this hypothesis by performing a series of computational investigations on H-shift reactions in a RO₂ derived from a hydrocarbon analogue to 1,2-DEE, octane (OCT 2-RO₂), and two RO₂ derived from a monoether analogue, ethoxypentane (EP 2-RO₂ and EP 7-RO₂). Calculation results for these systems, as well as their structures, are shown in Figure 4.4 and Section C.5.3 - C.5.6.

Comparison of 1,5 H-shift reaction energy barriers in all four systems shown in Figure 4.4a highlights the C-H bond deactivating effect of β -oxyl substitution: $\Delta^\ddagger E_0$ is ~ 1 and ~ 2 kcal mol⁻¹ higher for 1,2-DEE 2-RO₂ and EP 7-RO₂ relative to EP 2-RO₂ and OCT 2-RO₂ respectively. This trend is reflected in the site-specific local electrophilic index differences $\Delta\omega^+$, where the least negative values, which are associated with less nucleophilic abstraction sites,^{56,85,86} are those at β -oxyl positions (Fig. 4.4b). These findings agree with previous work investigating similar selectivity trends.^{81,84} Doing the same comparison with 1,6 H-shift reaction energy barriers, however, reveals the opposite behavior: $\Delta^\ddagger E_0$ is slightly lower (~ 0.4 kcal mol⁻¹) for 1,2-DEE 2-RO₂ and EP 2-RO₂ relative to EP 7-RO₂ and OCT 2-RO₂, respectively. Here, an effect associated with the fact that the β -heteroatom is endocyclic in the TS's ring-like structure, rather than exocyclic like in the case of 1,5 H-shifts, is possibly counteracting the effect of induction.

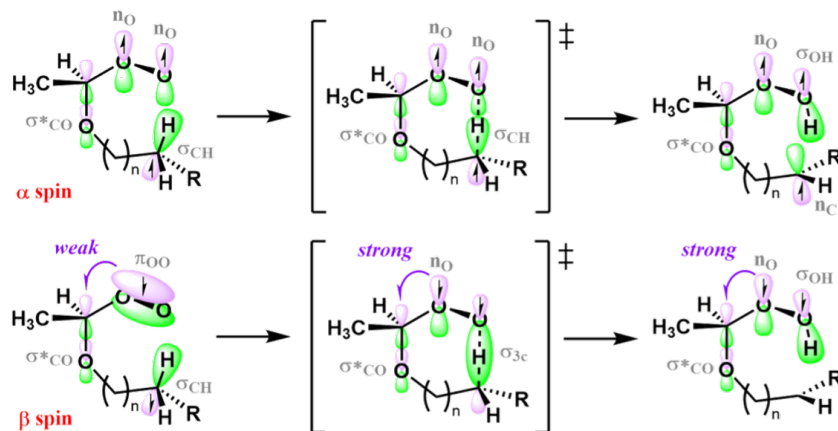
Previous studies⁸⁷⁻⁸⁹ have shown that cyclization reactions become more favorable when some of the methylene groups in the reactant's backbone are replaced by oxygen atoms. Experimental evidence⁹⁰ also suggests that such observation is associated with a decrease in transannular strain. While smaller rings, such as three-

or four-membered rings, suffer from a large degree of ring-strain associated with angle and torsional strain, larger rings such as seven- or eight-membered rings suffer from transannular strain, provoked by steric clashes between groups on opposite sides of the cycle.⁹¹ In the context of intramolecular H-shift reactions, some degree of transannular repulsion may destabilize the ring-like TS of longer-span pathways (1,7 or 1,8), as reported by Hao et al.⁸⁴ Our calculations for OCT 2-RO₂ H-shifts (Figure 4.4a) show that energy barriers initially decrease with increasing span, consistent

with a reduction in angle or torsional ring-strain in the TS, but then increase by ~ 2 kcal mol $^{-1}$ going from a 1,7 to a 1,8 H-shift span. An analogous increase in $\Delta^\ddagger E_0$ is not observed for the ether-derived 2-RO $_2$. Moreover, the calculated 1,8 H-shift reaction energy barriers ($\Delta^\ddagger E_0$) are more than 3 kcal mol $^{-1}$ lower for 1,2-DEE 2-RO $_2$ and EP 2-RO $_2$ relative to EP 7-RO $_2$ and OCT 2-RO $_2$ and respectively. Perhaps this indicates that replacing endocyclic methylene groups by oxygen atoms in longer-span RO $_2$ H-shift TSs reduces transannular strain.

The steric energy of activation $\Delta^\ddagger E_{steric}$ from Natural Steric Analysis^{65,66} and the analogue index $\Delta^\ddagger q_{bind}$ from NCI analysis⁶⁸ calculated for the H-shift reactions investigated here (Figure 4.4c and d) partly support the transannular strain hypothesis. For 1,8 H-shifts, both $\Delta^\ddagger E_{steric}$ and $\Delta^\ddagger q_{bind}$ are the largest for OCT 2-RO $_2$. These values are also the ones that see the largest increase when compared to the 1,6 H-shift, the optimal H-shift span from a TS ring-strain perspective. However, we observe some inconsistencies when comparing $\Delta^\ddagger E_{steric}$ and $\Delta^\ddagger q_{bind}$ for other systems and H-shift spans. First, the 1,8 H-shift $\Delta^\ddagger q_{bind}$ is larger for 1,2-DEE 2-RO $_2$ than it is for EP 7-RO $_2$, and the calculated $\Delta^\ddagger E_{steric}$ is almost the same for both systems, despite the lower $\Delta^\ddagger E_0$ calculated for the former. Second, ring-strain is unlikely to be the counteracting effect to induction in the 1,6 H-shift TS of 1,2-DEE 2-RO $_2$ and EP 2-RO $_2$ discussed above, given that transannular interactions are expected to be minimal in rings of this size, regardless of the system (see NCI domain plots in Section C.5.5). Thus, we argue that transannular strain (or lack thereof) can partly explain the disparate reactivity observed for longer-span H-shifts in ether- and hydrocarbon-derived RO $_2$, yet another structural factor is also playing a role. We hypothesize that this factor is a consequence of the generalized anomeric effect,⁹² and how the strength of this effect changes during the course of an H-shift reaction.

The generalized anomeric effect, often rationalized in terms of $n_O \rightarrow \sigma_{CO}^*$ hyperconjugative interactions,^{25,92,93} acts to enhance H-shift reaction rates in α -oxyl peroxy radicals, such as 1,2-DEE 2-RO $_2$ and EP 2-RO $_2$, as seen in the evolution of spin-orbitals occupied by β -spin electrons (Figure 4.5). As the hydrogen atom is transferred during the course of an H-shift reaction, the bonding π_{OO} spin-orbital in the reactant is replaced by a non-bonding n_O spin-orbital in the transition state. Since non-bonding orbitals are, in general, better electron donors than bonding orbitals, the $n_O \rightarrow \sigma_{CO}^*$ interaction is stronger than the $\pi_{OO} \rightarrow \sigma_{CO}^*$ interaction. The anomeric effect thus better stabilizes the transition state than it does for the reactant, lowering the reaction energy barrier. An analogous enhancement in hyperconjugation



Scheme 4.5: Generalized anomeric effect in the mechanism of intramolecular H-shift reactions of α -oxyl peroxy radicals. The relevant α spin-orbitals (top row) and β spin-orbitals (bottom row) are not shown to scale, and the wavefunction sign is indicated with purple/green color. Filled spin-orbitals are indicated with up or down arrows for α and β spin electrons respectively. As the system evolves along the reaction coordinate, a weak hyperconjugative $\pi_{OO} \rightarrow \sigma_{CO}^*$ interaction between β spin-orbitals in the reactant (bottom row, left structure) is replaced by a strong $n_O \rightarrow \sigma_{CO}^*$ interaction the transition state (bottom row, middle structure), stabilizing the latter relative to the former.

tive stabilization can also assist H-shift reactions in hydrocarbon-derived RO_2 , but to a lesser extent, because σ_{CC}^* orbitals are poor electron acceptors. Our hypothesis is supported by second-order perturbation theory analysis of NBO donor-acceptor interactions. Results from these calculations and a more detailed discussion of this effect are given in Section C.5.7.

In summary, our finding that the 1,8 H-shift reaction is the fastest amongst unimolecular pathways available to 1,2-DEE 2- RO_2 can be explained by a combination of factors. C-H bond activation via hyperconjugative stabilization of the TS by an α -oxyl group, and a strengthened generalized anomeric effect at the TS relative to the reactant, both of which act to enhance the reactivity towards intramolecular H-shift reactions overall. Partial C-H bond deactivation at the abstraction site of competing pathways (1,5 and 1,6 H-shifts) via inductive electron withdrawal by a β -oxyl group, and a weaker degree of transannular repulsion experienced by the system at the 1,8 H-shift TS (compared to a hydrocarbon-derived RO_2), act to enhance selectivity towards the 1,8 H-shift reaction in specific. We note that the calculated steric energy trends challenge the usual explanation that entropic factors alone are the cause for the typical lack of competitiveness of long-span RO_2 H-shifts. While the large entropic penalty from the loss of many internal rotors is certainly important, TS energy-raising transannular repulsion is apparently also part of the reason why 1,8

H-shifts are slower in hydrocarbon-derived RO₂.

Regarding the second-generation 1,8 H-shift, i.e. the 1,8 H-shift reaction of 2-OO-5-ROOH, we notice that it is much slower than the first-generation 2-RO₂ 1,8 H-shift (Table 4.2 and 4.3), despite that the H abstraction site is substituted with two π -donating functional groups: -OOH and -O-.^{25,77} Here, C-H bond activation via π -donation from both substituents may not be entirely additive, while being overwhelmed by inductive C-H bond deactivation via σ -withdrawal by two electronegative α -oxygen atoms.^{85,94} Moreover, the intramolecular hydrogen-bond (H-bond) between the -OOH and -O- groups in the RO₂ reactant, which is exchanged by a weaker H-bond between the -OOH and the -OO groups in the TS of H-abstraction from the α -OOH position, likely also plays a role (Section C.5.8). The additional energy which is required to break this intramolecular H-bond raises the energy barrier for this H-shift reaction pathway. Presence of this H-bond also makes the 1,8 H-shift a minor reaction channel for 2-OO-5-ROOH, outcompeted by its 1,5 and 1,6 H-shift pathways (Table 4.4 and Section C.8.3), whose reaction TS formation does not involve disrupting the intramolecular interaction.

4.3.3 Atmospheric Implications

Based on our estimation, the fast 2-RO₂ 1,8 H-shift reaction can rival their reactions with NO at a NO level of ~ 5 ppb at 294 K (with $k_{\text{RO}_2+\text{NO}} = 9.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on Jenkin et al.⁴). Since RO₂ H-shift rates generally increase with temperature due to the energy barrier associated with the H-shift reaction coordinate,^{3,12} we expect the H-shift reaction to be competitive with bimolecular reaction with NO at even higher NO levels under warmer conditions. As shown in Table 4.5, on warm summer afternoons when outdoor temperatures can exceed 30 °C and occasionally reach 40 °C, the H-shift pathway can proceed at rates greater than 2 s^{-1} and outrun bimolecular reactions at $[\text{NO}] > 9 \text{ ppb}$. As urban NO_x levels often fall below 1 ppb due to successful NO_x emission control,^{14,15} the H-shift reaction is expected to be the dominant reaction pathway for the RO₂ under most urban atmospheric conditions.

Atmospheric autoxidation chemistry produces low-volatility HOMs through consecutive RO₂ H-shift reactions and O₂ addition, which add multiple hydroperoxy functionalities onto the carbon backbone of the VOC until the reaction chain is terminated by H abstraction at an α -OOH position, forming a ketone group (Scheme 4.1). VOCs with sufficiently long carbon chain to support multi-generational H-shifts are

Table 4.5: 2-RO₂ 1,8 H-shift rate coefficients at varied temperatures based on temperature dependence calculated by MC-TST method (details in Section S5.2), and corresponding NO concentrations that lead to pseudo-first-order reaction rate constants $k'_{\text{NO}} = k_{\text{RO}_2+\text{NO}}[\text{NO}]$ equivalent to the H-shift rates. ^a Calculated with $k_{\text{RO}_2+\text{NO}} = 2.7 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (T in K)⁴ and sea-level atmospheric pressure of $1 \times 10^5 \text{ Pa}$.

Temperature (°C)	$k_{1,8 \text{ H-shift, 2-RO}_2} (\text{s}^{-1})$	[NO] (ppb) ^a
10	0.60	2.4
20	1.10	4.8
30	1.98	9.4
40	3.48	17.6

thus considered to have a high potential to produce di- or even trihydroperoxy oxidation products, which will have extremely low volatility and promote new particle formation.¹² The long-chain diether compound investigated here represents such a system, and the fast long-range H-shift reaction further enhances its potential for HOM and SOA formation by enabling rapid incorporation of hydroperoxy groups at all possible positions in the molecule. The reaction allows the formation of HOMs from long-chain VOCs with the diether moiety, such as long-chain glycol ethers,²⁸ at a much higher rate than previously believed. For long-chain VOCs containing other oxygenated functional groups or other heteroatoms, such long-range RO₂ H-shift may also be possible, expanding the range of viable autoxidation pathways that produce structurally complex HOMs.

4.4 Conclusions

We perform experimental and computational investigations on intramolecular H-shift reactions of RO₂ derived from OH-initiated oxidation of the diether 1,2-DEE, and identify an unexpectedly fast 1,8 H-shift reaction of 1,2-DEE 2-RO₂ occurs at $\sim 1 \text{ s}^{-1}$ at ambient temperature of 294 K. This long-span H-shift outruns not only all other H-shift reactions in 1,2-DEE-derived RO₂, but also their bimolecular chemistry under atmospheric conditions. Quantum chemical calculations attribute the exceptional rate of this long-range H-shift reaction to a combination of factors. Hyperconjugative C-H bond activation by an α -oxyl group, combined with a kinetic generalized anomeric effect involving the peroxy group, enhances the RO₂ reactivity towards H-shifts overall, while weakened transannular strain in the 1,8 H-shift TS, combined with inductive C-H bond deactivation by a β -oxyl group in competing shorter-span pathways, enhances the RO₂ selectivity towards the 1,8 H-shift in specific. A series of photo-oxidation experiments are conducted using both ordi-

nary and isotope-labeled 1,2-DEE, which provides validation for the computational predictions of various H-shift processes in the system.

Our findings highlight how heteroatom-induced electronic effects modulate the reactivity of RO₂, and in particular, how the presence and positioning of oxygen atoms and oxygen-containing functional groups in the carbon backbone influence RO₂ H-shift reactions. With the unusually fast H-shift reaction identified here, a substantial fraction of 1,2-DEE RO₂ (>60%) will undergo autoxidation pathways under modern urban atmospheric conditions, where typical RO₂ bimolecular lifetime exceeds 5 s,¹¹ leading to efficient formation of HOMs. We expect that similar intramolecular H-shift mechanisms can be important, yet have been previously overlooked, in many similar systems, especially long-chain ethers and glycol ethers that are important classes of volatile chemical products (VCPs),^{28,95} an emerging urban VOC emission source.^{96,97} It is also possible that the long-span H-shift chemistry is relevant in the atmospheric oxidation of non-hydrocarbon compounds containing other heteroatoms with similar electron-directing ability as oxygen,⁸¹ such as amines (R–NH–R') and sulfides (R–S–R'), which are emitted into the atmosphere from various sources^{98,99} and are shown to undergo autoxidation.^{21,100,101} Extending investigations to those systems are essential for constraining autoxidation mechanisms and improving predictive models of HOMs and SOA formation from diverse VOC precursors. Moreover, since autoxidation chemistry via RO₂ H-shift reactions is also important in low-temperature combustion, food industry, and biochemistry,^{102,103} our discovery here may have implications for radical chemistry in other chemical environments.

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Chapter 5

AUTOXIDATION OF ESTERS: ETHYL PROPIONATE

5.1 Introduction

Alkyl esters are compounds with molecular formula $R-C(O)O-R'$, an important class of oxygenated volatile organic compound (OVOC) that are emitted into the atmosphere from various anthropogenic and natural sources.¹ Esters are widely used as solvents in industry and as reagents in manufacture of perfumes and food flavorings. A number of esters are present in vegetation and fruits, where they contribute to characteristic pleasant odor, and thus are added to perfumes and consumer products.²⁻⁴ Some alkyl esters (e.g., methyl and ethyl esters) are major constituents of biofuels and are used as diesel blends.⁵⁻⁷ They are also produced in the atmosphere by oxidation of ether compounds.^{1,3}

In the atmosphere, the degradation of saturated alkyl esters is generally initiated by their reactions with OH radicals. Esters are substantially less reactive towards OH radicals compared to ethers of the same size.^{1,3} While reactions between OH and ether compounds typically have rate coefficients at $\sim 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at ambient temperature, OH + ester reactions proceed an order of magnitude more slowly, with rate coefficients of $\sim 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁸ The reduced reactivity arises from the ester functionality $-C(O)O-$ that deactivates the alkyl groups to which it is attached, with deactivation most pronounced for the alkyl group attached to the carbonyl group.^{3,9}

The overall lower atmospheric reactivity of alkyl esters compared to other OVOCs suggests that they may contribute less to the formation of secondary atmospheric pollutants, such as ozone (O_3) and secondary organic aerosol (SOA). Therefore, there have been growing interests in using esters as alternatives to traditional organic solvents used in industries and volatile chemical products (VCPs),¹⁰ such as ethers and glycol ethers that are more reactive and may have higher SOA formation potential upon their release into the atmosphere.¹¹ Increases in use of esters in industrial and consumer products will lead to corresponding increases in their emissions. Thus, it is important to evaluate the environmental impacts of volatile esters by elucidating their atmospheric oxidation pathways and their potential to produce secondary atmospheric pollutants.

OH radical abstracts a hydrogen atom on the alkyl groups of the ester, yielding an alkyl radical ($R\cdot$). Under atmospheric conditions, the alkyl radical then reacts with oxygen molecule (O_2) to produce a peroxy radical (RO_2). For most volatile organic compounds (VOCs), the subsequent reactions of RO_2 would determine their chemical fate in the atmosphere.¹² Traditionally, the bimolecular reactions between RO_2 and reactants, such as NO, HO_2 , and other RO_2 , are believed to be dominant.^{13,14} With the advancements in analytical techniques, oxidation products from pathways other than the bimolecular reactions are measured and their formation pathways are recognized.¹⁵ One exemplary non-canonical pathway is the atmospheric autoxidation chemistry, which is initiated by an intramolecular hydrogen shift (H-shift) process to the RO_2 . O_2 addition to the nascent hydroperoxyalkyl radical (QOOH) forms a hydroperoxy RO_2 , which can lead to the formation of highly oxygenated organic molecules (HOMs), contributing to SOA formation.^{14,16,17}

Our previous investigations on the autoxidation chemistry of simple ethers and glycol ethers have shown that H-shift reactions of RO_2 from those systems occurs at $\sim 0.1\text{ s}^{-1}$,^{18,19} which can be competitive with their bimolecular reactions under urban atmospheric conditions following NO_x emission controls where NO levels can fall below 1 ppb.^{20,21} Those relatively fast H-shifts are facilitated by the α -oxyl or hydroxyl group that activates the adjacent C-H bond from which the H atom is abstracted.²² In contrast, the ester functional groups $-C(O)O-$ deactivate adjacent C-H bonds,^{1,3} and are thereby expected to suppress autoxidation chemistry. Thus, we infer that ester compounds are unlikely to undergo efficient autoxidation, which reduce their potential to form HOMs and SOA.

To examine the potential of esters to be an environmentally friendly class of OVOC, this study aims at investigating the atmospheric oxidation pathways of saturated alkyl esters, with a focus on the unimolecular autoxidation chemistry. We use ethyl propionate (EP) as the model system for this investigation. We conduct a series of photo-oxidation experiments of EP by OH with differing HO_2 concentrations to explore the bimolecular and unimolecular chemistry of EP-derived RO_2 . The experimental results are analyzed with help from box model simulations to derive kinetic parameters for key pathways of EP oxidation.

5.2 Methods

We apply similar method as in our previous studies^{18,19} to investigate the oxidation mechanism of ethyl propionate. Briefly, photo-oxidation experiments of ethyl pro-

pionate (EP, 99% Sigma Aldrich) are conducted in a $\sim 0.7 \text{ m}^3$ Teflon environmental chamber. The chamber enclosure is covered with UV reflective metal and can be equipped with eight UV lamps, either 254 nm (Sankyo Denki G40T10) or 350 nm (Sylvania 350 Blacklight). Oxidation of EP are initiated by OH radicals, which are generated by photolysis of H_2O_2 through reaction: $\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$. We use HO_2 as the primary bimolecular reactants in the experiments, which is produced through reaction: $\text{CH}_3\text{OH} + \text{OH} \xrightarrow{\text{O}_2} \text{HO}_2 + \text{HCHO} + \text{H}_2\text{O}$. Differing concentrations of HO_2 are produced by adjusting the rate of this reaction. We adjust the type and number of UV lamps in the chamber enclosure to control the rate of photolysis reactions in the chamber, mainly the production of OH from H_2O_2 photolysis, which in turn governs the formation rate of HO_2 . More details about constraining $[\text{HO}_2]$ in the chamber are also discussed in our previous publications.^{18,19} The reactivity of CH_3OH with OH is kept much higher than that with EP to ensure production rate of HO_2 exceeds that of EP RO_2 to suppress RO_2 self-reactions. The HO_2 concentrations in our experiments are determined by box model simulations (described below). A list of experimental conditions is provided in Table D.1.

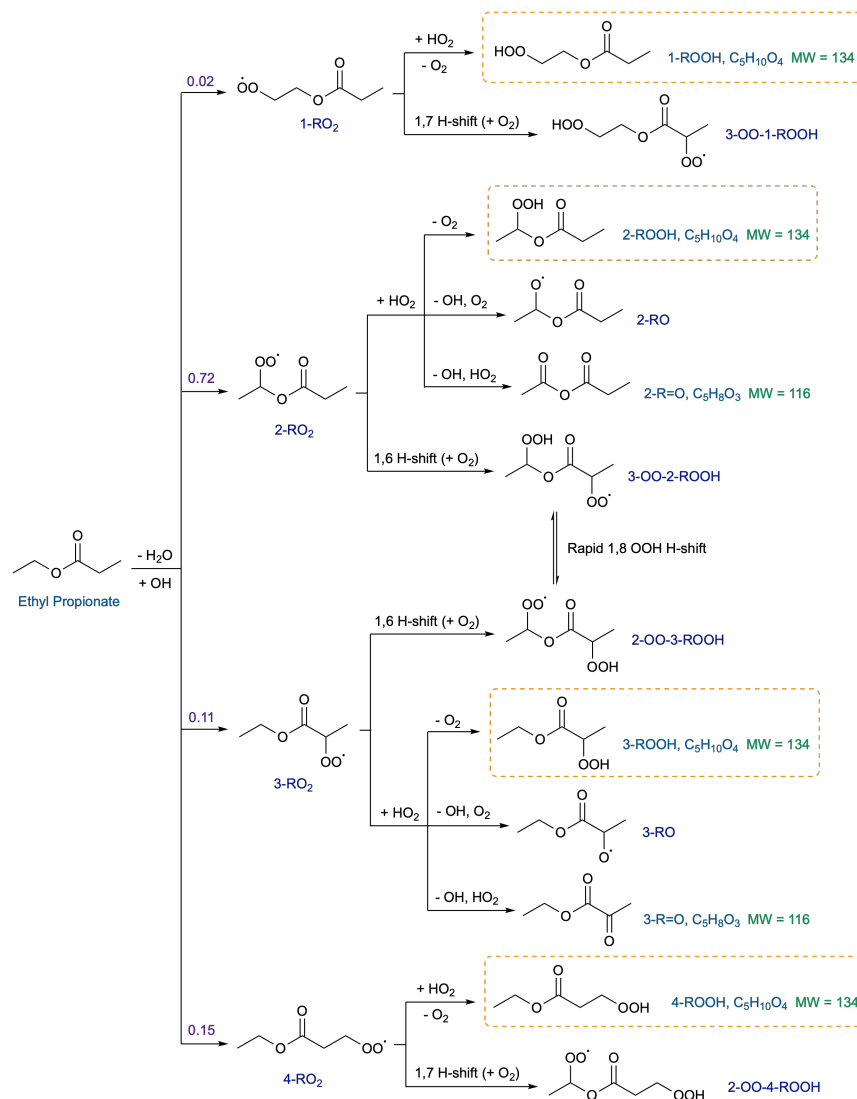
The oxidation products from EP are measured by a high-resolution time-of-flight chemical ionization mass spectrometer coupled with gas chromatography (GC-CIMS). The configuration of the instrument is described in detail elsewhere.²³ In brief, the instrument provides us isomer-resolved detection of gas-phase oxygenated organic compounds. CF_3O^- is used as the reagent ion for the CIMS, which makes the instrument sensitive to multifunctional oxygenated VOCs, such as hydroperoxides and nitrates.^{23,24} The analytes are mostly detected as cluster ions with CF_3O^- at m/z neutral mass + 85 amu. We estimate the CIMS sensitivity of the analytes by their ion-molecule collision rates with CF_3O^- , which can be determined by methods by Su and Chesnavich²⁵ using the calculated dipole moment and polarizability of the molecule.²⁶ In this preliminary study, we assume that all multifunctional reaction products from the system have the same CIMS sensitivity, based on our previous investigations on multifunctional organic compounds, which is discussed in detail in Section D.4.1.

A MATLAB-based gas-phase chemistry box model is used to simulate the experimental results. The model uses the MATLAB ode15s solver to calculate time-dependent concentrations of chemical species based on given initial conditions and a specified chemical mechanism. The reaction kinetics of bimolecular and unimolecular chemistry implemented in the model are initially adopted from the Master

Chemical Mechanism (MCM)²⁷ and estimations reported in literatures.^{8,12,28} The kinetics and branching ratios of those reactions in the implemented mechanism are then adjusted to minimize the difference between the experimental data and the simulations, providing optimized estimates of those reaction parameters.

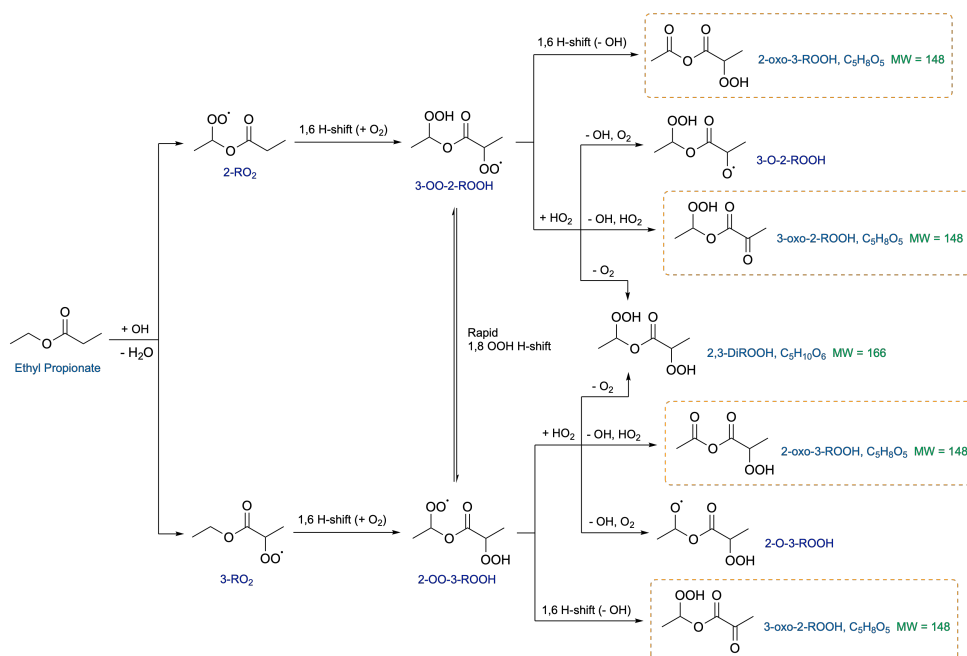
5.3 Results

5.3.1 Identity of Major EP Oxidation Products



Scheme 5.1: Oxidation of EP by OH radical. The branching fractions of the initial steps are denoted in purple (derived in Section D.6.1). Subsequent reactions of the peroxy radicals and respective reaction products are also shown, including RO₂ + HO₂ bimolecular reactions and unimolecular H-shift reactions. The molecular masses of major closed-shell products are shown in green. Products that are detected by our instrument are shown in orange boxes. Detailed oxidation mechanisms of EP are discussed in Section D.1.

Shown in Scheme 5.1 are the initiation step of EP oxidation chemistry, production of simple hydroperoxides (ROOH) from $\text{RO}_2 + \text{HO}_2$ reactions, and production of hydroperoxy RO_2 (OO-ROOH) from RO_2 H-shift reactions. Based on estimations by structure-activity relationship (SAR),^{12,29} the production of 2- RO_2 is likely the dominant pathway ($\sim 75\%$), followed by 4- RO_2 ($\sim 12\%$), 3- RO_2 ($\sim 10\%$), and 1- RO_2 ($< 3\%$). Thus, we infer that the dominant autoxidation pathways in our system proceed through the 1,6 H-shift reactions of 2- RO_2 and 3- RO_2 , which lead to formation of 3-OO-2-ROOH and 2-OO-3-ROOH. The subsequent reactions of 2-OO-3-ROOH and 3-OO-2-ROOH are shown in Scheme 5.2.



Scheme 5.2: Proposed autoxidation mechanisms of EP 2- RO_2 and 3- RO_2 . Subsequent bimolecular reaction with HO_2 , H-shift reactions, and respective products are also shown. The molecular masses of major closed-shell products are denoted in green. Products that are detected by our instrument are shown in orange boxes. Detailed reaction mechanisms of 2-OO-3-ROOH and 3-OO-2-ROOH are shown in Section D.1.

Shown in Figure 5.1 are the gas chromatograms of major EP oxidation products from an experiment with $[\text{HO}_2]$ of 1 ppb ($\sim 2.5 \times 10^{10}$ molecules cm^{-3}). The reaction products of interest include the hydroperoxides (ROOH, m/z 219) resulted from $\text{RO}_2 + \text{HO}_2$ reactions (Scheme 5.1) and the ketohydroperoxides (oxoROOH, m/z 233) resulted from autoxidation chemistry (Scheme 5.2). We identify ROOH and oxoROOH isomers by oxidizing a partially deuterated ethyl propionate (ethyl propionate- d_5 , 98% D, CDN isotopes), which enables us to determine the positions of different functionalization. More details are discussed in Section D.2.1.

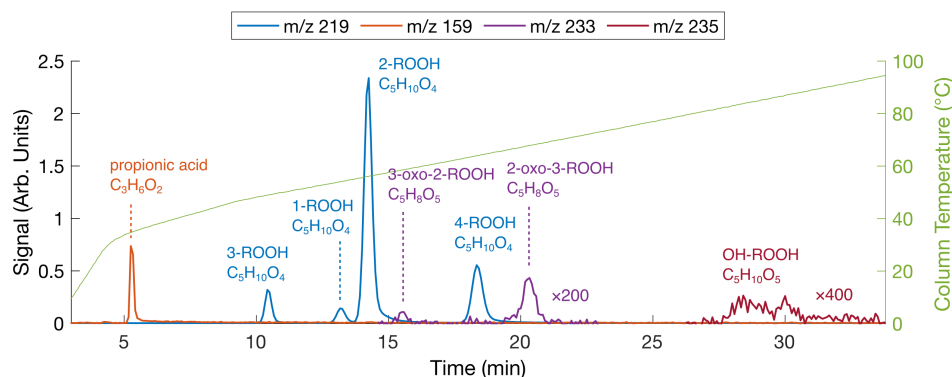
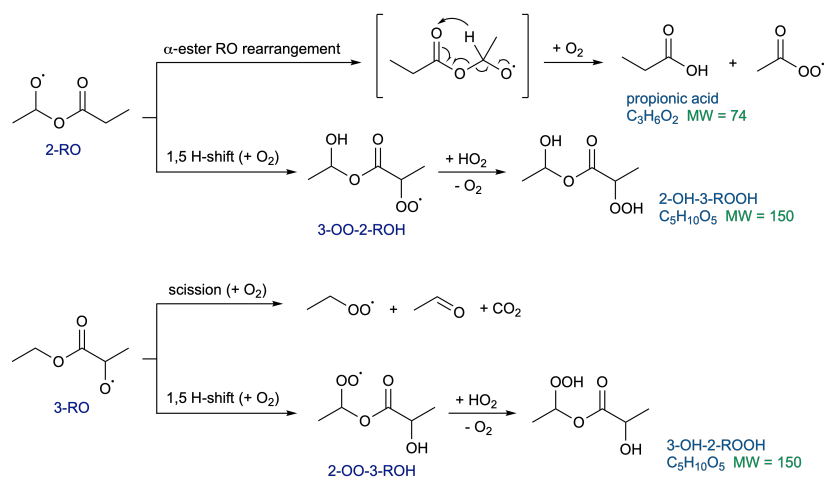


Figure 5.1: Gas chromatograms of EP oxidation products from an experiment with $[\text{HO}_2]$ ~ 1 ppb. Certain signals are scaled up by a factor denoted in the figure.

We also identify products from reactions of EP-derived alkoxy radicals (RO): propionic acid (m/z 159) and isomers of hydroxy ROOH (OH-ROOH, m/z 235). We propose their formation pathway in Scheme 5.3. The propionic acid is likely produced through an α -ester RO rearrangement reaction.³⁰ It is a decomposition reaction that occurs through a concerted mechanism of a RO radical with α -ester functionality, which leads to formation of an organic acid and an acyl radical. This pathway likely dominates over other reaction pathways of 2-RO and produces propionic acid. A minor isomerization pathway of 2-RO may lead to formation of a hydroxy RO₂ (OO-ROH), 3-OO-2-ROH. The isomerization pathway of 3-RO also forms a hydroxy RO₂, 2-OO-3-ROH. Both OO-ROH can further react with HO₂ and contribute to formation of OH-ROOH. The reaction pathways of alkoxy radicals are

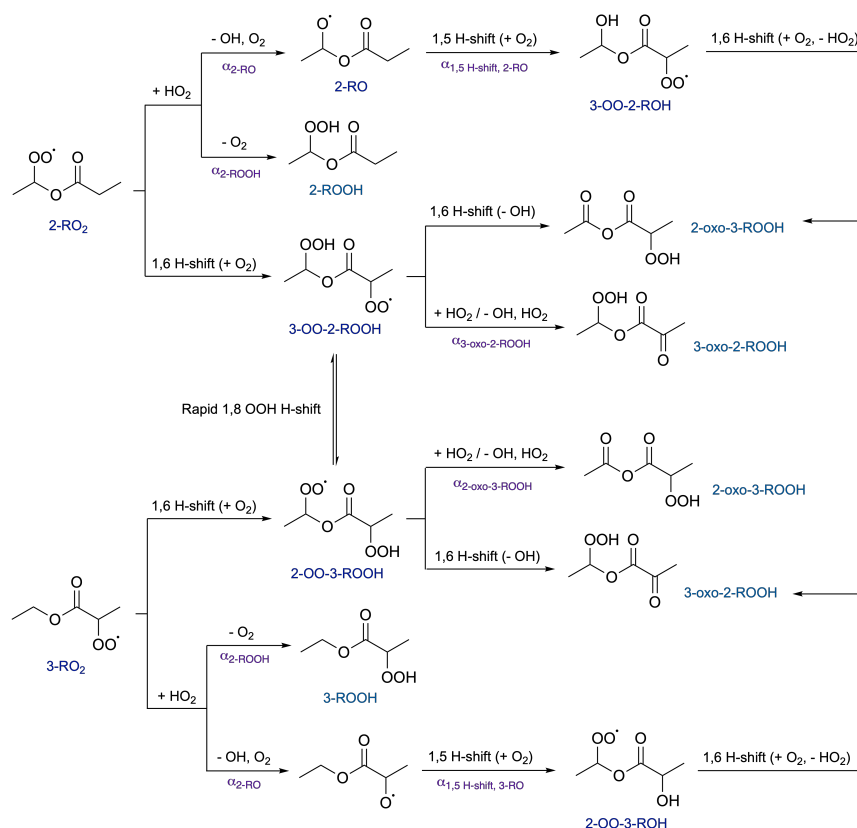


Scheme 5.3: Reactions of EP-derived alkoxy radicals. The molecular masses of major closed-shell products are denoted in green. More details regarding these reactions are discussed in Section D.6.

also verified by an EP oxidation experiment with presence of NO (Section D.2.2).

5.3.2 Rate Coefficients of EP RO₂ Unimolecular Reactions

As shown in Figure 5.1, we only detect minimal amount of reaction products from EP autoxidation pathway, which is consistent with our expectation that autoxidation chemistry will be slow in ester compounds. We estimate the rate coefficients of H-shift reactions of EP-derived RO₂ by comparing the yields of EP ROOH and oxoROOH. Shown in Scheme 5.4 are the detailed formation pathways of 2-oxo-3-ROOH and 3-oxo-2-ROOH. The oxoROOH can be produced from the H-shift reactions of 2-RO₂, 3-RO₂, as well as those of the hydroxy RO₂, 3-OO-2-ROH and 2-OO-3-ROH.



Scheme 5.4: Proposed formation pathways of 2-oxo-3-ROOH and 3-oxo-2-ROOH. Reaction parameters of certain reactions are denoted in purple and are derived in Section D.6.

Here, we propose two possible mechanisms that may account for the observed yields of EP-derived oxoROOH, each of which implies a different set of estimated EP RO₂ H-shift rate coefficients.

5.3.2.1 EP oxoROOH produced mainly from H-shifts of simple RO₂

We compare the rates of 2-RO₂ and 3-RO₂ bimolecular pathways and the total production rates of oxoROOH by:

$$\frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[\text{oxo-ROOH}]} = \frac{k_{\text{RO}_2+\text{HO}_2}[\text{RO}_2][\text{HO}_2]}{\alpha_{\text{oxoROOH}}k_{\text{OO-ROOH}+\text{HO}_2}[\text{OO-ROOH}][\text{HO}_2] + k_{\text{H-shift,OO-ROOH}}[\text{OO-ROOH}] + k_{\text{H-shift,OO-ROH}}[\text{OO-ROH}]} \quad (5.1)$$

where $\alpha_{2\text{-ROOH}}$ and $\alpha_{3\text{-ROOH}}$ indicates the branching fractions to formation of corresponding simple ROOH through RO₂ + HO₂ reactions, $k_{\text{RO}_2+\text{HO}_2}$ is the overall rate coefficient of reactions between simple RO₂ and HO₂, $k_{\text{OO-ROOH}+\text{HO}_2}$ is the overall rate coefficient of reactions between hydroperoxy RO₂ and HO₂, α_{oxoROOH} indicates the average branching fractions to formation of oxoROOH from OO-ROOH+HO₂ reactions, $k_{\text{H-shift,OO-ROOH}}$ is the average H-shift rate coefficient of OO-ROOH, and $k_{\text{H-shift,OO-ROH}}$ indicate the average H-shift rate coefficient of OO-ROH.

In order to derive rate coefficients of H-shift rate coefficients of 2-RO₂ and 3-RO₂ from Equation 5.1, we assume that under high [HO₂] conditions, the H-shift reactions of OO-ROOH and OO-ROH are negligible. Thus, we can simplify Equation 5.1 to:

$$\frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[\text{oxo-ROOH}]} \simeq \frac{k_{\text{RO}_2+\text{HO}_2}[\text{RO}_2][\text{HO}_2]}{\alpha_{\text{oxoROOH}}k_{\text{OO-ROOH}+\text{HO}_2}[\text{OO-ROOH}][\text{HO}_2]} \quad (5.2)$$

By assuming steady state for OO-ROOH, in Equation 5.2, we replace the loss of [OO-ROOH] by their bimolecular reaction with their production from H-shifts of 2-RO₂ and 3-RO₂: $k_{\text{H-shift,RO}_2}[\text{RO}_2]$, where $k_{\text{H-shift,RO}_2}$ indicate the average H-shift rate coefficient of 2-RO₂ and 3-RO₂ 1,6 H-shifts:

$$\begin{aligned} & \frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[\text{oxo-ROOH}]} \\ & \simeq \frac{k_{\text{RO}_2+\text{HO}_2}[\text{RO}_2][\text{HO}_2]}{\alpha_{\text{oxoROOH}}k_{\text{H-shift,RO}_2}[\text{RO}_2]} \\ & \simeq \frac{k_{\text{RO}_2+\text{HO}_2}}{\alpha_{\text{oxoROOH}}k_{\text{H-shift,RO}_2}}[\text{HO}_2] \end{aligned} \quad (5.3)$$

Based on Equation 5.3, we observe a rough linear relationship between the yields of 2-ROOH and 3-ROOH divided by their branching fractions (derived in Section D.6.1) from RO₂+HO₂ reactions and the yields of 2-oxo-3-ROOH and 3-oxo-2-ROOH at high [HO₂], as shown in Figure 5.2. The slope of the linear relationship is found to be $(7.98 \pm 3.53) \times 10^{-9} \text{ cm}^3 \text{ molecules}^{-1}$. The rate coefficient $k_{\text{RO}_2+\text{HO}_2}$

can be estimated based on method in Jenkin et al.¹² and Wennberg et al.³¹ to be $1.86 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 294 K. Since we fail to detect all products from $\text{OO-ROOH} + \text{HO}_2$ reactions, we assume α_{oxoROOH} to equal ~ 0.28 based on values reported in previous studies on carbonyl- and OH-substituted RO_2 . Thus, we estimate $k_{\text{H-shift,RO}_2}$ to be $\sim 0.008 \text{ s}^{-1}$, which is consistent with our expectation.

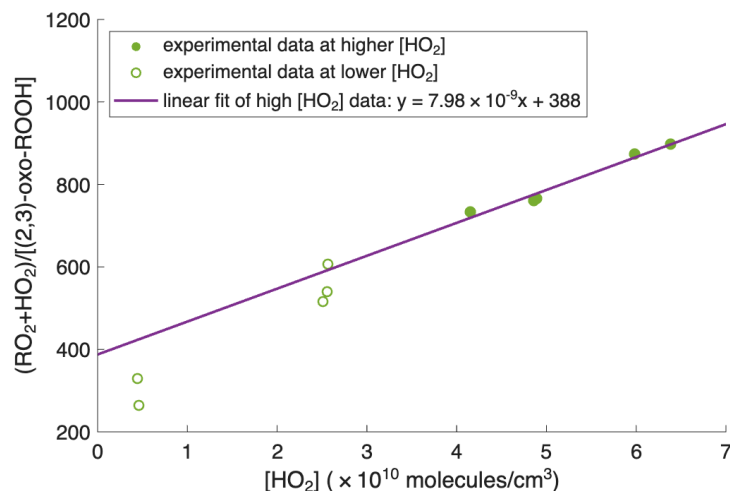


Figure 5.2: $k_{\text{RO}_2+\text{HO}_2} ([2\text{-RO}_2] + [3\text{-RO}_2]) [\text{HO}_2] / ([2\text{-oxo-3-ROOH}] + [3\text{-oxo-2-ROOH}])$ vs. $[\text{HO}_2]$ at ambient temperature (294 K), and the result from linear regression fit ($R^2 = 0.971$) of data with $[\text{HO}_2] > 4 \times 10^{10} \text{ molecules cm}^{-3}$.

Still, we are confused by the large intercept of the linear regression fit in Figure 5.2, since based on Equation 5.3, we expect an approximate linear relationship with an intercept close to 0. Given the major uncertainties in the measured concentrations of reaction products in this system (discussed in Section D.7), the large intercept could arise from propagation and compounding of these uncertainties. The other hypothesis for this phenomenon suggests the potential existence of a unimolecular reaction that consumes 2-OO-3-ROOH and/or 3-OO-2-ROOH, which leads to smaller yields of oxoROOH at all $[\text{HO}_2]$. By box model simulation, as shown in Figure 5.3, we propose that this reaction could occur at $\sim 1.5 \text{ s}^{-1}$.

We propose one possible reaction that could result in this phenomenon: an intramolecular RO_2 cyclization with π -bonds in the carbonyl group. The peroxy radical center attacks the carbonyl carbon, yielding a cyclic alkoxy radical with a secondary ozonide structure (Scheme 5.5). This reaction is suggested by previous computational work to have a low energy barrier, and can be important in compounds with a ketone functionality when the cyclic transition state has five or more atoms.^{32,33} We thus propose that this reaction is possible for both 2- RO_2 and 2-OO-3-ROOH in our system. While the cyclization of 2- RO_2 is likely reversible through

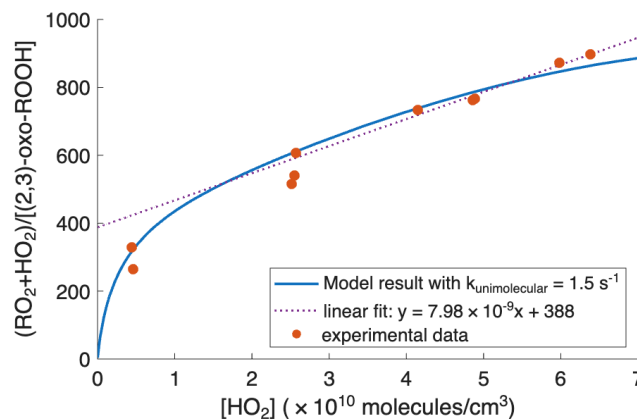
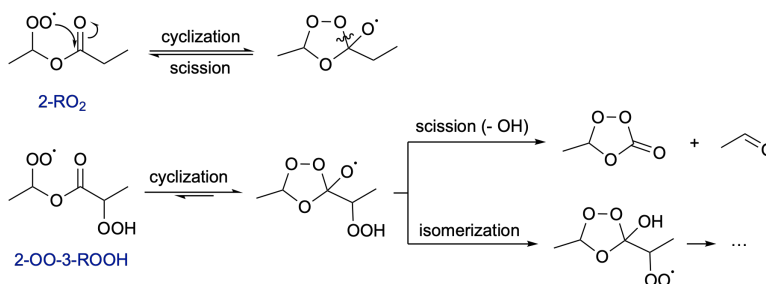


Figure 5.3: $k_{\text{RO}_2+\text{HO}_2} ([2\text{-RO}_2] + [3\text{-RO}_2]) [\text{HO}_2] / ([2\text{-oxo-3-ROOH}] + [3\text{-oxo-2-ROOH}])$ vs. $[\text{HO}_2]$ at ambient temperature (294 K). The linear fit from Figure 5.2 is shown as the purple dotted line. The result from box model simulation with the fast unimolecular reaction is shown as the blue line. The reaction parameters we use for model simulation are listed and discussed in Section D.6.

dissociation of the C-O bond in the cyclic alkoxy radical derived from 2-RO₂, the presence of the hydroperoxy group in 2-OO-3-ROOH might enable additional reaction pathways for the corresponding cyclic alkoxy radical, as proposed in Scheme 5.5. However, we failed to detect signatures of potential reaction products from the proposed cyclization process of 2-OO-3-ROOH. The hypothesized secondary ozonide-like products could either decompose upon formation or undergo multi-phase processes and partition into the particle phase.



Scheme 5.5: Proposed cyclization pathways of 2-RO₂ and 2-OO-3-ROOH

5.3.2.2 EP oxoROOH produced mainly from H-shifts of OO-ROH radicals

Here, we propose an alternative hypothesis that could explain the large intercept in the linear regression shown in Figure 5.2, in which oxoROOH products are formed mainly from H-shift reactions of OO-ROH radicals (Scheme 5.4), such that the H-shift rate coefficients of OO-ROH radicals are much faster, while those of RO₂ are negligible. Thus, the ratio between the yields of simple ROOH and oxoROOH

(e.g. 2-ROOH and 2-oxo-3-ROOH) can be formulated as:

$$\frac{[2\text{-ROOH}]}{[2\text{-oxo-3-ROOH}]} = \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [2\text{-RO}_2] [\text{HO}_2]}{k_{\text{H-shift},3\text{-OO-2-ROH}} [3\text{-OO-2-ROH}]} \quad (5.4)$$

where $k_{\text{H-shift},3\text{-OO-2-ROH}}$ is the H-shift rate coefficient of 3-OO-ROH. According to Scheme 5.4, 3-OO-2-ROH can be produced from a 1,5 H-shift reaction of the alkoxy radical 2-RO, and undergo a 1,6 H-shift reaction to form 2-oxo-3-ROOH. Thus we have the rate equation of 3-OO-2-ROH:

$$\begin{aligned} \frac{d[3\text{-OO-2-ROH}]}{dt} = & \alpha_{3\text{-OO-2-ROH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{RO}_2] [\text{HO}_2] \\ & - k_{\text{H-shift},3\text{-OO-2-ROH}} [3\text{-OO-2-ROH}] \\ & - k_{3\text{-OO-2-ROH}+\text{HO}_2} [3\text{-OO-2-ROH}] [\text{HO}_2] \end{aligned} \quad (5.5)$$

where $\alpha_{3\text{-OO-2-ROH}}$ is the branching fraction to formation of 3-OO-2-ROH from $2\text{-RO}_2 + \text{HO}_2$ reaction, and $k_{3\text{-OO-2-ROH}+\text{HO}_2}$ is the overall rate coefficient of reaction between 3-OO-2-ROH and HO_2 . By assuming steady state for [3-OO-2-ROH] gives:

$$[3\text{-OO-2-ROH}] = \frac{\alpha_{3\text{-OO-2-ROH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{RO}_2] [\text{HO}_2]}{k_{\text{H-shift},3\text{-OO-2-ROH}} + k_{3\text{-OO-2-ROH}+\text{HO}_2} [\text{HO}_2]} \quad (5.6)$$

Plugging Equation 5.6 into Equation 5.8 gives us:

$$\begin{aligned} & \frac{[2\text{-ROOH}]}{[2\text{-oxo-3-ROOH}]} \\ &= \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [2\text{-RO}_2] [\text{HO}_2]}{k_{\text{H-shift},3\text{-OO-2-ROH}} \times \frac{\alpha_{3\text{-OO-2-ROH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{RO}_2] [\text{HO}_2]}{k_{\text{H-shift},3\text{-OO-2-ROH}} + k_{3\text{-OO-2-ROH}+\text{HO}_2} [\text{HO}_2]}} \end{aligned} \quad (5.7)$$

which can be further simplified to be:

$$\begin{aligned} & \frac{[2\text{-ROOH}]}{[2\text{-oxo-3-ROOH}]} \\ &= \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [2\text{-RO}_2] [\text{HO}_2] \times (k_{\text{H-shift},3\text{-OO-2-ROH}} + k_{3\text{-OO-2-ROH}+\text{HO}_2} [\text{HO}_2])}{k_{\text{H-shift},3\text{-OO-2-ROH}} \times \alpha_{3\text{-OO-2-ROH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{RO}_2] [\text{HO}_2]} \\ &= \frac{\alpha_{2\text{-ROOH}} \times (k_{\text{H-shift},3\text{-OO-2-ROH}} + k_{3\text{-OO-2-ROH}+\text{HO}_2} [\text{HO}_2])}{k_{\text{H-shift},3\text{-OO-2-ROH}} \times \alpha_{3\text{-OO-2-ROH}}} \\ &= \frac{\alpha_{2\text{-ROOH}}}{\alpha_{3\text{-OO-2-ROH}}} + \frac{\alpha_{2\text{-ROOH}} \times k_{3\text{-OO-2-ROH}+\text{HO}_2}}{\alpha_{3\text{-OO-2-ROH}} \times k_{\text{H-shift},3\text{-OO-2-ROH}}} [\text{HO}_2] \end{aligned} \quad (5.8)$$

Thus, with the H-shift reactions of OO-ROH radicals being much faster than those of the simple RO_2 from which they are derived, there should be a linear relationship

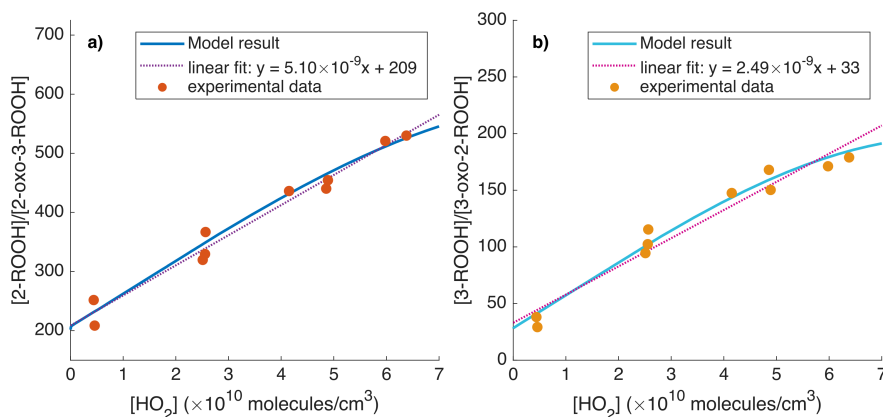


Figure 5.4: (a) $[2\text{-ROOH}]/[2\text{-oxo-3-ROOH}]$ vs. $[\text{HO}_2]$ and (b) $[3\text{-ROOH}]/[3\text{-oxo-2-ROOH}]$ vs. $[\text{HO}_2]$ at ambient temperature. Repsective linear regression fits are shown as dotted line, and model results based on estimated reaction parameters in Table 5.1 are shown as solid line.

between the ratio of the yields of simple ROOH to oxoROOH and HO_2 concentrations. The linear relationship enables us to derive the H-shift rate coefficients, as well as parameters of other reactions, for the OO-ROH radicals.

Figure 5.4 shows the linear regression fits of $[2\text{-ROOH}]/[2\text{-oxo-3-ROOH}]$ and $[3\text{-ROOH}]/[3\text{-oxo-2-ROOH}]$ versus $[\text{HO}_2]$. Based on Equation 5.8, the intercept of the linear fit equals the ratio between the branching fraction of ROOH and OO-ROH formation pathways in the $\text{RO}_2 + \text{HO}_2$ reaction. The slope of the linear fit can be used to calculate the H-shift rate coefficients of respective OO-ROH based on the value of the slope and the rate coefficient of the bimolecular rate coefficient of OO-ROH+ HO_2 reaction:

$$k_{\text{H-shift,OO-ROH}} = \frac{(\text{intercept in Figure 5.4}) \times k_{\text{OO-ROH}+\text{HO}_2}}{(\text{slope in Figure 5.4})} \quad (5.9)$$

The rate coefficient of OO-ROH+ HO_2 can be estimated based on method in Jenkin et al.¹² and Wennberg et al.³¹ to be $1.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K.

Table 5.1: Estimations of key parameters of reactions involving OO-ROH radicals at 294 K. Here, the rate coefficients of H-shift reactions of 2- RO_2 and 3- RO_2 are set to be 0. ^a Branching fraction of ROOH formation from RO_2+HO_2 reactions are derived in Section D.6.1.

2- RO_2	3-OO-2-ROH	
$\alpha_{2\text{-ROOH}} = 0.52 \pm 0.09^{\text{a}}$	$\alpha_{3\text{-OO-2-ROH}} = (25 \pm 9) \times 10^{-4}$	$k_{1,6 \text{ H-shift, 3-OO-2-ROH}} = 0.72 \pm 0.52 \text{ s}^{-1}$
3- RO_2	2-OO-3-ROH	
$\alpha_{3\text{-ROOH}} = 0.40 \pm 0.16^{\text{a}}$	$\alpha_{2\text{-OO-3-ROH}} = (14 \pm 7) \times 10^{-3}$	$k_{1,6 \text{ H-shift, 2-OO-3-ROH}} = 0.19 \pm 0.14 \text{ s}^{-1}$

Shown in Table 5.1 are our estimates of the relevant reaction parameters derived from the linear fits in Figure 5.4 and Equation 5.9. The derived H-shift rate coefficients for 2-OO-3-ROH and 3-OO-2-ROH are exceptionally fast, which appears unlikely for ester-derived RO₂. Nevertheless, this hypothesis suggests that relatively fast H-shift reactions of hydroxy RO₂ radicals formed via RO radical isomerization may partially account for the non-zero intercept observed in the linear relationship between the ratio of bimolecular to autoxidation product yields and the concentration of the bimolecular reactant.

5.4 Atmospheric Implications

In this study, we estimate the rate coefficients of H-shift reactions of simple RO₂ derived from ethyl propionate likely to be $<0.008\text{ s}^{-1}$, which is approximately one order of magnitude lower than those of RO₂ from the more reactive compound classes, such as ethers, glycol ethers, and alcohols. Autoxidation chemistry of ester-derived RO₂ is suppressed by the ester functionality and is unlikely to compete with their bimolecular chemistry unless under very clean air conditions ($[\text{NO}] < 0.05\text{ ppb}$).

By analyzing the yields of EP autoxidation products at varied $[\text{HO}_2]$, we propose that there could be a fast unimolecular reaction pathway ($\sim 1\text{ s}^{-1}$) that is consuming the hydroperoxy RO₂ formed from the ester. We were unable to detect potential reaction products from this hypothesized pathway, despite this chemistry should be dominant over most experimental conditions considering its exceptional rate. One possible explanation is that this pathway produces species that either fragment readily or partition into the condensed phase. Determining whether the pathway leads to decomposition or formation of low-volatility organics has important implications regarding the aerosol formation potential of the compound. Thus, more comprehensive studies, such as aerosol yield measurements, are crucial to fully assess the atmospheric oxidation potential and evaluate the environmental compatibility of this compound, and more broadly, saturated alkyl esters as a class.

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Chapter 6

CONCLUSIONS AND FUTURE WORK

This thesis examined the atmospheric autoxidation chemistry of volatile organic compounds (VOCs) associated with volatile chemical products (VCPs). The work focused on four representative molecules spanning three VCP classes – ethers, glycol ethers, and esters – to investigate the autoxidation mechanisms of those classes of compounds, the resulting formation of highly oxygenated organic molecules (HOMs), and, in particular, the influence of specific functional groups on the unimolecular H-shift chemistry of organic peroxy radicals (RO_2). Gas-phase oxidation experiments, complemented by computational analyses and box model simulations, were used to quantify RO_2 H-shift rate coefficients and assess the extent to which RO_2 autoxidation can compete with their bimolecular reactions under modern urban atmospheric conditions.

The investigations in Chapters 2 and 3 on simple ether and glycol ether compounds (diethyl ether and 2-ethoxyethanol) demonstrate that H-shift reactions from carbons α to hydroxyl ($-\text{OH}$), ether ($-\text{OCH}_2-$), and hydroperoxyl ($-\text{OOH}$) groups are accelerated and occur at a rate of $0.05\text{--}0.2\text{ s}^{-1}$ at ambient temperature. These H-shifts are facilitated by the electron-donating α -oxygen atoms, which increase the lability of the neighboring C-H bonds and stabilize the H-shift transition states (TSSs) via hyperconjugation,^{51,52} enabling autoxidation chemistry in those systems to proceed on atmospherically relevant timescales. In contrast, ester groups ($-\text{C}(\text{O})\text{O}-$) suppress RO_2 H-shift chemistry and limit the formation of HOMs. As shown in Chapter 5, the electron-withdrawing carbonyl group deactivates the adjacent C-H bonds, resulting in RO_2 H-shift rate coefficients that are approximately an order of magnitude lower than those associated with electron-donating substituents.

In Chapter 4, the autoxidation chemistry of a long-chain diether compound, 1,2-diethoxyethane (1,2-DEE), is examined, revealing an unexpectedly rapid long-range 1,8 H-shift in a simple RO_2 derived from this system. While the 1,5 and 1,6 H-shift rates of 1,2-DEE-derived RO_2 are comparable to those observed for simple ethers and glycol ethers (Chapters 2 and 3), the entropically less favorable^{11,41} 1,8 H-shift proceeds at approximately 1 s^{-1} , outcompeting RO_2 bimolecular processes under most urban atmospheric conditions. Computational analyses indicate that the diether

structural motif facilitates this long-range H-shift through a combination of effects. Activation of the C-H bond by the α -oxyl substituent and stereoelectronic effects involving the peroxy group⁵³ act to enhance reactivity towards H-shifts in the system overall. Weaker transannular strain in the 1,8 H-shift transition state, combined with inductive deactivation of C-H bonds by a β -oxyl group at the abstraction site of competing 1,5 and 1,6 H-shifts,^{54,55} enhance the selectivity towards the 1,8 H-shift in specific. Another potentially rapid unimolecular reaction noticed in this work is an intramolecular cyclization of a RO₂ radical derived from the ester ethyl propionate (Chapter 5). Although the outcome of this reaction are not yet known, the presence of such a cyclization pathway may have important implications for the atmospheric chemical fate and secondary organic aerosol (SOA) formation potential of alkyl esters.

In summary, the findings in this thesis highlight the key role of functional group chemistry in determining whether VCP-derived oxygenated VOCs undergo extensive autoxidation and contribute to HOM and SOA formation in urban environments. While the results presented here advance mechanistic understanding of autoxidation chemistry of functionalized VOCs, several important questions remain. Addressing these questions will be essential for evaluating the growing importance of VCP emissions and VOC autoxidation chemistry, as well as informing future environmental policy decisions.

Characterization of SOA yields and properties from investigated VCP precursors under atmospheric-relevant conditions

Direct measurements of SOA yields under atmospherically relevant conditions are needed to quantitatively connect investigated autoxidation kinetics to particle formation. Future environmental chamber and flow tube studies should evaluate SOA yields and resolve the contribution of HOM formation from the investigated VCP precursors across a range of NO_x levels, relative humidity, and temperatures representative of urban environments.

The production of HOMs from autoxidation is expected to increase under lower NO_x conditions, when RO₂ radicals are less efficiently terminated by bimolecular reactions with NO, and at higher temperatures, when RO₂ H-shift rates will increase due to the high energy barrier along the H-shift reaction coordinate,⁴ as shown in Chapter 3. However, more efficient H-shift chemistry at higher temperatures does not necessarily lead to higher SOA yield, since the volatility of HOMs also increases

with temperature. Systematic characterization of how these environmental factors influence HOM production and SOA yields will therefore be crucial for constraining the contribution of VCP-derived VOCs to urban aerosol burdens and their further impact on air quality and human health.

Gas-phase oxidation of more diverse VOC classes

This thesis focused on ethers, glycol ethers, and esters that are important VCP-relevant compound classes. However, many other anthropogenic VOCs may also exhibit distinct autoxidation behavior. One notable example is aldehydes, which are emitted from fossil fuel and biomass burning, cooking activities, and produced from VOC oxidation processes.^{42,56} Studies have shown that aldehyde-derived RO₂ undergo rapid H-shift reactions.^{42,57} Terpenoids from fragranced products, such as limonene, are also shown to produce HOMs from autoxidation pathways.⁵⁸ The presence of conjugated systems in terpene compounds are expected to facilitate H-shift reactions of RO₂ from those systems.^{41,59} Expanding investigations to a broader ranges of VOC classes and evaluating their underlying H-shift reaction mechanisms would help develop a more general structure–reactivity framework for RO₂ autoxidation chemistry.

Certain functional groups may enable other reaction channels of the VOCs beyond RO₂ autoxidation, such as α -ester alkoxy rearrangement,⁶⁰ epoxide formation from hydroperxy-substituted alkyl radical,⁶¹ and intramolecular radical addition to π -bonds (as described in Chapter 5).^{59,62,63} Many of these pathways are predicted to be sufficiently fast to dominate the overall VOC reactivity under a wide range of atmospheric conditions.³⁸ It is likely that many more reactions of functionalized intermediates are yet to be characterized. Identifying and quantifying those pathways will be important for accurately predicting product distributions and volatility from atmospheric oxidation of functionalized VOCs.

Incorporation of autoxidation reaction rates into atmospheric models

Ultimately, improved kinetic descriptions of RO₂ H-shift reactions, as well as other unimolecular processes, and resulting product formation need to be incorporated into the chemical mechanisms used in air-quality and climate models. Recent implementation of VCP emission inventories and VCP-relevant chemistry in Community Multiscale Air Quality (CMAQ) model by Pennington et al.³¹ and Seltzer et al.⁶⁴

substantially improved the model's prediction of SOA mass concentrations in the Los Angeles area. Still, there remains large discrepancy between predicted and observed VCP-derived SOA, which likely reflects incomplete representation of oxidation pathways for oxygenated VOCs (OVOCs).³¹ Therefore, incorporating a more detailed description of autoxidation chemistry for VCP-derived VOCs in climate models would help address the persistent discrepancies between model prediction and observations of urban SOA. Moreover, including functional-group-dependent autoxidation rate coefficients, with a more refined urban OVOC emission inventory, has the potential to further improve predictions of oxidant budgets and SOA burdens in urban environments.

RO₂ H-shift reactions are not well represented in atmospheric chemistry models, as they remain poorly characterized for many substrates, and there is a lack of applicable quantitative structure-activity relationships (SARs) to support mechanism construction by providing reliable prediction of H-shift reaction rate coefficients of RO₂ with varied functionalities.³⁵ One work by Vereecken and Nozière⁴¹ provides a starting framework for SAR describing RO₂ H-shift reactions. The SAR is developed not by rigorously incorporating all available literature data, but by including lower-level theoretical predictions, and, where necessary, building on reactivity trends of analogous compound classes, the transferability of which could not always be validated. As such, the SAR can serve as a foundational framework that offers practical usability within its expected accuracy, while leaving room for improvements as more data become available. Results from new theoretical calculations at high levels of theory and especially experimental work shall further refine this SAR.

Thus, we expect the results in this work would represent an initial step toward providing validation and constraints to build upon the existing SAR. In particular, this work provides experimental validation for autoxidation reaction kinetics of simple VOCs with ether, alcohol, and hydroperoxide groups (Chapter 2 and 3). Theoretical calculations by multi-conformer transition state theory (MC-TST)⁵⁰ are also shown to have relatively high level of accuracy in predicting RO₂ H-shift rate coefficients. The combination of experimental and computational investigation can serve as a benchmark for further development and refinement of SARs for RO₂ H-shift reactions. Still, we expect major challenges remain in predicting reaction parameters for large, multifunctional RO₂ species (e.g. Chapter 4). In such systems, the influence of multiple substitutions on C-H bond strengths can be complex, and the interplay among different functional groups must be carefully characterized

to achieve reliable predictions. The temperature dependence of H-shift reactions of various RO₂ systems also needs to be evaluated in order to accurately assess the competitiveness of autoxidation chemistry in the atmosphere under real-world conditions.

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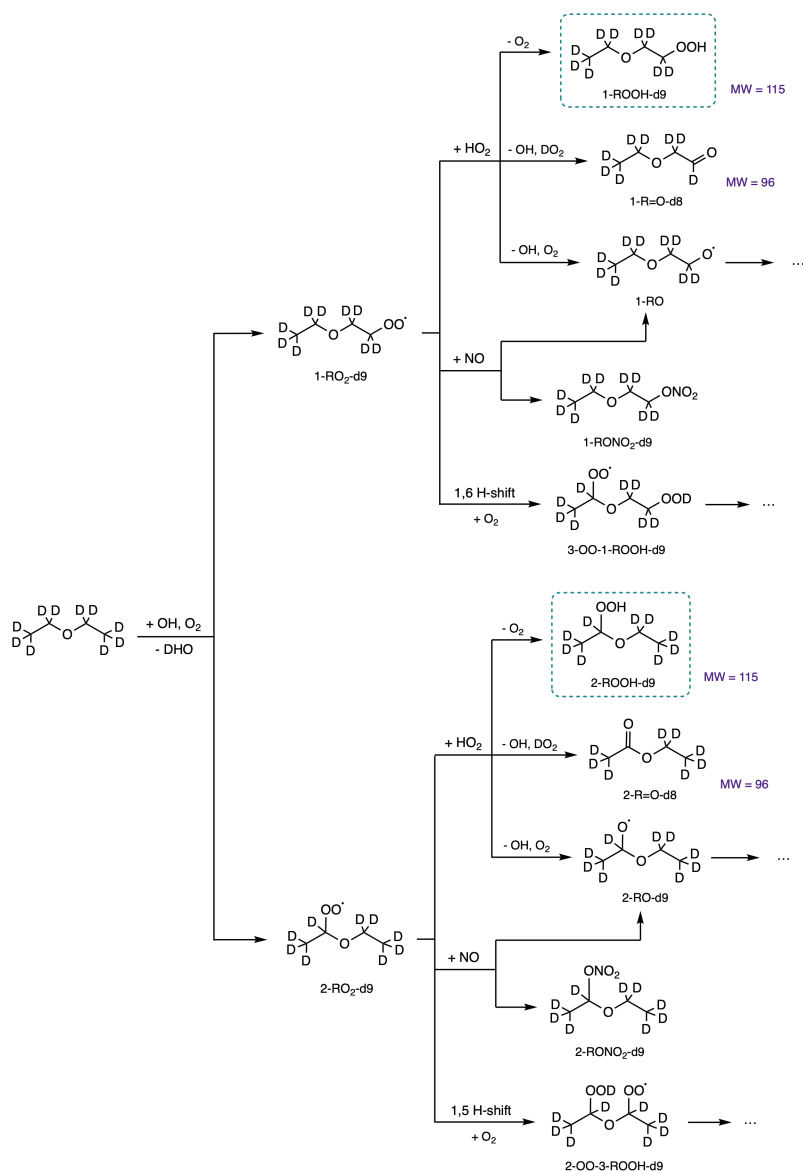
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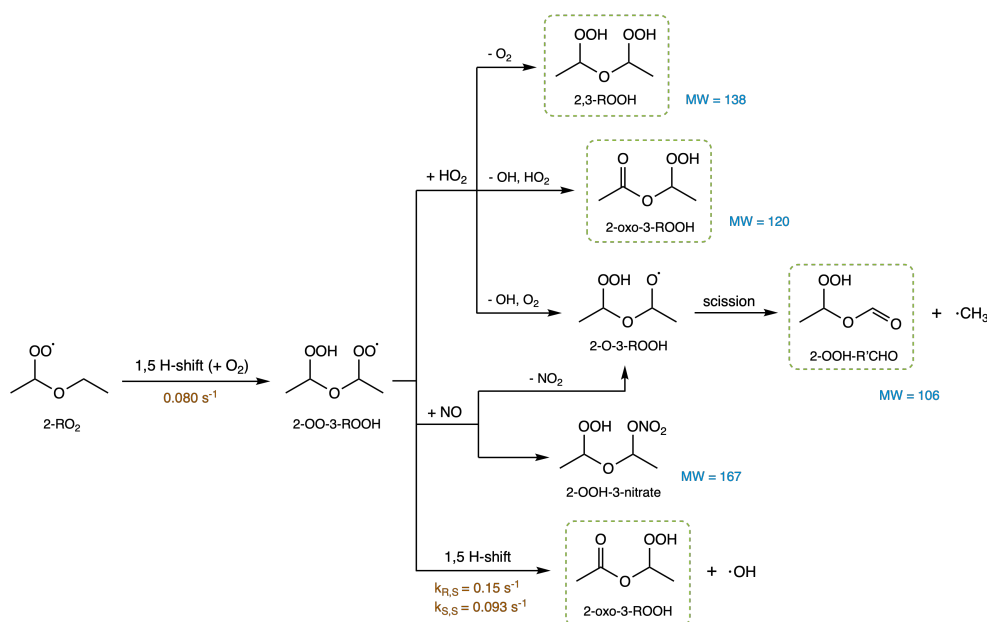
Appendix A

SUPPLEMENTARY INFORMATION FOR CHAPTER 2

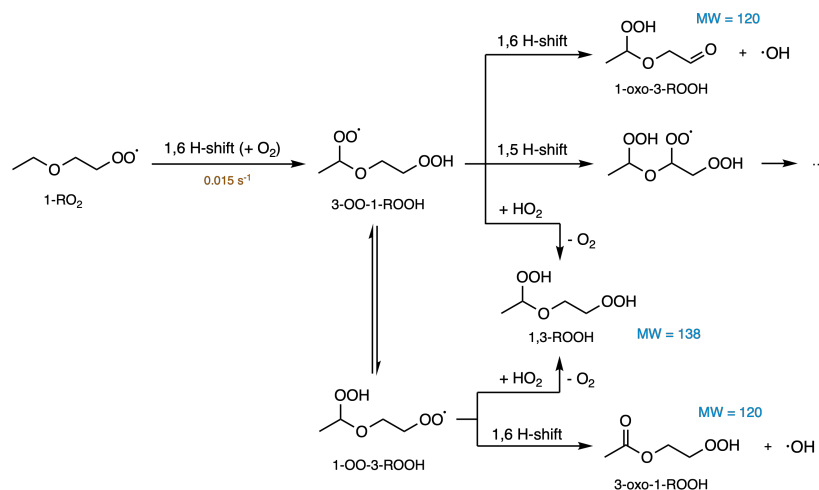
A.1 Additional Oxidation Mechanisms



Scheme A.1: Initiation step of diethyl ether- d_{10} (DE- d_{10}) oxidation by OH radical, as well as subsequent reactions of the generated peroxy radicals, including: RO $_2$ + HO $_2$ /NO bimolecular reactions and unimolecular H-shift reactions. Further pathways from H-shift reactions are shown in Scheme A.2. The molecular masses of major closed-shell products are denoted in purple. Products that are detectable by our instrument are shown in teal boxes.



Scheme A.2: Autoxidation mechanism of 2-RO₂-d₉ from DE-d₁₀ system based on calculated H-shift rate coefficients at 294 K. Subsequent reactions, including 2-OO-3-ROOH-d₉ + HO₂/NO reactions and fast D/H exchange of hydroperoxide deuterium atom, and their respective products are also shown. The molecular masses of major closed-shell products are denoted in purple. Products that are detectable by our instrument are shown in teal boxes.



Scheme A.3: The autoxidation mechanism proposed for 1-RO₂ from diethyl ether (DE) system. The H-shift rate coefficient is calculated at 294 K. The molecular masses of major closed-shell products are denoted in blue. None of the products in the proposed mechanism is observed above detection limit in our experiments.

A.2 Experimental Conditions

Table A.1: Experimental conditions. All concentrations are in ppb. All experiments are conducted at ambient temperature of 294 ± 1 K.

Exp. No.	[DE] ₀	[DE-d10] ₀	[CH ₃ OH] ₀	[H ₂ O ₂] ₀	Bulb Type	Bulb #	Oxidation time
1	528	0	45294	2088	254 nm	1	8
2	523	0	45563	2172	350 nm	8	120
3	0	1052	45371	1961	254 nm	1	8 18
4	0	1119	45266	2032	350 nm	1	180
5	354	0	46378	2070	350 nm	1	180
6	315	931	46713	2051	254 nm	8	1 2
7	322	920	45409	2020	350 nm	8	100
8	303	906	45074	2113	254 nm	8	1 4
9	309	912	45477	2073	254 nm	1	8 16
10	329	968	47932	2039	254 nm	4	2 8
11	293	872	46052	2095	254 nm	2	4 12
12	318	857	44967	1817	350 nm	8	100
13	203	969	45691	1871	350 nm	1	200
14	324	994	42974	1896	350 nm	4	150
15	350	981	43990	2082	350 nm	2	180
16	294	962	45151	2154	350 nm	2	180
17	360	1313	45232	2205	254 nm	2	4

Table A.2: Ramp rate of GC runs in DE/DE-d10 oxidation experiments.

GC step	Temperature (°C)	Ramp rate (°C/min)	Time (min)
1	−30 – 30	15	4
2	30 – 95	2	32.5
3	95 – 130	10	3.5
Soak	130		3

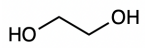
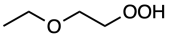
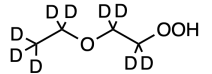
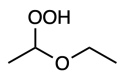
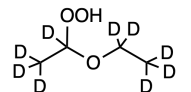
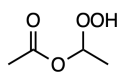
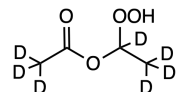
A.3 CIMS Calibration

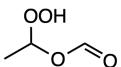
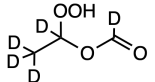
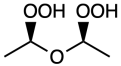
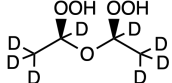
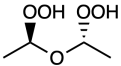
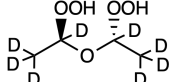
Quantification of oxidation products from the experiments requires us knowledge of their sensitivities in the CIMS instrument. The compounds are mainly detected as product ions clustered with CF_3O^- reagent ion (m/z 85), with a detection limit of ~ 10 ppt and with a 1 s integration period. First we normalize the CIMS signal for each compound by the sum of the signals for the reagent ions, including CF_3O^- and its clusters with H_2O and H_2O_2 (detected at m/z 85, m/z 103, and m/z 119). Because of the high number of these reagent ions, in order to remain in a linear regime, we use the isotopologues of these reagent ion clusters at $m/z + 1$ (i.e. the clusters with $^{13}\text{CF}_3\text{O}^-$ at $m/z = 86$) to normalize the analyte signals. Therefore, the sensitivities listed in Table... below are normalized by the sum of m/z 86 + m/z 104 + m/z 120.

Since most species discussed in this study lack authentic standards, we estimate their instrumental sensitivities by calculating their CF_3O^- -molecule collision rate coefficients using calculated dipole moments and polarizabilities, assuming that all collisions leads to formation of quantifiable product ions. The ion-molecule collision rate coefficients are calculated using the parameterization by Su et al.¹ The dipole moments and polarizabilities are calculated at the B3LYP/cc-pVTZ level following the method by Garden et al.² In summary, all conformers are generated via 3-fold of all dihedral angles, and first screened at B3LYP/6-31+G(d) level, the conformers have electronic energy within the 15 kJ/mol cut-off are further optimized at the B3LYP/cc-pVTZ level. Conformers with an electronic energy difference of less than 0.00005 Hartree and dipole moment difference of less than 0.015 Debye are recognized as duplicated conformers. Subsequently, the dipole moment and polarizability are calculated for each unique conformer at the same level. The dipole moment is calculated based on the weighted averages of the low energy conformers, and the polarizabilities are based on the lowest-energy conformer.

The sensitivities of oxidation products listed in Table D.2 are calibrated based on the calculated ion-molecule collision rate and measured sensitivity of ethylene glycol. The compound ethylene glycol is chosen as the standard for determining the sensitivities of other compounds given its ability to form well-bound cluster with CF_3O^- . The CIMS sensitivity of ethylene glycol (Sigma-Aldrich, 99.8%) is determined by evaporating a known amount of ethylene glycol into the Teflon chamber and measuring the gas phase standard by the CIMS.

Table A.3: Calculated dipole moments (μ_D), polarizabilities (α), CF_3O^- -molecule collision rate coefficients (k_c), and CIMS sensitivities for molecules of interests in the system. ^a Normalized relative to that of ethylene glycol. ^b measured sensitivity data and uncertainties.

Molecule	m/z	μ_D (D)	α ($\text{\AA}^3$)	k_c ($10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Relative k_c ^a	Sensitivity (10^{-4} cts/pptv)
Ethylene glycol 	147	2.08	5.11	1.90	1	3.25 (± 0.26) ^b
1-ROOH 	191	3.34	9.60	2.55	1.34	4.36 (± 0.35)
1-ROOH-d9 	200	3.34	9.60	2.50	1.32	4.28 (± 0.34)
2-ROOH 	191	2.12	9.51	1.85	0.98	3.17 (± 0.25)
2-ROOH-d9 	200	2.12	9.51	1.82	0.96	3.11 (± 0.25)
2-oxo-3-ROOH 	205	3.62	9.55	2.63	1.39	4.50 (± 0.36)
2-oxo-3-ROOH-d7 	212	3.62	9.55	2.60	1.37	4.45 (± 0.36)

Molecule	m/z	μ_D (D)	α (Å ³)	k_c (10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹)	Relative k_c	Sensitivity (10 ⁻⁴ cts/pptv)
2-OOH-R'CHO 	191	3.01	7.75	2.29	1.21	3.92 (± 0.31)
2-OOH-R'CHO-d5 	196	3.01	7.75	2.27	1.20	3.88 (± 0.31)
(<i>R,S</i>)-2,3-ROOH 	223	2.61	10.79	2.06	1.08	3.52 (± 0.28)
(<i>R,S</i>)-2,3-ROOH-d8 	231	2.61	10.79	2.04	1.07	3.48 (± 0.28)
(<i>S,S</i>)-2,3-ROOH 	223	2.63	10.74	2.07	1.09	3.54 (± 0.28)
(<i>S,S</i>)-2,3-ROOH-d8 	231	2.63	10.74	2.05	1.08	3.50 (± 0.28)

A.4 Computational Results

A.4.1 Calculated H/D-shift rate coefficients

The RO₂ H/D-shift rate coefficients are calculated by the MC-TCT approach as described in Møller et al.³ The B3LYP/6-31+G(d) level calculations serve as a pre-screening. For reactions with a rate slower than 10⁻³ s⁻¹, higher-level calculations were not performed. The difference in the rates between the ω B97X-D/aug-cc-pVTZ level and the ROCCSD(T)-F12/VDZ-F12// ω B97X-D/aug-cc-pVTZ level roughly reflects the uncertainty in our calculations - about a factor of 5. Among them the ROCCSD(T)-F12/VDZ-F12// ω B97X-D/aug-cc-pVTZ level is recommended.

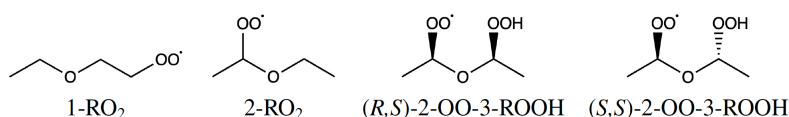


Table A.4: Calculated 1,5 H-shift and D-shift rate coefficients at different levels of theory at 298.15 K.

		barrier [kcal mol ⁻¹]	<i>k</i> [s ⁻¹]	barrier [kcal mol ⁻¹]	<i>k</i> [s ⁻¹]	barrier [kcal mol ⁻¹]	<i>k</i> [s ⁻¹]
Level/ Basis set		B3LYP/ 6-31+G(d)		ω B97X-D/ aug-cc-pVTZ		ROCCSD(T)-F12a/ VDZ-F12	
2-RO ₂	H-shift	20.0	4.25×10 ⁻²	19.7	4.73×10 ⁻²	19.4	1.11×10 ⁻¹
	D-shift	21.1	5.30×10 ⁻⁴	20.8	1.25×10 ⁻³	20.4	2.30×10 ⁻³
(R,S)-2-OO-3-ROOH	H-shift	20.7	6.15×10 ⁻²	20.2	1.53×10 ⁻¹	20.1	1.93×10 ⁻¹
	D-shift	21.9	7.39×10 ⁻⁴	21.4	1.69×10 ⁻³	21.3	2.14×10 ⁻³
(S,S)-2-OO-3-ROOH	H-shift	20.1	2.10×10 ⁻¹	21.0	3.13×10 ⁻²	20.2	1.23×10 ⁻¹
	D-shift	21.2	1.61×10 ⁻³	22.2	4.57×10 ⁻⁴	21.4	1.60×10 ⁻³

Table A.5: Temperature dependence of calculated H and D-shift rate coefficients calculated at the ROCCSD(T)-F12a/VDZ-F12// ω B97X-D/aug-cc-pVTZ level.

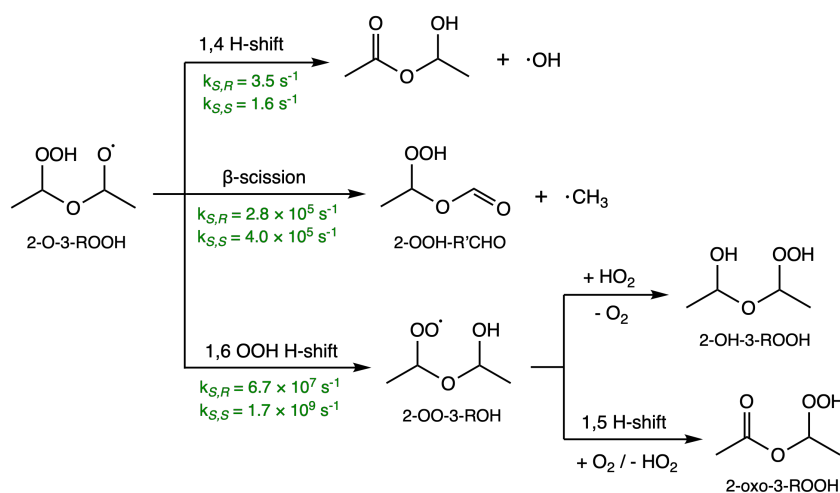
Reaction	<i>k</i> _{298.15K} [s ⁻¹]	<i>k</i> _{294.00K} [s ⁻¹]	<i>k</i> _{260K-320K} [s ⁻¹]
2-RO ₂ 1,5 H-shift	1.11×10 ⁻¹	7.99×10 ⁻²	3.37×10 ¹¹ exp(-9.56×10 ³ /T) exp(8.76×10 ⁷ /T ³)
2-RO ₂ -d9 1,5 D-shift	2.30×10 ⁻³	1.60×10 ⁻³	1.84×10 ¹¹ exp(-1.01×10 ⁴ /T) exp(5.03×10 ⁷ /T ³)
1-RO ₂ 1,6 H-shift	2.11×10 ⁻²	1.53×10 ⁻²	9.54×10 ¹⁰ exp(-9.79×10 ³ /T) exp(9.76×10 ⁷ /T ³)
(R,S)-2-OO-3-ROOH 1,5 H-shift	1.93×10 ⁻¹	1.48×10 ⁻¹	1.22×10 ¹² exp(-1.02×10 ⁴ /T) exp(1.26×10 ⁸ /T ³)
(R,S)-2-OO-3-ROOH-d9 1,5 D-shift	2.14×10 ⁻³	1.30×10 ⁻³	1.07×10 ¹² exp(-1.08×10 ⁴ /T) exp(6.08×10 ⁷ /T ³)
(S,S)-2-OO-3-ROOH 1,5 H-shift	1.23×10 ⁻¹	9.34×10 ⁻²	6.22×10 ¹¹ exp(-1.00×10 ⁴ /T) exp(1.14×10 ⁸ /T ³)
(S,S)-2-OO-3-ROOH-d9 1,5 D-shift	1.60×10 ⁻³	1.01×10 ⁻³	5.79×10 ¹¹ exp(-1.06×10 ⁴ /T) exp(5.27×10 ⁷ /T ³)

Table A.6: Eckart tunneling factors for RO₂ 1,5 H/D-shift reactions calculated at 294 K.

Reaction	Eckart tunneling factor
2-RO ₂ 1,5 H-shift	73.8
2-RO ₂ -d9 1,5 D-shift	9.6
(<i>R,S</i>)-2-OO-3-ROOH 1,5 H-shift	179.1
(<i>R,S</i>)-2-OO-3-ROOH-d9 1,5 D-shift	11.2
(<i>S,S</i>)-2-OO-3-ROOH 1,5 H-shift	101.8
(<i>S,S</i>)-2-OO-3-ROOH-d9 1,5 D-shift	8.7

A.4.2 Fate of 2-O-3-ROOH

Additional calculations were carried out to investigate the fate of the alkoxy radical 2-O-3-ROOH, formed from reaction of 2-OO-3-ROOH with HO₂, following the same methodology described above, adapted for alkoxy radical reactions.⁴ The investigated pathways, shown in Scheme A.4, were: 1) 1,4 H-shift followed by spontaneous OH radical elimination; 2) β -scission leading to the aldehyde 2-OOH-R'CHO, measured by the experiments, plus methyl radical (CH₃·); and 3) 1,6 H-shift involving abstraction of the OOH hydrogen, leading to peroxy radical 2-OO-3-ROH. The 2-OO-3-ROH will undergo subsequent reactions such as bimolecular reaction with HO₂/NO, as well as a 1,5 H-shift to yield the ketone 2-oxo-3-ROOH, which is also measured in the experiments. The fully deuterated form of the reactant, 2-O-3-ROOH-d9, are also included in the analysis. The rate coefficients calculated at the ω B97X-D/aug-cc-pVTZ level and at the ROCCSD(T)-F12a/VDZ-F12// ω B97X-D/aug-cc-pVTZ level are shown in Table A.7.

**Scheme A.4:** Investigated 2-O-3-ROOH reaction pathways. Rate coefficients calculated at 294 K and 1 atm are shown in green.

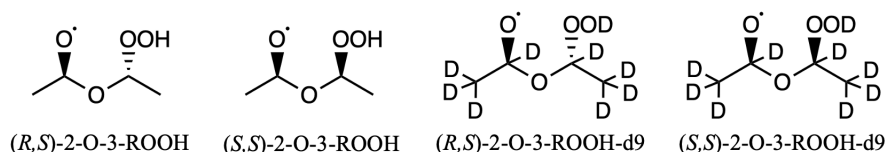


Table A.7: Energy barriers and rate coefficients calculated for 2-O-3-ROOH/2-O-3-ROOH-d9 reaction pathways.

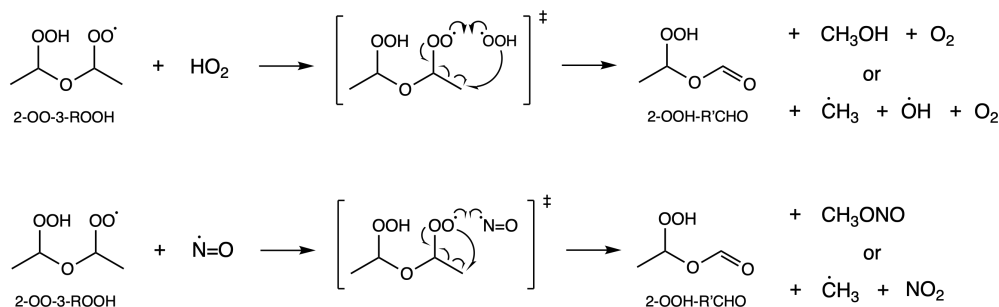
		Barrier [kcal mol ⁻¹]	$k_{298.15\text{K}}$ [s ⁻¹]	$k_{294.00\text{K}}$ [s ⁻¹]	Barrier [kcal mol ⁻¹]	$k_{298.15\text{K}}$ [s ⁻¹]	$k_{294.00\text{K}}$ [s ⁻¹]
Level/Basis set		$\omega\text{B97X-D/}a\text{ug-cc-pVTZ}$			ROCCSD(T)-F12a/VDZ-F12		
$(R,S)\text{-}2\text{-O-}3\text{-ROOH}$	1,4 H-shift	16.1	3.71×10^1	2.89×10^1	17.3	4.65	3.54
	β -scission	9.1	2.96×10^5	2.39×10^5	9.0	3.47×10^5	2.81×10^5
	1,6 H-shift	7.6	7.10×10^7	6.70×10^7	—	—	—
$(S,S)\text{-}2\text{-O-}3\text{-ROOH}$	1,4 H-shift	16.8	5.24×10^1	3.99×10^1	18.7	2.24	1.64
	β -scission	9.2	9.39×10^5	7.56×10^5	9.5	4.98×10^5	3.97×10^5
	1,6 H-shift	5.4	1.79×10^9	1.71×10^9	—	—	—
$(R,S)\text{-}2\text{-O-}3\text{-ROOH-d}_9$	1,4 H-shift	16.9	1.56	1.11	18.7	8.63×10^{-2}	5.89×10^{-2}
	β -scission	9.2	2.28×10^5	1.83×10^5	9.6	1.29×10^5	1.03×10^5
	1,6 H-shift	8.6	3.29×10^6	2.95×10^6	—	—	—
$(S,S)\text{-}2\text{-O-}3\text{-ROOH-d}_9$	1,4 H-shift	17.7	2.25	1.55	19.6	8.83×10^{-2}	5.84×10^{-2}
	β -scission	9.3	7.03×10^5	5.61×10^5	9.7	3.72×10^5	2.94×10^5
	1,6 H-shift	6.4	1.20×10^8	1.10×10^8	—	—	—

In all cases, our calculations predict that the β -scission is fast enough ($k(294\text{K}) = 1\text{--}5 \times 10^5 \text{ s}^{-1}$) to outcompete direct H-abstraction by O_2 , with a typical pseudo-first-order rate coefficient of $\sim 10^4 \text{ s}^{-1}$ at 298 K and 1 atm.⁵ Albeit fast, the 1,4 H-shift is much slower than the β -scission, and is expected to be a negligible pathway. The 1,6 H-shift, on the other hand, is predicted to be much faster, outcompeting the β -scission even for the fully deuterated form, 2-OO-3-ROOH-d9. This reaction is significantly exothermic and can thus be assumed to be irreversible. Previous studies⁶ indicate that the energetics calculated at the F12 level of theory for reactions where the H migrates between two O atoms, such as the 1,6 H-shift investigated here, may not be as reliable as it is for H-shifts involving a C atom as a hydrogen donor/acceptor. For this reason, rate coefficients for the 1,6 H-shift reaction analyzed here are predicted at the $\omega\text{B97X-D}$ level of theory only. This level of theory is, however, inherently less accurate overall and predicted rate coefficients are expected to be more uncertain, by a factor of up to ~ 100 .

We failed to observe subsequent products from 2-OO-3-ROH, such as 2-OH-3-ROOH which would appear at m/z 207, above the detection limit, and thus we

are unable to provide a reliable experimental estimation regarding the branching fractions of the scission and 1,6 H-shift pathways of 2-O-3-ROOH. Moreover, in a high NO experiment (discussed in Section A.8), the yield of the scission product 2-OOH-R'CHO increases, and yet still no products from 2-OO-3-ROH are observed. It is possible that, given the high level of uncertainty in our calculation, the reaction rate of 1,6 H-shift is much slower than calculated, and thus the yields of products from 2-OO-3-ROH are too low to be detected. Thus, the interpretation of the experimental measurement of 2-OOH-R'CHO as the major product of the 2-O-3-ROOH β -scission is not entirely in conflict with computational predictions.

Another possibility is that the reaction $2\text{-OO-3-ROOH} + \text{HO}_2/\text{NO} \rightarrow 2\text{-OOH-R'CHO}$ involves a concerted mechanism such that the intermediate 2-O-3-ROOH is not produced at all (proposed mechanism in Scheme A.5), which may explain the disparity between the computational and experimental results. Unfortunately, with our instrumentation, we are unable to verify or deny this claim. In such case, $\alpha_{2\text{-O-3-ROOH}}$ discussed in the main text and later in this document should be equivalent to $\alpha_{2\text{-OOH-R'CHO}}$.



Scheme A.5: Proposed concerted mechanism of 2-OOH-R'CHO formation.

A.4.3 Molecular Structures of (*R,S*)- and (*S,S*)-2,3-ROOH

The molecular structures of the lowest-free-energy conformations of the dihydroperoxide stereoisomers, optimized at the $\omega\text{B97X-D/aug-cc-pVTZ}$ level of theory are shown in Figure A.1. The -OOH groups in the (*R,S*) isomer interact via an intramolecular H-bond, whereas in the (*S,S*) isomer they do not, and instead the functionalities point at opposite directions. This observation indicates that the (*S,S*) isomer may interact more strongly with the GC column's stationary phase and therefore elute later than the (*R,S*) stereoisomer.

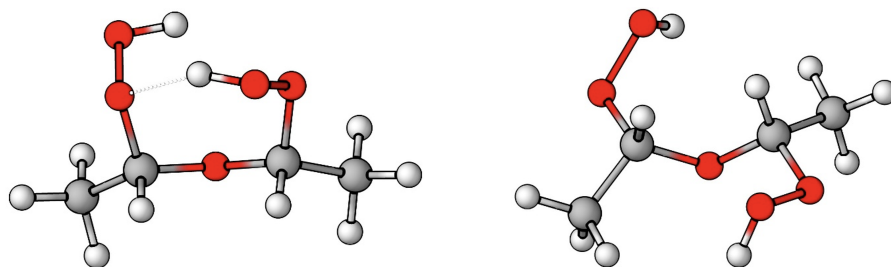


Figure A.1: Molecular structure of *(R,S)*-2,3-ROOH (left) and *(S,S)*-2,3-ROOH (right). Color code: Gray = C; Red = O; White = H.

A.4.4 Intramolecular Hydrogen-Bond in 2-OO-3-ROOH Radical

The molecular structures of the lowest-energy conformations of the *(R,S)*-2-OO-3-ROOH and its connected 1,5 H-shift transition state, optimized at the ω B97X-D/aug-cc-pVTZ level of theory, are shown in Figure A.2. The -OOH and -OO groups in the reactant interact via an intramolecular H-bond, which is broken as the molecule distorts itself towards the 1,5-shift transition state. The loss of the H-bond, and the stabilization it brings, translates into an additional energy penalty, raising the barrier for the reaction pathway. A very similar situation is observed with the *(S,S)* isomer.

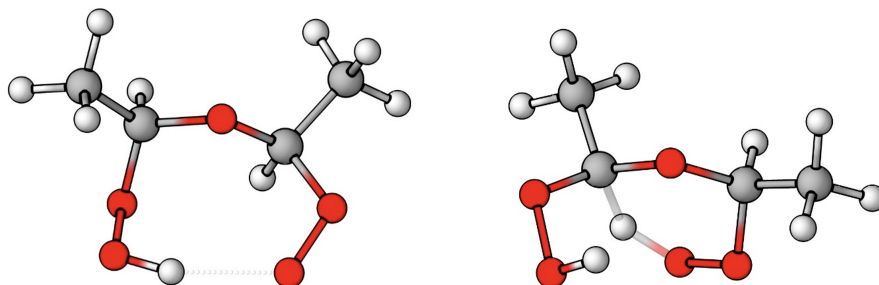


Figure A.2: Molecular structure of *(R,S)*-2-OO-3-ROOH reactant (left) and its connected 1,5 H-shift transition state (right). Faded bonds are partially broken. Color code: Gray = C; Red = O; White = H.

A.5 Box Model Implementation

We implement in the photochemical box model a photo-oxidation mechanism of DE and DE-d10, including the reactions of major peroxy radicals, formation of the first-generation closed-shell products, and important secondary reactions of those products. The full mechanism in .txt is available at: doi.org/10.22002/671m3-rky11. The reaction kinetics regarding the formation of key oxidation products discussed in this work are listed in Table A.8. The secondary chemical reactions included are discussed later.

Table A.8: Major bimolecular and unimolecular reactions and respective rate constants. All rate constants are evaluated at 294 K and 993 hPa. ^a Calculated based on formulation from MCM ^b Inferred from experimental results and box model simulations. ^c Calculated based on Jenkin et al.,⁷ with rate coefficients of deuterated RO₂+HO₂ reactions assumed to be similar to their undeuterated counterparts. ^d Rate coefficients of unimolecular reactions of alkoxy radicals are calculated based on methods detailed in Zhao et al.⁴ ^e Branching ratios of bimolecular reactions and rate coefficients of RO₂ H-shift reactions come from derivations in this work.

Bimolecular Reaction	Rate Constant ($10^{-11} \frac{\text{cm}^3}{\text{molecule}\cdot\text{s}}$)	Branching Ratio ^e (α)
DE + OH $\rightarrow$ 1-RO ₂	1.46 ^a	0.03
$\rightarrow$ 2-RO ₂		0.97
DE-d10 + OH $\rightarrow$ 1-RO ₂ -d9	0.37 ^b	0.014
$\rightarrow$ 2-RO ₂ -d9		0.986
1-RO ₂ + HO ₂ $\rightarrow$ 1-ROOH + O ₂	1.58 ^c	1
1-RO ₂ -d9 + HO ₂ $\rightarrow$ 1-ROOH-d9 + O ₂	1.58 ^c	1
2-RO ₂ + HO ₂ $\rightarrow$ 2-ROOH + O ₂	1.58 ^c	0.87
2-RO ₂ -d9 + HO ₂ $\rightarrow$ 2-ROOH-d9 + O ₂	1.58 ^c	0.90
2-OO-3-ROOH + HO ₂ $\rightarrow$ 2,3-ROOH + O ₂	1.86 ^c	0.83
$\rightarrow$ 2-oxo-3-ROOH + OH + HO ₂		0.14
$\rightarrow$ 2-O-3-ROOH + OH + O ₂		0.03
2-OO-3-ROOH-d8 + HO ₂ $\rightarrow$ 2,3-ROOH-d8 + O ₂	1.86 ^c	0.87
$\rightarrow$ 2-oxo-3-ROOH-d7 + OH + HO ₂		0.10
$\rightarrow$ 2-O-3-ROOH-d8 + OH + O ₂		0.03
Unimolecular Reaction of Alkoxy Radicals	Rate Constant ^d (s ⁻¹)	
(R,S)-2-O-3-ROOH $\xrightarrow{\text{scission (+O}_2)}$ 2-OOH-R'CHO + CH ₃ OO	2.81 $\times 10^5$	
(S,S)-2-O-3-ROOH $\xrightarrow{\text{scission (+O}_2)}$ 2-OOH-R'CHO + CH ₃ OO	3.97 $\times 10^5$	
(R,S)-2-O-3-ROOH-d8 $\xrightarrow{\text{scission (+O}_2)}$ 2-OOH-R'CHO-d5 + CD ₃ OO	1.97 $\times 10^5$	
(S,S)-2-O-3-ROOH-d8 $\xrightarrow{\text{scission (+O}_2)}$ 2-OOH-R'CHO-d5 + CD ₃ OO	2.82 $\times 10^5$	
Unimolecular H-shift of Peroxy Radicals	Rate Constant ^e (s ⁻¹)	
1-RO ₂ $\xrightarrow{\text{O}_2}$ 3-OO-1-ROOH	0.015	
1-RO ₂ -d9 $\xrightarrow{\text{O}_2, \text{H}_2\text{O} / -\text{DHO}}$ 3-OO-1-ROOH-d8	0.002	

$2\text{-RO}_2 \xrightarrow{\text{O}_2} 2\text{-OO-3-ROOH}$	0.094
$2\text{-RO}_2\text{-d9} \xrightarrow{\text{O}_2, \text{H}_2\text{O}/-\text{DHO}} 2\text{-OO-3-ROOH-d8}$	0.012
$2\text{-OO-3-ROOH} \xrightarrow{\text{O}_2} 2\text{-oxo-3-ROOH} + \text{HO}_2$	0.090
$2\text{-OO-3-ROOH-d8} \xrightarrow{\text{O}_2, \text{H}_2\text{O}/-\text{DHO}} 2\text{-oxo-3-ROOH-d7} + \text{HO}_2$	0.006

A.5.1 Secondary Chemistry

Major secondary reactions of first-generation closed-shell products include their reactions with OH and photolysis. The reaction kinetics of the OH reactions are directly adopted from Master Chemical Mechanism (MCM, mcm.york.ac.uk/home.htm). For compounds that lack information regarding their OH reactions, the kinetics of structurally similar compounds are used.

Table A.9: Estimated photolysis reaction rate coefficients of relevant compound classes in the system. ^a H_2O_2 photolysis rate coefficient in our chamber at 254 nm is calculated by Murphy et al.⁸ by measuring OH production via the decay of 2,3-butanediol. The photolysis rate coefficient at 350 nm is calculated in Yu et al.⁹ using similar method via the decay of ethylene glycol. ^b The photolysis rate coefficients of ketohydroperoxides are estimated through the combined UV absorption cross sections of the hydroperoxides and structurally similar organic carbonyls.¹⁰

Molecules	Wavelength	
	254 nm	350 nm
H_2O_2 ^a	$2.7 (\pm 0.4) \times 10^{-4} \text{ s}^{-1}$	$1.7 (\pm 0.2) \times 10^{-6} \text{ s}^{-1}$
Hydroperoxides	$2.7 (\pm 0.4) \times 10^{-4} \text{ s}^{-1}$	$1.7 (\pm 0.2) \times 10^{-6} \text{ s}^{-1}$
Ketohydroperoxides ^b	$3.0 (\pm 0.4) \times 10^{-4} \text{ s}^{-1}$	$1.9 (\pm 0.2) \times 10^{-6} \text{ s}^{-1}$

Most oxidation products discussed in this study contain photo-sensitive moieties, such as hydroperoxide and/or carbonyl (aldehyde and ketone) groups, making those compounds undergo photolysis during irradiation. The photolytic properties of many of the functional groups as well as their combinations have so far been understudied. The photolysis rate coefficients of organic hydroperoxides are expected to be close to that of H_2O_2 , given the similar absorption cross sections for H_2O_2 and organic hydroperoxides in the 200-350 nm range.¹⁰ The photolysis rate coefficients of H_2O_2 in our chamber are measured to be $1.7 \times 10^{-6} \text{ s}^{-1}$ under eight 350 nm bulbs and $2.7 \times 10^{-4} \text{ s}^{-1}$ under eight 254 nm bulbs.^{8,9} These rates are applied to all hydroperoxides in the box model. For compounds with multiple functional groups, such as the ketohydroperoxides (2-oxo-3-ROOH and 2-OOH-R'CHO), their

photolysis rates are estimated assuming additivity of the absorption cross sections of carbonyls and hydroperoxides.¹⁰ Due to lack of knowledge of potential enhancements in the cross section by the interaction between the functional groups,¹¹ we may underestimate the photolysis rates of the multifunctional products. Our estimation of the photolysis rate coefficients are in Table A.9. On average, ~2-4% of the oxidation products is lost under irradiation during our experiments.

A.6 Additional Data Processing

A.6.1 Vapor Wall Loss

Vapor wall loss refers to the partitioning of organic vapor products onto chamber walls, thereby removing them from the system. We quantify the wall loss of the oxidation products by measuring their decay after irradiation, and then correct the yields of the oxidation products using the estimated wall loss rate. The wall loss rate is estimated by fitting the dark decay of the compounds of interests, which gives $1.22 \times 10^{-6} \text{ s}^{-1}$ for ROOH's, and $1.88 \times 10^{-5} \text{ s}^{-1}$ for ketohydroperoxides (2-oxo-3-ROOH and 2-oxo-3-ROOH-d7). We failed to observe a decay higher than $1.88 \times 10^{-5} \text{ s}^{-1}$ for dihydroperoxides (2,3-ROOH and 2,3-ROOH-d8), likely due to the short equilibrium timescale for low-volatility vapor between the gas-phase and the wall-phase.^{12,13} The smaller the vapor-wall equilibrium timescale of a compound, the earlier the wall loss process starts to affect its detectable gas phase concentration. The compound likely already approaches gas-wall equilibrium during the oxidation period, which would result in a smaller decay observed after oxidation.

We use the rate $1.88 \times 10^{-5} \text{ s}^{-1}$ to account for the wall loss of dihydroperoxides. The potential underestimation of wall loss of the compounds can lead to biases in our estimations of some parameters. For example, overestimation in the slope in Figure 2.2 and underestimation of 1,5 H-shift rate coefficients of 2-RO₂'s, underestimation of the branching fraction to its formation ($\alpha_{2,3\text{-ROOH}}$), and overestimation in the ratio of [2-oxo-3-ROOH]/[2,3-ROOH] and 1,5 H-shift rate coefficients of 2-OO-3-ROOH's.

A.6.2 Chromatographic Analysis of Dihydroperoxides

Shown in Figure A.3 are the GC chromatograms of major product ions of the stereoisomers of dihydroperoxides, 2,3-ROOH and 2,3-ROOH-d8, from an experiment with both DE and DE-d10, including the CF₃O⁻ products (m/z 223 and 231), the fluorine transfer products (m/z 157 and 165), and major fragment ions (m/z 63, 81, and 79). In this study, we refer to the diastereomers with the same configuration

at both chiral centers as (*S,S*) [(*R,R*) and (*S,S*) isomers] and those with different configuration as (*R,S*) [(*S,R*) and (*R,S*) isomers]. For (*R,S*) isomers, the product ions (m/z 223:157:63:81:79 and m/z 231:165:63:81:79) are produced in an approximate ratio of 1.2:1:1:1:1, while for (*S,S*) isomers, the ratio is approximately 1:3.5:1:1:1.5. To quantify the yields of the two dihydroperoxides, we sum up all the CIMS signals of their product ions. For experiments with both VOCs, the respective contribution of the two dihydroperoxides to the fragment ions is estimated based on the ratio of the yields of their major parent ions, (m/z 223 + m/z 157):(m/z 231 + m/z 165). Our results show that the ratio of the (*R,S*) to (*S,S*) stereoisomers of both dihydroperoxides is ~ 1 , which is consistent with our expectation since the dihydroperoxides are derived from the racemic mixture of 2-OO-3-ROOH's.

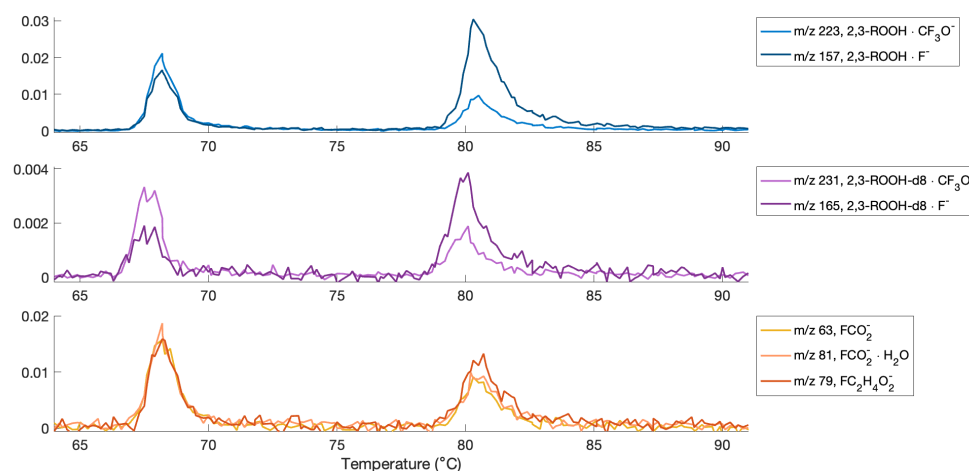


Figure A.3: GC chromatograms of major product ions of 2,3-ROOH and 2,3-ROOH-d8 stereoisomers from experiment No.9.

A.7 Experimental Results

Table A.10: Experimental results with all data corrected. All concentrations are in ppb. HO₂ concentrations are determined by the box model.

Exp. No.	[HO ₂]	[1-ROOH]	[2-ROOH]	[2-oxo-3-ROOH]	[2-OOH-R'CHO]	[(<i>R,S</i>)-2,3-ROOH]	[(<i>S,S</i>)-2,3-ROOH]
1	1.01	0.36	8.55	0.64	0.07	0.75	0.76
2	0.19	0.18	2.57	2.64	0.08	0.87	0.86
5	0.07	0.02	0.19	0.73	0.01	0.10	0.10
6	2.27	0.15	3.97	0.10	0.02	0.20	0.19
		0.32	8.37	0.20	0.04	0.40	0.39
7	0.18	0.06	0.89	0.85	0.03	0.29	0.29
8	2.30	0.18	4.54	0.09	0.02	0.21	0.21
		0.69	17.7	0.39	0.08	0.81	0.82
9	0.98	0.19	4.45	0.26	0.04	0.39	0.38
		0.59	14.04	0.88	0.13	1.16	1.16
10	1.83	0.20	4.99	0.17	0.03	0.30	0.30
		0.80	19.9	0.81	0.12	1.24	1.23
11	1.36	0.22	5.47	0.22	0.04	0.36	0.36
		0.68	16.5	0.77	0.12	1.10	1.09
12	0.17	0.06	0.91	0.95	0.03	0.30	0.30
13	0.06	0.01	0.08	0.39	0.004	0.05	0.05
14	0.12	0.07	0.84	1.70	0.04	0.38	0.37
15	0.09	0.05	0.47	1.25	0.02	0.24	0.22
16	0.09	0.04	0.38	1.07	0.01	0.18	0.17
17	1.32	0.27	6.73	0.37	0.05	0.53	0.53

	[HO ₂]	[1-ROOH-d9]	[2-ROOH-d9]	[2-oxo-3-ROOH-d7]	[2-OOH-R'CHO-d5]	[(R,S)-2,3-ROOH-d8]	[(S,S)-2,3-ROOH-d8]
3	1.03	0.11	6.95	0.03	0.01	0.09	0.09
		0.25	15.3	0.06	0.02	0.20	0.20
4	0.06	0.01	0.40	0.07	0.008	0.10	0.10
6	2.27	0.06	3.67	0.006	0.002	0.02	0.02
		0.12	7.71	0.012	0.004	0.05	0.05
7	0.18	0.02	1.17	0.05	0.01	0.13	0.13
8	2.30	0.07	4.10	0.007	0.003	0.03	0.03
		0.29	17.7	0.029	0.010	0.11	0.11
9	0.98	0.08	5.00	0.02	0.005	0.07	0.07
		0.27	16.5	0.06	0.016	0.22	0.22
10	1.83	0.08	4.91	0.01	0.003	0.04	0.04
		0.32	19.8	0.04	0.013	0.14	0.14
11	1.36	0.08	5.09	0.02	0.005	0.06	0.06
		0.26	15.8	0.05	0.015	0.18	0.18
12	0.17	0.03	1.39	0.05	0.01	0.14	0.14
13	0.06	0.01	0.33	0.06	0.006	0.08	0.08
14	0.12	0.03	1.50	0.11	0.02	0.21	0.21
15	0.09	0.02	0.92	0.09	0.01	0.17	0.17
16	0.09	0.02	0.76	0.07	0.01	0.13	0.13
17	1.32	0.12	7.21	0.02	0.007	0.08	0.08

A.8 Additional Results

A.8.1 An experiment with NO

Figure A.4 shows the gas chromatograms of an experiment with ~300 ppb DE, ~900 ppb DE-d10, ~2000 ppb H₂O₂, and ~5 ppb NO. Compared to HO₂ only experiments, we observe lower yields of hydroperoxides and higher yields of the potential alkoxy radical scission products (e.g. 2-OOH-R'CHO at m/z 191 and 196). Simple organic nitrates (RONO₂'s) that do not contain an additional functional group are not sensitive to our instrument, and are thus not detected. Low signals of hydroperoxynitrates (2-OOH-3-nitrate) is detected through the direct sampling mode of GC-CIMS, but the compound is not captured by the GC.

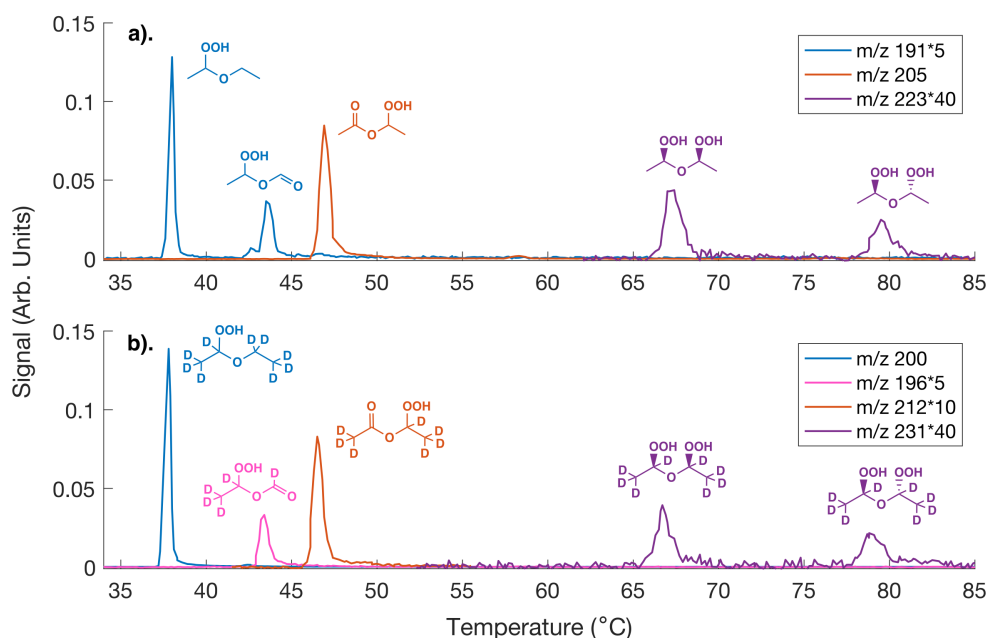


Figure A.4: Gas chromatograms of an experiment with low [NO] (a) GC traces of DE oxidation products and (b) GC traces of DE-d10 oxidation products. Certain signals in the figure are scaled up by a factor denoted in the figure.

A.8.2 [2-ROOH]/[1-ROOH]

The ratio of the yields of 2-ROOH and 1-ROOH is equal to the ratio of their formation rates, which can be formulated as:

$$\frac{[2\text{-ROOH}]}{[1\text{-ROOH}]} = \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [2\text{-RO}_2]_{ss} [\text{HO}_2]}{\alpha_{1\text{-ROOH}} k_{1\text{-RO}_2+\text{HO}_2} [1\text{-RO}_2]_{ss} [\text{HO}_2]} = \frac{\alpha_{2\text{-ROOH}} [2\text{-RO}_2]_{ss}}{\alpha_{1\text{-ROOH}} [1\text{-RO}_2]_{ss}} \quad (\text{A.1})$$

where $\alpha_{2\text{-ROOH}}$ and $\alpha_{1\text{-ROOH}}$ indicate the branching fraction to respective ROOH's

from $\text{RO}_2 + \text{HO}_2$ reaction, and $[2\text{-RO}_2]_{ss}$ and $[1\text{-RO}_2]_{ss}$ indicates steady state concentrations of $[2\text{-RO}_2]$ and $[1\text{-RO}_2]$. To derive the expression for $[2\text{-RO}_2]_{ss}$ and $[1\text{-RO}_2]_{ss}$, we start with the rate equations of $[2\text{-RO}_2]$ and $[1\text{-RO}_2]$:

$$\begin{aligned} \frac{d}{dt}[2\text{-RO}_2] &= \alpha_{2\text{-RO}_2} k_{\text{DE}+\text{OH}}[\text{DE}][\text{OH}] - k_{2\text{-RO}_2+\text{HO}_2}[2\text{-RO}_2][\text{HO}_2] \\ &\quad - k_{1,5 \text{ H-shift}, 2\text{-RO}_2}[2\text{-RO}_2] \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} \frac{d}{dt}[1\text{-RO}_2] &= \alpha_{1\text{-RO}_2} k_{\text{DE}+\text{OH}}[\text{DE}][\text{OH}] - k_{1\text{-RO}_2+\text{HO}_2}[1\text{-RO}_2][\text{HO}_2] \\ &\quad - k_{1,6 \text{ H-shift}, 1\text{-RO}_2}[1\text{-RO}_2] \end{aligned} \quad (\text{A.3})$$

where $\alpha_{2\text{-RO}_2}$ and $\alpha_{1\text{-RO}_2}$ are the branching fractions of 2-RO_2 and 1-RO_2 formation in the initiation step. Assuming steady states for equation A.2 and A.3 gives:

$$[2\text{-RO}_2]_{ss} = \frac{\alpha_{2\text{-RO}_2} k_{\text{DE}+\text{OH}}[\text{DE}][\text{OH}]}{k_{2\text{-RO}_2+\text{HO}_2}[\text{HO}_2] + k_{1,5 \text{ H-shift}, 2\text{-RO}_2}} \quad (\text{A.4})$$

$$[1\text{-RO}_2]_{ss} = \frac{\alpha_{1\text{-RO}_2} k_{\text{DE}+\text{OH}}[\text{DE}][\text{OH}]}{k_{1\text{-RO}_2+\text{HO}_2}[\text{HO}_2] + k_{1,6 \text{ H-shift}, 1\text{-RO}_2}} \quad (\text{A.5})$$

Plugging equation A.4 and A.5 into equation A.1 gives:

$$\begin{aligned} \frac{[2\text{-ROOH}]}{[1\text{-ROOH}]} &= \frac{\alpha_{2\text{-ROOH}}[2\text{-RO}_2]_{ss}}{\alpha_{1\text{-ROOH}}[1\text{-RO}_2]_{ss}} \\ &= \frac{\alpha_{2\text{-ROOH}}}{\alpha_{1\text{-ROOH}}} \cdot \frac{\alpha_{2\text{-RO}_2}}{\alpha_{1\text{-RO}_2}} \cdot \frac{k_{1\text{-RO}_2+\text{HO}_2}[\text{HO}_2] + k_{1,6 \text{ H-shift}, 1\text{-RO}_2}}{k_{2\text{-RO}_2+\text{HO}_2}[\text{HO}_2] + k_{1,5 \text{ H-shift}, 2\text{-RO}_2}} \end{aligned} \quad (\text{A.6})$$

Following Equation A.6, the yield of the two hydroperoxides in the system is mainly governed by the following parameters: 1) the branching ratio of 1-RO_2 and 2-RO_2 in the initiation step (Scheme 2.1), 2) the branching ratio of $\text{RO}_2 + \text{HO}_2$ reaction to ROOH formation, and 3) the unimolecular H-shift reaction rate coefficients of 1-RO_2 and 2-RO_2 . When $[\text{HO}_2]$ is sufficiently high that the RO_2 bimolecular reaction rates vastly exceed their H-shift reaction rates, the ratio of the yields of 2-ROOH and 1-ROOH should equal to the ratio of branching fractions of the ROOH formation pathways $((\alpha_{2\text{-RO}_2} \cdot \alpha_{2\text{-ROOH}})/(\alpha_{1\text{-RO}_2} \cdot \alpha_{1\text{-ROOH}}))$. As $[\text{HO}_2]$ decreases, the H-shift reactions become more significant in influencing the $[2\text{-ROOH}]/[1\text{-ROOH}]$ ratio. We use box model simulations to facilitate our estimation of those parameters to produce the best model fit to experimental data.

Figure A.5 shows the variation of $[2\text{-ROOH}]/[1\text{-ROOH}]$ as a function of $[\text{HO}_2]$ from both DE and DE-d10 system. Since the 1,5 H-shift rate coefficient of 2-RO_2 is

much higher than the 1,6 H-shift rate coefficient of 1-RO₂, as HO₂ levels decrease, the yield of 2-ROOH will decrease more substantially than that of 1-ROOH, leading to a lower [2-ROOH]/[1-ROOH] ratio. The resulted reaction parameters from the best fit of the model to the experimental data are in Table A.8. Here we assume that $\alpha_{1\text{-ROOH}}$ and $\alpha_{1\text{-ROOH-d9}} = 1$ based on our observation of reaction products from 1-RO₂+HO₂ reaction, and other parameters are estimated relative to this assumption. This assumption may lead to a slight overestimation of $\alpha_{2\text{-ROOH}}$, $\alpha_{2\text{-ROOH-d9}}$, and 2-RO₂ and 2-RO₂-d9 H-shift rates. However, the observed yields of relevant reaction products and previous studies^{7,14} suggest that $\alpha_{1\text{-ROOH}}$ and $\alpha_{1\text{-ROOH-d9}}$ is likely >0.9, and thus our assumption here should not contribute significantly to the overall uncertainty in our estimated reaction parameters.

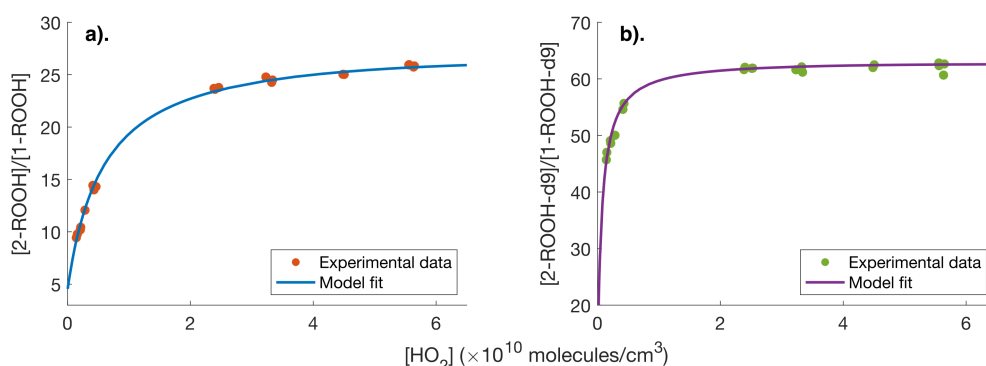


Figure A.5: (a) [2-ROOH]/[1-ROOH] vs. [HO₂], and (b) [2-ROOH-d9]/[1-ROOH-d9] vs. [HO₂]. The solid lines represent the optimized model fit to the data. The uncertainties in the data are dominated by common systematic errors as detailed in Section A.9 (~28% for concentration ratios and ~16% for [HO₂]).

A.8.3 2-oxo-3-ROOH and 2-OOH-R'CHO

Shown in Figure A.6 is the experimental and model result of the ratios of [2-oxo-3-ROOH]/[2,3-ROOH] and [2-OOH-R'CHO]/[2,3-ROOH] from DE and DE-d10 system. As detailed in the main text, the two ratios enable us to estimate the branching fractions of three channels of bimolecular reaction 2-OO-3-ROOH + HO₂ (Scheme 2.2 and A.2), as well as the 1,5 H-shift rate coefficient of 2-OO-3-ROOH. With the decrease of [HO₂], the yield of 2-oxo-3-ROOH increases compared to that of 2,3-ROOH as 1,5 H-shift reaction of 2-OO-3-ROOH increasingly dominates the formation of 2-oxo-3-ROOH. The variation in [2-OOH-R'CHO]/[2,3-ROOH] is small, since both products are produced through reaction 2-OO-3-ROOH + HO₂ and the ratio is largely determined by the ratio between the branching fraction $\alpha_{2\text{-O-3-ROOH}}/\alpha_{2,3\text{-ROOH}}$ (or $\alpha_{2\text{-OOH-R'CHO}}/\alpha_{2,3\text{-ROOH}}$). Small variation in experimental

data and model outputs is likely due to minor reaction pathways that also produce 2-O-3-ROOH, such as secondary reactions of 2,3-ROOH and permutation reactions of 2-OO-3-ROOH.

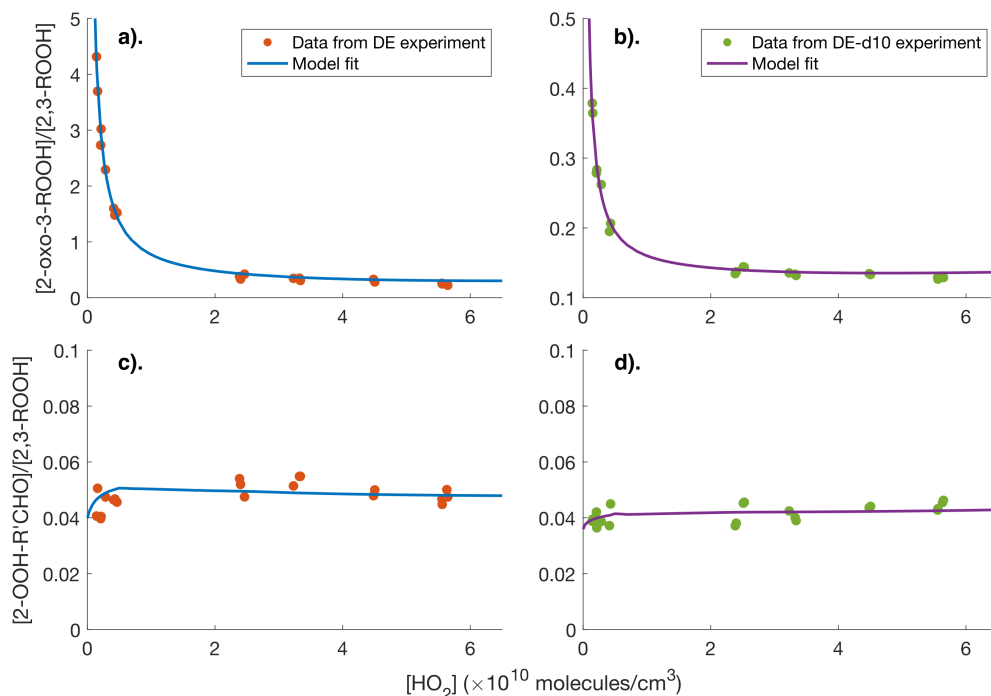


Figure A.6: Yields of 2-oxo-3-ROOH and 2-OOH-R'CHO compared to that of 2,3-ROOH from DE and DE-d10 system. Model results are based on derived parameters shown in Table A.8. (a) $[2\text{-oxo-3-ROOH}]/[2,3\text{-ROOH}]$, (b) $[2\text{-oxo-3-ROOH-d7}]/[2,3\text{-ROOH-d8}]$, (c) $[2\text{-OOH-R'CHO}]/[2,3\text{-ROOH}]$, (d) $[2\text{-OOH-R'CHO-d5}]/[2,3\text{-ROOH-d8}]$. The uncertainties in the data are dominated by common systematic errors as detailed in Section A.9 ($\sim 28\%$ for concentration ratios and $\sim 16\%$ for $[HO_2]$).

A.8.4 (*R,S*)- and (*S,S*)-2,3-ROOH

Our estimation of the 1,5 H-shift rate coefficient of 2-OO-3-ROOH's listed in Table 2.2 and Table A.8, which is derived from ratio between the yield of 2-oxo-3-ROOH and the total yield of 2,3-ROOH (sum of both diastereomers), is an average for (*R,S*) and (*S,S*) diastereoisomers. The stereoisomer-specific H-shift rate coefficient can be derived by comparing the yields of (*R,S*) and (*S,S*)-2,3-ROOH as a function of HO_2 concentrations.. The stereoisomer with higher H-shift rate coefficient should produce less corresponding dihydroperoxides at lower HO_2 level.

Figure A.7 shows the ratios between the yields of the two diastereomers from DE and DE-d10 experiments based on our tentative peak assignment in Figure 2.1. If our tentative peak assignment in Figure 2.1 is incorrect, the following analysis of

(*R,S*) and (*S,S*) diastereomers would be reversed. The ratio is close to 1 across the range of HO₂ concentrations. There is no obvious trend, except a slight increase at lower HO₂ levels, which is within the uncertainties of experimental data. The small increase can be fitted with a slightly lower 1,5 H-shift rate coefficients of the (*R,S*) diastereomer, as shown by the dashed line in Figure A.7. However, the difference between the proposed H-shift rate coefficients of the two diastereomers is minimal and well within the uncertainties of our estimations of the rate coefficients. Therefore, based on our experimental results, we do not observe a major difference between the H-shift rate coefficients of the two diastereomers of 2-OO-3-ROOH's.

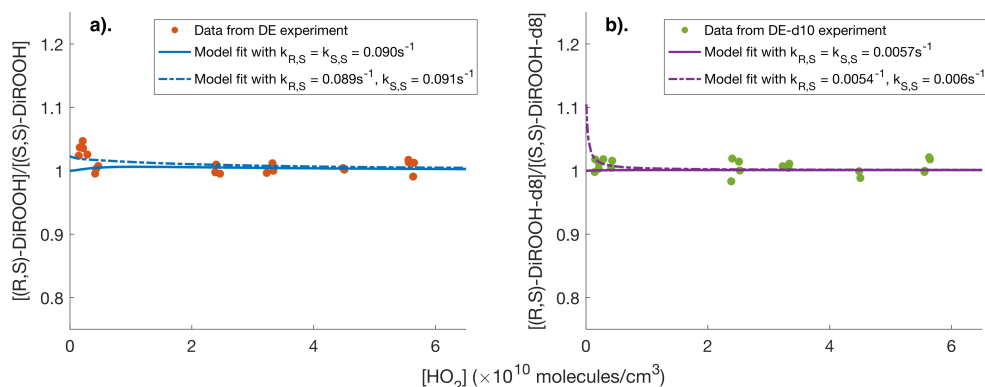


Figure A.7: (a) [(*R,S*)-2,3-ROOH]/[(*S,S*)-2,3-ROOH] vs. [HO₂], (b) [(*R,S*)-2,3-ROOH-d8]/[(*S,S*)-2,3-ROOH-d8] vs. [HO₂]. The solid lines represent the model output with 1,5 H-shift rate coefficients of both diastereomers to be the same. The dashed lines represent the model output with the H-shift rate coefficient of the (*R,S*) diastereomer to be slightly smaller than that of the (*S,S*) diastereomer. The uncertainties in the data are dominated by common systematic errors as detailed in Section A.9 (~28% for concentration ratios and ~16% for [HO₂]).

A.9 Estimation of Uncertainties

A.9.1 HO₂ Concentrations

The rate equations for the dominant production and loss pathways of HO_x species in our experiments are formulated as follows:

$$P(\text{OH}) = 2J_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] \quad (\text{A.7})$$

$$L(\text{OH}) = (k_{\text{OH}+\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + k_{\text{OH}+\text{CH}_3\text{OH}}[\text{CH}_3\text{OH}] + k_{\text{OH}+\text{VOC}}[\text{VOC}])[\text{OH}] \quad (\text{A.8})$$

$$P(\text{HO}_2) = (k_{\text{OH}+\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + k_{\text{OH}+\text{CH}_3\text{OH}}[\text{CH}_3\text{OH}] + \alpha \cdot k_{\text{OH}+\text{VOC}}[\text{VOC}])[\text{OH}] \quad (\text{A.9})$$

$$L(\text{HO}_2) = 2k_{\text{HO}_2+\text{HO}_2}[\text{HO}_2]^2 + k_{\text{RO}_2+\text{HO}_2}[\text{RO}_2][\text{HO}_2] \quad (\text{A.10})$$

where α in Equation A.9 indicates the branching ratio for HO_2 production through reactions of VOCs and OH, $k_{\text{OH}+\text{H}_2\text{O}_2} = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ based on Vakhtin et al.,¹⁵ $k_{\text{OH}+\text{CH}_3\text{OH}} = 8.8 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 294 K based on MCM, $k_{\text{OH}+\text{DE}} = 1.46 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 294 K based on MCM, and $k_{\text{OH}+\text{DE-d10}} = 3.65 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 294 K derived from our experimental results. In our experiments, the concentration of CH_3OH is kept much higher than that of the VOCs in order to suppress RO_2+RO_2 chemistry. On average, $\sim 85\%$ of OH radical reacts with H_2O_2 and CH_3OH , and $\sim 15\%$ reacts with DE and DE-d10. We thereby simplify equations A.8 to A.10 as:

$$L(\text{OH}) \simeq (k_{\text{OH}+\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + k_{\text{OH}+\text{CH}_3\text{OH}}[\text{CH}_3\text{OH}])[\text{OH}] \quad (\text{A.11})$$

$$P(\text{HO}_2) \simeq (k_{\text{OH}+\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + k_{\text{OH}+\text{CH}_3\text{OH}}[\text{CH}_3\text{OH}])[\text{OH}] \quad (\text{A.12})$$

$$L(\text{HO}_2) \simeq 2k_{\text{HO}_2+\text{HO}_2}[\text{HO}_2]^2 \quad (\text{A.13})$$

Therefore, consumption of OH in our system mostly leads to formation of HO_2 , and assuming steady state for OH and HO_2 equalizes the equations above and gives:

$$2k_{\text{HO}_2+\text{HO}_2}[\text{HO}_2]^2 \simeq 2J_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]$$

$$[\text{HO}_2] \simeq \sqrt{\frac{J_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}{k_{\text{HO}_2+\text{HO}_2}}} \quad (\text{A.14})$$

which indicates that $[\text{HO}_2]$ in our system is approximately proportional to the square root of the photolysis rate coefficient of H_2O_2 , which can be modified by changing the number and wavelengths of the UV lamps in our chamber enclosure.

Based on Equation A.14, the HO_2 concentrations in our system are mainly constrained by the photolysis rate coefficients of H_2O_2 , H_2O_2 concentrations, and the rate coefficient of the self-reaction of HO_2 . The uncertainties in the photolysis rate coefficients of H_2O_2 are determined by the uncertainties in the fitted slopes used to evaluate these rate coefficients (Table A.9). The major source of uncertainties in the concentrations of H_2O_2 comes from our sample preparation procedure and instrumentation, which we estimate to introduce a $\sim 20\%$ systematic error in the measured $[\text{H}_2\text{O}_2]$. The uncertainty in $k_{\text{HO}_2+\text{HO}_2}$ is evaluated using the method in JPL documentation¹⁶ to be $\pm 21\%$ at ambient temperature. As a result, propagation of error gives an uncertainty of $\sim 16\%$ in the estimated $[\text{HO}_2]$ in our experiments.

A.9.2 Product Concentrations and Ratios of Product Yields

The major source of uncertainties in the measured concentrations of oxidation products lies in the instrument sensitivity of the product. The uncertainty in the measured sensitivity of ethylene glycol (Table D.2) is calculated as the standard deviation of replicate measurements, which is $\sim 8\%$. This part of uncertainty is then propagated to the calculated sensitivities of other oxidation products. However, since this component of error is correlated by common measurements, it cannot be used to propagate the error in the ratios between product concentrations.

Another source of uncertainty in the sensitivities comes from the error in the calculated ion-molecule collision rate coefficients, which can be derived from the error in the calculated polarizabilities and dipole moments.² The resulted $\sim 20\%$ error is not correlated and thus can be used to infer the uncertainties in the ratios between the yields of different products. Therefore, we estimate the uncertainties in the concentrations of detected products to be $\sim 22\%$, and the uncertainties in the ratios between product concentrations to be $\sim 28\%$.

A.9.3 Comparing H-shift and D-shift rate coefficients

As discussed in the main text, we determine the H-shift rate coefficients in the system based on the following expressions:

$$\frac{[2\text{-ROOH}]}{[\text{all products from } 2\text{-OO-3-ROOH}]} = \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{HO}_2]}{k_{1,5 \text{ H-shift}, 2\text{-RO}_2}} \quad (\text{A.15})$$

$$\frac{[2\text{-oxo-3-ROOH}]}{[2,3\text{-ROOH}]} = \frac{\alpha_{2\text{-oxo-3-ROOH}}}{\alpha_{2,3\text{-ROOH}}} + \frac{k_{1,5 \text{ H-shift}, 2\text{-OO-3-ROOH}}}{\alpha_{2,3\text{-ROOH}} k_{2\text{-OO-3-ROOH}+\text{HO}_2}} \cdot \frac{1}{[\text{HO}_2]} \quad (\text{A.16})$$

For simplicity, here we denote the left-hand side of Equation A.15 and A.16 as $Ratio_{2\text{-RO}_2}$ and $Ratio_{2\text{-OO-3-ROOH}}$, and their deuterated version as $Ratio_{2\text{-RO}_2\text{-d9}}$ and $Ratio_{2\text{-OO-3-ROOH-d8}}$. Equation A.15 and A.16 can then be rearranged as:

$$k_{1,5 \text{ H-shift}, 2\text{-RO}_2} = \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{HO}_2]}{Ratio_{2\text{-RO}_2}} \quad (\text{A.17})$$

$$k_{1,5 \text{ H-shift}, 2\text{-OO-3-ROOH}} \simeq \alpha_{2,3\text{-ROOH}} k_{2\text{-OO-3-ROOH}+\text{HO}_2} [\text{HO}_2] \cdot Ratio_{2\text{-OO-3-ROOH}} \quad (\text{A.18})$$

The ratio between H-shift and D-shift rate coefficients can then be expressed as:

$$\frac{k_{1,5 \text{ H-shift, 2-RO}_2}}{k_{1,5 \text{ H-shift, 2-RO}_2\text{-d9}}} = \frac{\alpha_{2\text{-ROOH}} k_{2\text{-RO}_2+\text{HO}_2} [\text{HO}_2]}{\text{Ratio}_{2\text{-RO}_2}} / \frac{\alpha_{2\text{-ROOH-d9}} k_{2\text{-RO}_2\text{-d9}+\text{HO}_2} [\text{HO}_2]}{\text{Ratio}_{2\text{-RO}_2\text{-d9}}} \quad (\text{A.19})$$

$$\frac{k_{1,5 \text{ H-shift, 2-OO-3-ROOH}}}{k_{1,5 \text{ H-shift, 2-OO-3-ROOH-d8}}} \simeq \frac{\alpha_{2,3\text{-ROOH}} k_{2\text{-OO-3-ROOH}+\text{HO}_2} [\text{HO}_2] \cdot \text{Ratio}_{2\text{-OO-3-ROOH}}}{\alpha_{2,3\text{-ROOH-d8}} k_{2\text{-OO-3-ROOH-d8}+\text{HO}_2} [\text{HO}_2] \cdot \text{Ratio}_{2\text{-OO-3-ROOH-d8}}} \quad (\text{A.20})$$

Since most of the experiments conducted in this study have both DE and DE-d10 in the chamber, these experiments have the same $[\text{HO}_2]$ for DE and DE-d10 system. Also, we assume that the rate coefficients for $\text{RO}_2 + \text{HO}_2$ reactions are the same for non-deuterated and deuterated RO_2 . Equation A.19 and A.20 can thereby be simplified to:

$$\frac{k_{1,5 \text{ H-shift, 2-RO}_2}}{k_{1,5 \text{ H-shift, 2-RO}_2\text{-d9}}} = \frac{\alpha_{2\text{-ROOH}}}{\alpha_{2\text{-ROOH-d9}}} \cdot \frac{\text{Ratio}_{2\text{-RO}_2\text{-d9}}}{\text{Ratio}_{2\text{-RO}_2}} \quad (\text{A.21})$$

$$\frac{k_{1,5 \text{ H-shift, 2-OO-3-ROOH}}}{k_{1,5 \text{ H-shift, 2-OO-3-ROOH-d8}}} \simeq \frac{\alpha_{2,3\text{-ROOH}}}{\alpha_{2,3\text{-ROOH-d8}}} \cdot \frac{\text{Ratio}_{2\text{-OO-3-ROOH}}}{\text{Ratio}_{2\text{-OO-3-ROOH-d8}}} \quad (\text{A.22})$$

The uncertainties in the ratio between the rate coefficients of H-shifts and D-shifts can thereby be calculated based on the uncertainties reported for relevant reaction parameters in Table A.11, which are:

$$\frac{k_{1,5 \text{ H-shift, 2-RO}_2}}{k_{1,5 \text{ H-shift, 2-RO}_2\text{-d9}}} = 7.8 \pm 6.1, \quad \frac{k_{1,5 \text{ H-shift, 2-OO-3-ROOH}}}{k_{1,5 \text{ H-shift, 2-OO-3-ROOH-d8}}} = 15.0 \pm 8.3$$

Table A.11: Sources of uncertainties for reaction parameters determined in this study. ^a Uncertainty in $k_{RO_2+HO_2}$ are derived from that of $k_{C_2H_5O_2+HO_2}$ based on method in JPL documentation.¹⁶

Quantity	Constraints	Sources of Uncertainty	Value
α_{1-RO_2}	$\frac{[1-ROOH]}{[1-ROOH]+[\text{all products from } 2-RO_2]} (28\%)$		0.03 ± 0.01
α_{1-RO_2-d9}	$\frac{[1-ROOH-d9]}{[1-ROOH-d9]+[\text{all products from } 2-RO_2-d9]} (28\%)$		0.014 ± 0.004
α_{2-RO_2}	$1 - \alpha_{1-RO_2}$	α_{1-RO_2}	0.97 ± 0.01
α_{2-RO_2-d9}	$1 - \alpha_{1-RO_2-d9}$	α_{1-RO_2-d9}	0.986 ± 0.004
α_{2-ROOH}	$\frac{[2-ROOH]}{[1-ROOH]} (28\%), \frac{\alpha_{2-RO_2}}{\alpha_{1-RO_2}} (28\%)$		$0.87 + 0.13 / - 0.34$
$\alpha_{2-ROOH-d9}$	$\frac{[2-ROOH-d9]}{[1-ROOH-d9]} (28\%), \frac{\alpha_{2-RO_2-d9}}{\alpha_{1-RO_2-d9}} (28\%)$		$0.90 + 0.10 / - 0.36$
Slope Fig. 2.2 $(\frac{\alpha_{2-ROOH} \cdot k_{2-RO_2+HO_2}}{k_{1,5 \text{ H-shift, } 2-RO_2}})$ and $(\frac{\alpha_{2-ROOH-d9} \cdot k_{2-RO_2-d9+HO_2}}{k_{1,5 \text{ H-shift, } 2-RO_2-d9}})$	slope fit Fig. 2.2 (2.7%), $\frac{[2-ROOH]}{[\text{all products from } 2-OO-3-ROOH]} (28\%), [HO_2] (16\%)$ slope fit Fig. 2.2 (2.2%), $\frac{[2-ROOH-d9]}{[\text{all products from } 2-OO-3-ROOH-d8]} (28\%), [HO_2] (16\%)$		$(1.5 \pm 0.5) \times 10^{-10}$ $(1.2 \pm 0.4) \times 10^{-9}$
$k_{1,5 \text{ H-shift, } 2-RO_2}$	$\alpha_{2-ROOH} k_{2-RO_2+HO_2} / (\text{slope Fig. 2.2})$	slope Fig. 2.2 (32%), α_{2-ROOH} (39%), $k_{RO_2+HO_2}$ (52%) ^a	0.094 ± 0.068
$k_{1,5 \text{ H-shift, } 2-RO_2-d9}$	$\alpha_{2-ROOH-d9} k_{2-RO_2-d9+HO_2} / (\text{slope Fig. 2.2})$	slope Fig. 2.2 (32%), $\alpha_{2-ROOH-d9}$ (39%), $k_{RO_2+HO_2}$ (52%)	0.012 ± 0.009
Slope Fig. 2.3 $(\frac{k_{1,5 \text{ H-shift, } 2-OO-3-ROOH}}{\alpha_{2,3-ROOH} \cdot k_{2-OO-3-ROOH+HO_2}})$	slope fit Fig. 2.3 (1.4%), $\frac{[2-oxo-3-ROOH]}{[2,3-ROOH]} (28\%), [HO_2] (16\%)$		$(5.8 \pm 1.9) \times 10^9$

Quantity	Constraints	Sources of Uncertainty	Value
and $\left(\frac{k_{1,5} \text{ H-shift, 2-OO-3-ROOH-d8}}{\alpha_{2,3}\text{-ROOH-d8} \cdot k_{2\text{-OO-3-ROOH-d8+HO}_2}} \right)$	slope fit Fig. 2.3 (1.9%), $\frac{[2\text{-oxo-3-ROOH-d7}]}{[2,3\text{-ROOH-d8}]}$ (28%), $[\text{HO}_2]$ (16%)		$(3.6 \pm 1.1) \times 10^8$
Intercept Fig. 2.3 $\left(\frac{\alpha_{2\text{-oxo-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}} \right)$ and $\left(\frac{\alpha_{2\text{-oxo-3-ROOH-d7}}}{\alpha_{2,3}\text{-ROOH-d8}} \right)$	intercept fit Fig. 2.3 (15%), $\frac{[2\text{-oxo-3-ROOH}]}{[2,3\text{-ROOH}]}$ (28%) intercept fit Fig. 2.3 (1.6%), $\frac{[2\text{-oxo-3-ROOH-d7}]}{[2,3\text{-ROOH-d8}]}$ (28%)		0.16 ± 0.05 0.12 ± 0.03
$\frac{\alpha_{2\text{-O-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}}$	$\frac{[2\text{-OOH-R'CHO}]}{[2,3\text{-ROOH}]}$ (28%)		0.05 ± 0.02
$\frac{\alpha_{2\text{-O-3-ROOH-d8}}}{\alpha_{2,3}\text{-ROOH-d8}}$	$\frac{[2\text{-OOH-R'CHO-d5}]}{[2,3\text{-ROOH-d8}]}$ (28%)		0.04 ± 0.01
$\alpha_{2,3}\text{-ROOH}$	$\frac{1}{1 + \frac{\alpha_{2\text{-oxo-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}} + \frac{\alpha_{2\text{-O-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}}}$		$0.83 + 0.06 / - 0.05$
$\alpha_{2,3}\text{-ROOH-d8}$	$\frac{1}{1 + \frac{\alpha_{2\text{-oxo-3-ROOH-d7}}}{\alpha_{2,3}\text{-ROOH-d8}} + \frac{\alpha_{2\text{-O-3-ROOH-d8}}}{\alpha_{2,3}\text{-ROOH-d8}}}$		$0.87 + 0.02 / - 0.04$
$\alpha_{2\text{-oxo-3-ROOH}}$	$\alpha_{2,3}\text{-ROOH} \times \frac{\alpha_{2\text{-oxo-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}}$	$\alpha_{2,3}\text{-ROOH}$ (6%), $\frac{\alpha_{2\text{-oxo-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}}$ (32%)	0.14 ± 0.05
$\alpha_{2\text{-oxo-3-ROOH-d7}}$	$\alpha_{2,3}\text{-ROOH-d8} \times \frac{\alpha_{2\text{-oxo-3-ROOH-d7}}}{\alpha_{2,3}\text{-ROOH-d8}}$	$\alpha_{2,3}\text{-ROOH-d8}$ (4%), $\frac{\alpha_{2\text{-oxo-3-ROOH-d7}}}{\alpha_{2,3}\text{-ROOH-d8}}$ (28%)	0.10 ± 0.03
$\alpha_{2\text{-O-3-ROOH}}$	$\alpha_{2,3}\text{-ROOH} \times \frac{\alpha_{2\text{-O-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}}$	$\alpha_{2,3}\text{-ROOH}$ (6%), $\frac{\alpha_{2\text{-O-3-ROOH}}}{\alpha_{2,3}\text{-ROOH}}$ (28%)	0.03 ± 0.01
$\alpha_{2\text{-O-3-ROOH-d8}}$	$\alpha_{2,3}\text{-ROOH-d8} \times \frac{\alpha_{2\text{-O-3-ROOH-d8}}}{\alpha_{2,3}\text{-ROOH-d8}}$	$\alpha_{2,3}\text{-ROOH-d8}$ (4%), $\frac{\alpha_{2\text{-O-3-ROOH-d8}}}{\alpha_{2,3}\text{-ROOH-d8}}$ (28%)	0.03 ± 0.01
$k_{1,5} \text{ H-shift, 2-OO-3-ROOH}$	(slope Fig. 2.3) $\times \alpha_{2,3}\text{-ROOH} k_{2\text{-OO-3-ROOH+HO}_2}$	slope Fig. 2.3 (32%), $\alpha_{2,3}\text{-ROOH}$ (6%), $k_{\text{RO}_2+\text{HO}_2}$ (52%)	0.090 ± 0.055
$k_{1,5} \text{ H-shift, 2-OO-3-ROOH-d8}$	(slope Fig. 2.3) $\times \alpha_{2,3}\text{-ROOH-d8} k_{2\text{-OO-3-ROOH-d8+HO}_2}$	slope Fig. 2.3 (32%), $\alpha_{2,3}\text{-ROOH-d8}$ (4%), $k_{\text{RO}_2+\text{HO}_2}$ (52%)	0.006 ± 0.004

References

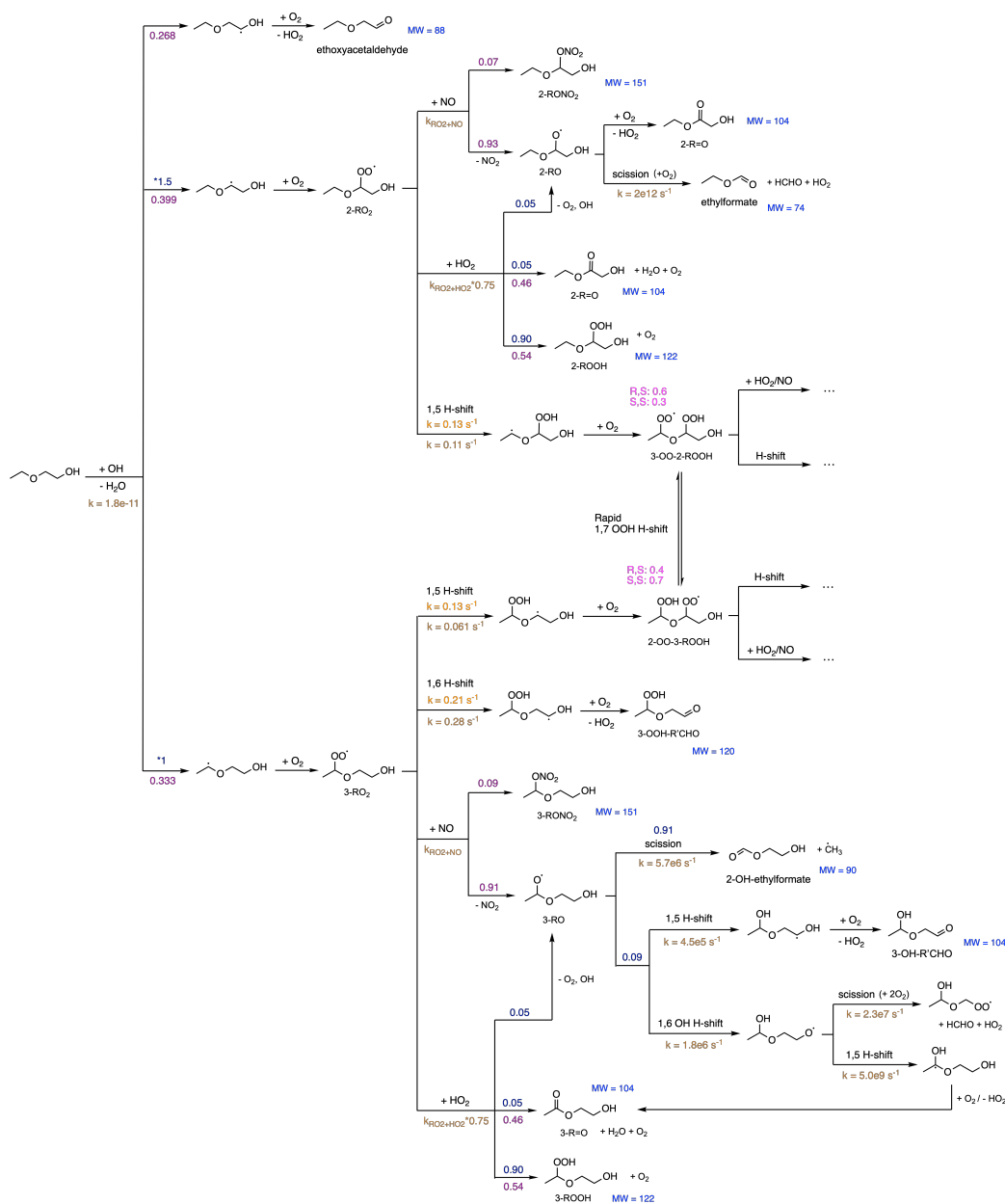
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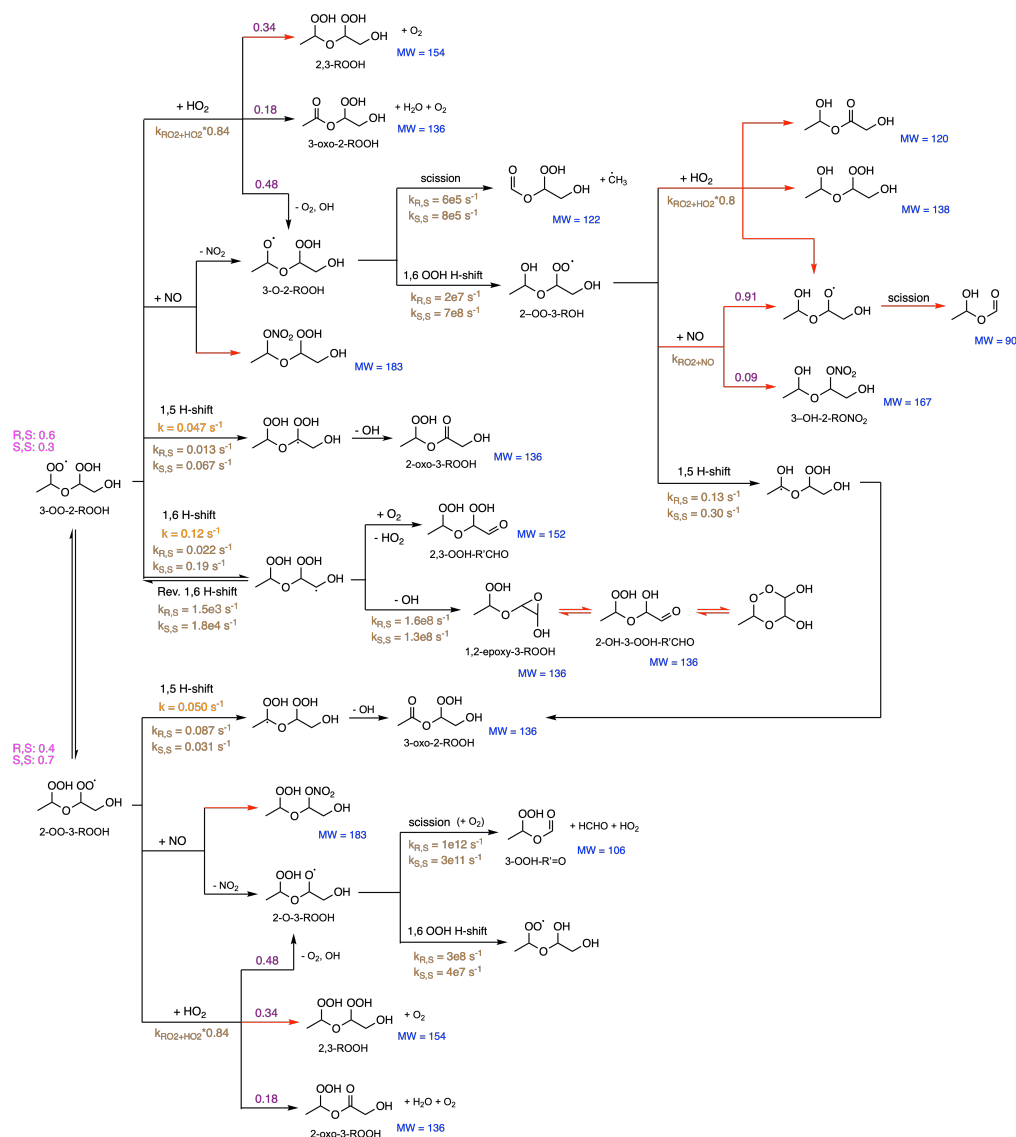
Appendix B

SUPPLEMENTARY INFORMATION FOR CHAPTER 3

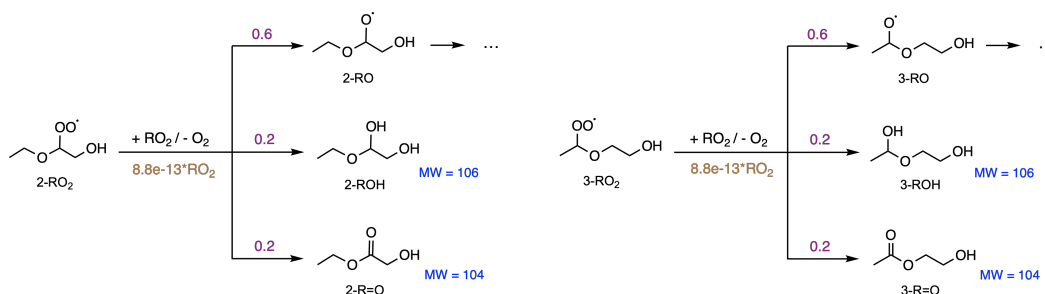
B.1 Photo-oxidation Mechanisms of 2-ethoxyethanol (2-EE)



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Scheme B.1: A mechanism of the initial steps in 2-EE photo-oxidation initiated by OH radical (except RO₂ self-reactions). Molecular weights of the products are indicated in blue. The branching ratios and rate coefficients that come from Master Chemical Mechanism (MCM), Jenkin et al.,¹ and quantum-chemical calculations are in purple and brown. $k_{RO_2+NO} = 2.7 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. $k_{RO_2+HO_2} = 2.8 \times 10^{-13} \exp(1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The branching ratios and rate coefficients determined in this study are in dark blue and orange. The MC-TST H-shift rate coefficients are at 298.15 K and the experimental-derived ones are at 294 K. The experimental-derived branching fractions of 2-RO₂ and 3-RO₂ formation is normalized by the branching to 3-RO₂, and we are not able to constrain the branching to ethoxyacetaldehyde. The product branching ratios for 2-OO-3-ROOH/3-OO-2-ROOH + HO₂ reactions come from Praske et al.² Red arrows indicate reaction pathways yet to be verified.



Scheme B.2: Mechanism for self-reaction of 2-EE peroxy radicals (RO₂). The branching ratios and rate coefficients come from MCM.

B.1.1 Box Model Implementation

We implement in the box model a full mechanism of photo-oxidation of 2-EE, i.e., from the starting material (2-EE) to the end-products (CO₂ and H₂O). The full mechanism in .txt is available at: <https://doi.org/10.22002/q0x9c-6kr07>. The reaction kinetics regarding the formation of first-generation closed-shell products are shown in Scheme B.1 and B.2. The reaction mechanisms involving multi-generational oxidation products are directly adopted from Master Chemical Mechanism (MCM).³ The following discussion only considers the reactions in Scheme B.1, which we can directly examine in this study.

The rate coefficients and branching fractions of initiation reaction 2-EE+OH is initially referred from MCM and Calvert et al.,⁴ and is later adjusted based on our experimental results. The estimation of the rate coefficients of bimolecular reactions (RO₂+HO₂/NO) relies on the method from Jenkin et al.¹ The branching ratio of RO₂+NO reaction is also adopted from Jenkin et al.,¹ while that of RO₂+HO₂ reaction is adopted from the results in this study (Section 3.3.2.1), except the 2-OO-3-ROOH/3-OO-2-ROOH + HO₂ reactions whose kinetic information are derived using constraints from the study of methyl vinyl ketone (MVK) by Praske et al.² The rate coefficients and branching fractions of unimolecular reactions, including the H-shifts, the reactions of alkoxy radicals, and the equilibrium between 2-OO-3-ROOH and 3-OO-2-ROOH, are initially adopted from quantum-chemical calculations, with some of them adjusted later based on experimental results. The kinetics of photolytic reactions of photo-sensitive compounds, such as hydroperoxides and carbonyls, are detailed in Section B.4.1. Other secondary processes, such as vapor wall loss (also see Section B.4.2), are not explicitly included in the model but are treated separately.

B.2 Experimental Conditions

All experiments are conducted in a $\sim 0.7 \text{ m}^3$ Teflon chamber. Gas-phase reagents (2-EE, CH_3OH , NO , etc.) were prepared in 500 cm^3 glass bulbs. Desired mixing ratios were achieved through serial dilution using a vacuum/ N_2 system, with pressure in the bulbs measured by pressure sensors (MKS 1000 and 10 Torr baraton pressure transducers). Reagents in liquid and solution phase (H_2O_2 , ethylene glycol, and other low-volatility organics) were pipetted into three-way glass vials. Their initial mixing ratios in the chamber were determined by weighing the 3-way vial before and after injection. Injection of the reagents was achieved by passing dry air through the bulbs and the vials into the chamber at 20 SLM. The time required to inject the reagents depends on the bag volume and their volatility. For reagents with low volatility, the flow rate of dry air is turned down and their injection time is extended accordingly to facilitate their total evaporation.

After collecting CIMS background signals, we turned the UV lights on to initiate photo-oxidation. The chamber is illuminated ranging from 1 minute to 2 hours depending on the types of UV bulbs used, i.e., the OH radical production rate in the chamber. The oxidation time in the chamber when we use multiple 254 nm lights (high OH production rate) was kept short to minimize secondary chemistry. We extended the oxidation time accordingly when fewer bulbs and/or bulbs at lower wavelengths were used so that similar amounts of 2-EE would be oxidized across all experiments. On average, less than 5% of 2-EE was reacted in our experiments (see Table B.9).

Upon eluted from the column, the GC effluent is transmitted to the CIMS instrument, either through a Teflon-coated glass flow tube or directly into the ion source, to interact with the CF_3O^- reagent ion to form product ions. We named the former GC operation “normal mode” and the latter “high sensitivity (HS) mode”. During normal mode operation, the eluted analytes are mixed with CF_3O^- downstream from the ion source, while in HS mode, the analytes interact with the ions as soon as it forms. Thus, the increase in analyte-reagent ion interaction time in HS mode operation leads to an enhancement in instrument sensitivity of the analytes compared to that in the normal mode. On the other hand, analytes in HS mode are more easily subject to fragmentation due to analyte interactions with the metal walls of the ionizer and the direct electron attachment to analytes. Unless otherwise noted, the experiments listed in the following tables are conducted with normal mode operation.

Table B.1: Experimental conditions for 2-EE HO₂ experiments. All concentrations are in ppb. Oxidation time are in minutes. Room temperature (RT) experiments are conducted at 294 ± 1 K. High temperature experiments at conducted at 309.5 ± 2 K.

Experimental. No.	[2-EE] ₀	[H ₂ O ₂] ₀	[CH ₃ OH] ₀	[Ethylene Glycol] ₀	Bulb Type	Bulb #	Oxidation time	Temperature
1	677	2379	45675	133	254 nm	2	5	RT
2	662	2320	45725	286	254 nm	1	8 16	RT
3	559	2133	46539	188	254 nm	7	1.5 3	RT
4	675	2297	45771	94	350 nm	8	96	RT
5	631	2488	45771	168	350 nm	8	17 96	RT
6	529	2106	46427	197	350 nm	2	68	RT
7	506	2050	48004	222	350 nm	1	136	RT
8	557	1948	47765	221	254 nm	2	5 12	RT
9	639	2557	46183	140	254 nm	7	1.5 2.5	RT
10	606	2033	46234	206	254 nm	1	8 16	RT
11	591	2442	46860	310	254 nm	1	8	HT
12	606	2620	46494	216	254 nm	4	4	HT
13	591	2159	46636	239	350 nm	8	15 100	HT
14	626	2389	46697	281	350 nm	1	120	HT
15	602	2284	46254	174	254 nm	8	1	HT

Table B.2: Experimental conditions for 2-EE NO experiments. All experiments are conducted at room temperature. Experiment No.18 are conducted with high sensitivity mode.

Experimental. No.	[2-EE] ₀	[H ₂ O ₂] ₀	[NO] ₀	[Ethylene Glycol] ₀	Bulb Type	Bulb #	Oxidation time
16	544	2123	106	347	350 nm	8	16
17	549	2472	592	304	350 nm	8	20
18	667	2073	518	0	350 nm	8	24

Table B.3: Experimental conditions for ethyl vinyl ether (EVE) experiments. All experiments are conducted at room temperature. Experiment No. 23 are conducted with high sensitivity mode.

Experimental. No.	[EVE] ₀	[H ₂ O ₂] ₀	[CH ₃ OH] ₀	[NO] ₀	[Ethylene Glycol] ₀	Bulb Type	Bulb #	Oxidation time
19	167	2617	123648	0	261	254 nm	4	5.5
20	181	2267	124266	0	223	350 nm	8	100
21	165	2763	122952	0	172	350 nm	1	120
22	499	1886	0	546	337	350 nm	8	10
23	533	2073	0	522	0	350 nm	8	11

Table B.4: Experimental conditions for oxidation of ethyl glycolate (2-R=O) and 2-hydroxyethyl acetate (3-R=O). All experiments are conducted at room temperature.

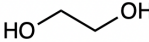
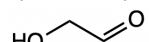
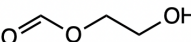
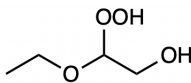
Experimental. No.	[VOC] ₀	[H ₂ O ₂] ₀	[CH ₃ OH] ₀	Bulb Type	Bulb #	Oxidation time	
24	2-R=O	885	2504	50580	254 nm	8	6
25	3-R=O	>822	2342	63240	254 nm	8	8

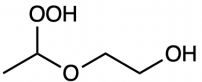
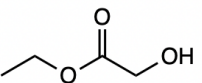
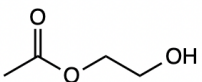
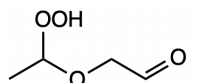
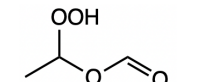
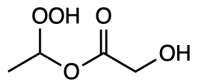
Notes: GC for experiment No.5, 8, and 20 are shown in Figure 3.1; Experiment No.12 are in Figure B.1; Experiment No.5, 20, 24, and 25 are in Figure B.2; Experiment No. 17 and 22 are in Figure B.3; Experiment No. 18 and 23 are in Figure B.4.

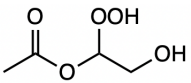
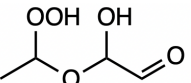
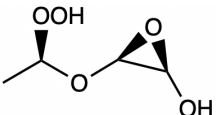
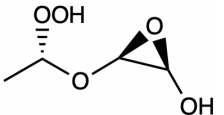
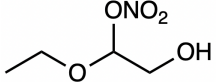
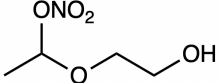
B.3 CIMS Calibration

The method of CIMS calibration in this work is the same as that documented in Section A.3. The following table list the CIMS sensitivities of 2-EE oxidation products calibrated based on their calculated ion-molecule collision rates and the measured sensitivity of ethylene glycol (Sigma-Aldrich, 99.8%).

Table B.5: Calculated dipole moments (μ_D), polarizabilities (α), CF_3O^- -molecule collision rate coefficients (k_c), and CIMS sensitivities for molecules of interests in 2-EE system. ^a Normalized relative to that of ethylene glycol. ^b measured sensitivity data and uncertainties for ethylene glycol and glycoaldehyde come from Murphy et al.⁵ ^c (*R,R*) and (*R,S*) stereoisomers of 2-OH-3-OOH-R'CHO have the same dipole moment, polarizability, and thus the same CIMS sensitivity.

Molecule	m/z	μ_D (D)	α ($\text{\AA}^3$)	k_c ($10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Relative k_c^a	Sensitivity (10^{-4} cts/ppTV)
Ethylene glycol 	147	2.08	5.11	1.90	1	2.50 (± 0.20) ^b
Glycoaldehyde 	145	2.33	4.64	2.06	1.08	2.71 (± 0.22) ^b
2-OH-ethylformate 	175	3.77	7.06	2.80	1.47	3.69 (± 0.30)
2-ROOH 	207	2.72	10.0	2.14	1.13	2.82 (± 0.23)

Molecule	m/z	μ_D (D)	α (Å ³)	k_c (10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹)	Relative k_c	Sensitivity (10 ⁻⁴ cts/pptv)
3-ROOH 	207	2.97	10.1	2.29	1.20	3.01 (± 0.24)
2-R=O 	189	3.15	8.77	2.42	1.27	3.19 (± 0.26)
3-R=O 	189	2.76	8.70	2.20	1.16	2.89 (± 0.23)
3-OOH-R'CHO 	205	4.14	9.55	2.92	1.54	3.84 (± 0.31)
3-OOH-R'=O 	191	3.01	7.76	2.30	1.21	3.02 (± 0.24)
2-oxo-3-ROOH 	221	3.08	10.1	2.29	1.21	3.02 (± 0.24)

Molecule	m/z	μ_D (D)	α (Å ³)	k_c (10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹)	Relative k_c	Sensitivity (10 ⁻⁴ cts/pptv)
3-oxo-2-ROOH 	221	3.48	10.1	2.51	1.32	3.31 (± 0.27)
2-OH-3-OOH-R'CHO 	221	2.79	10.2	2.14	1.12	2.81 (± 0.23) ^c
(<i>R,R,R</i>)-epoxide 	221	2.93	10.0	2.21	1.16	2.91 (± 0.23) ^c
(<i>S,R,R</i>)-epoxide 	221	2.91	9.92	2.20	1.16	2.89 (± 0.23) ^c
2-RONO ₂ 	236	2.69	11.7	2.09	1.10	2.75 (± 0.22) ^c
3-RONO ₂ 	236	2.80	11.6	2.15	1.13	2.82 (± 0.23) ^c

B.4 Secondary Losses

To evaluate the production rate of 2-EE oxidation products from the measured yields, we need to account for their secondary losses. The loss processes we considered in this study include: photolysis, vapor wall loss, and loss during GC transmission.

B.4.1 Photolysis

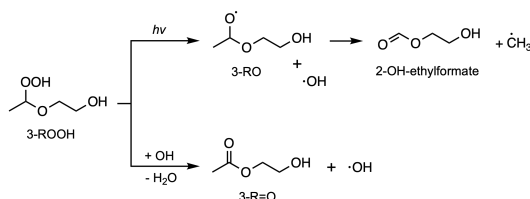
The major compound classes we considered to potentially undergo photolysis during irradiation are the hydroperoxides and carbonyls (ketones and aldehydes). We estimate the photolysis rates of those compounds as follows (similar procedure also described in Murphy et al.⁵):

We first synthesized the oxidation products at relatively higher yields in the chamber (by oxidizing under 254 nm UV lights for an extended period). Then we evacuated the chamber through a coil made from Teflon tubes while submerging the coil in an ethanol/liquid nitrogen bath maintained at approximately -30°C . In this way, we expect that the low-volatility products, most of which consist of hydroperoxide and carbonyl moieties, would be trapped in the coil and 2-EE, H_2O_2 , and other high-volatility products to be pumped away. After that, we cleaned out the chamber by flushing it thoroughly with clean air, and returned the contents trapped in the Teflon coil back to the chamber by slowly passing dry air through the coil. Finally, we injected ~ 90 ppm CH_3OH into the chamber as a $\cdot\text{OH}$ scrubber to minimize the influence from secondary chemistry other than photolysis. We then turned on the UV lights and examine the evolution of relevant compounds.

From the photolysis experiment, we observe a decrease in $[\text{3-ROOH}]$, which approximately equals to the sum of the increase in $[\text{2-OH-ethylformate}]$ and $[\text{3-R=O}]$ (Table B.6). 2-OH-ethylformate is likely a product from photolysis of 3-ROOH, while 3-R=O is formed by oxidation of 3-ROOH by OH radical (Scheme B.3). From the production of 2-OH-ethylformate, we manage to estimate the photolysis frequency for the ROOH's (Table B.7). We expect that the true photolysis rate coefficients of the peroxides to be close to that of H_2O_2 , which is $1.7 \times 10^{-6} \text{ s}^{-1}$ under eight 350 nm bulbs and $2.7 \times 10^{-4} \text{ s}^{-1}$ under eight 254 nm bulbs in our chamber. Our estimate is within reasonable agreement of the expected values. Still, under conditions when we lack necessary data to evaluate the photolytic loss, we assume that the photolysis rate coefficients of all other ROOH's is equal to that of H_2O_2 .

We were unable to identify any trends in the concentrations of aldehydes or ketones that could be useful for quantifying their photolytic loss. Therefore, for photolysis

frequencies of those compounds, we adopt measurements of similar compounds from the literature.⁶⁻⁹ For compounds with multiple types of moieties, we account for their photolysis frequencies from the sum of the photolysis rate coefficients of relevant compound classes.



Scheme B.3: Potential secondary chemistry pathways of 3-ROOH

Table B.6: Results from the photolysis experiment. Change in the abundance of selected oxidation products before and after photolysis. All concentrations are in ppb. The experiment is conducted using 8 350 nm bulbs and photolyzed for 60 min.

	[2-OH-ethylformate]	[2-ROOH]	[3-ROOH]	[3-R=O]
initial	0.093	0.51	0.28	0.36
final	0.106	0.32	0.17	0.45
Δ	0.013	-0.19	-0.11	0.09

Table B.7: Estimated photolysis frequencies (in s^{-1}) of relevant compound classes in the system. ^a H_2O_2 photolysis frequency in our chamber at 254 nm is calculated by Murphy et al.⁵ by measuring OH production via the decay of 2,3-butanediol, and scaled to fit our experiment conditions. The photolysis frequency at 350 nm is calculated using similar method via the decay of ethylene glycol. ^b Photolysis frequency of ROOH at 350 nm is evaluated from the results of photolysis experiments. ^c Photolysis frequency of aldehydes at 254 nm is adopted from measurements by Murphy et al.⁵ on the photolysis of glycoaldehyde. The rate coefficient at 350 nm is inferred from UV absorption spectrum of similar aldehydes with long carbon chain.^{6,9} ^d Photolysis frequencies of ketones are inferred from UV absorption spectrum of similar compounds⁷ based on literature values of their photolysis frequencies at different wavelengths.⁸

Wavelength	H_2O_2 ^a	Hydroperoxides ^b (ROOH)	Aldehydes ^c (R'CHO & R'=O)	Ketones ^d R=O
254 nm	$2.7 (\pm 0.4) \times 10^{-4}$	$2.7 (\pm 0.4) \times 10^{-4}$	$1.7 (\pm 0.1) \times 10^{-4}$	$7.3 (\pm 0.8) \times 10^{-5}$
350 nm	$1.7 (\pm 0.2) \times 10^{-6}$	$1.4 (\pm 0.2) \times 10^{-5}$	$1.7 (\pm 0.1) \times 10^{-6}$	$6.1 (\pm 0.7) \times 10^{-6}$

We list the estimates for the photolysis rate coefficients of the hydroperoxides and carbonyls in Table B.7. The photolysis frequencies listed in the table are evaluated under our chamber conditions with eight 254 nm bulbs and eight 350 nm bulbs. Since the light intensities of the bulbs increase as they warm up over time, the photolysis frequencies for different experiments with varied light intensities and

oxidation time are evaluated based on the mean irradiance in the chamber during oxidation, using time-dependent measurements of cosine-corrected irradiance of the bulbs (Ocean Optics spectrometer integrated between 224 and 284 nm). The H_2O_2 photolysis frequencies at 254 nm in Table B.7 were calculated based on the mean irradiance of the bulbs over the 90 s time period of our experiments, and the photolysis frequencies of other compounds are scaled accordingly. For the photolysis frequencies of the compounds at 350 nm with lower light intensities, since we lack time-dependent data of bulb irradiation, they are directly scaled from the values evaluated with eight light bulbs. As a result, based on our estimations of the photolysis frequencies, we calculate that around 2–5% of those potentially photo-sensitive compounds were lost during the experiments due to photolysis.

B.4.2 Vapor Wall Loss

Vapor wall loss is the partition of organic vapor products onto the chamber walls. We attempt to estimate the wall loss of 2-EE oxidation products by measuring the dark decay of those compounds after oxidation. Fitting the decay of the low-volatility compounds gives a wall loss rate for the ROOH's to be $2.5(\pm 0.4)\times 10^{-6} \text{ s}^{-1}$, and the ketohydroperoxides (2-oxo-3-ROOH and 3-oxo-2-ROOH) to be $6.1(\pm 0.9)\times 10^{-6} \text{ s}^{-1}$, which would on average lead to around 2% loss for the compounds over 1 hour. Those values are smaller than our expectation, especially for the ketohydroperoxides, as these compounds are both highly oxygenated and functionalized. They are expected to have low volatility and would readily partition into the condensed phase.¹⁰

One reason for the potential underestimation is likely that the low-volatility vapor equilibrates relatively fast between the gas-phase and the wall-phase. For low vapor pressure species, vapor-wall equilibrium can be established in relatively short timescale (~ 10 min in bag).¹¹ Smaller the vapor-wall equilibrium timescale of the compounds, earlier the wall loss process starts to take effect on their detectable gas phase concentration.^{11–13} The compound likely already starts to approach gas-wall equilibrium during the oxidation period, which would result in a smaller decay observed after the oxidation. Thus, the detected long-timescale wall-loss likely only encompasses a portion of vapor-wall partitioning. Other dark loss processes, e.g., reactive uptake by the walls, diffusion of species into the Teflon, or dilution due to potential leaks, may also account for the detected decay. Still, we expect that the underestimation in vapor-wall losses of the compounds will not greatly affect our results. Most analysis in this study is based on the ratios between concentrations of relevant hydroperoxides (e.g. [2-ROOH]/[3-ROOH] in Section 3.3.2.3, and [3-

oxo-2-ROOH]/[2-oxo-3-ROOH] in Section 3.3.2.5), so as long as the wall loss of those compounds are similar (see Table B.8 for a list of vapor pressure estimated by EVAPORATION¹⁴), it should have small impact on our results.

However, the potential underestimation in wall partitioning for certain compounds can lead to biases in our estimations of some parameters. For example, 3-ROOH may have larger vapor-wall loss than our estimation here, which would lead to underestimation in its branching fraction in Section 3.3.2.1, underestimation in [3-ROOH]/[3-OOH-R'CHO] and overestimation in $k_{1,6 \text{ H-shift}, 3\text{-RO}_2}$ in Section 3.3.2.2, and overestimation in [2-ROOH]/[3-ROOH] and biases in the 1,5 H-shift rate coefficients in Section 3.3.2.3. Moreover, the ketohydroperoxides also likely have higher magnitude of wall loss, which may lead to biases in [3-oxo-2-ROOH]/[2-oxo-3-ROOH] in Section 3.3.2.5.

Table B.8: Vapor pressure (in atm) of major oxidation products in 2-EE system estimated by EVAPORATION method¹⁴ at 294 K. (<https://tropo.aeronomie.be/index.php/models/evaporation>)

	2-ROOH	3-ROOH	2-R=O	3-R=O
Vapor pressure	2.8×10^{-6}	2.0×10^{-6}	6.3×10^{-4}	5.3×10^{-4}
	3-OOH-R'CHO	3-OOH-R'=O	2-oxo-3-ROOH	3-oxo-2-ROOH
Vapor pressure	1.9×10^{-4}	6.8×10^{-4}	4.0×10^{-7}	5.4×10^{-7}

B.4.3 GC transmission

A certain portion of the oxidation products are lost by decomposition and/or reaction with the column surface as they are travelling through the column. The GC transmission rates of the products are evaluated by comparing their detected concentrations from direct sampling mode and GC mode. Losses are often greater for compounds eluting later at higher temperature. On average, the products elute before ~10 min (2-OH-ethylformate, 3-R=O, and 3-OOH-R'=O) have GC transmission rates of ~90%. The products with hydroperoxy group (3-OOH-R'CHO, 2-ROOH, and 3-ROOH) have transmission rates of 60–70%. The ketohydroperoxides (2-oxo-3-ROOH and 3-oxo-2-ROOH), due to their low volatility and multifunctionality as mentioned in Section 3.3.2.5, have low GC transmission rates of 25–30%.

B.5 Table of Results

Table B.9: Experimental results with all data corrected. All concentrations are in ppb. HO₂ concentrations are determined by the box model.

Exp. No.	[HO ₂]	Δ[2-EE]	[2-OH-ethylformate]	[3-R=O]	[3-ROOH]	[2-ROOH]	[3-OOH-R'CHO]	[3-OOH-R'=O]	[3-oxo-2-ROOH]/ [2-oxo-3-ROOH]
1	1.42	20.2	0.31	0.24	4.88	9.51	1.63	0.53	
2	1.04	10.0	0.15	0.12	2.49	5.08	1.29	0.39	
		19.0	0.29	0.24	4.73	9.46	2.46	0.88	
3	2.27	8.95	0.12	0.13	2.89	4.70	0.69	0.20	
		18.5	0.25	0.28	5.59	9.41	1.30	0.43	
4	0.19	15.4	0.09	0.09	0.76	2.19	1.58	0.84	
5	0.20	1.84		0.01	0.11	0.34	0.21	0.09	
		11.7	0.05	0.07	0.50	1.59	1.19	0.63	1.54
6	0.10	1.50	0.02	0.005	0.05	0.18	0.17	0.07	1.45
7	0.07	1.62		0.002	0.05	0.18	0.20	0.07	1.29
8	1.33	9.39	0.13	0.15	3.25	6.38	1.26	0.39	1.67
		25.0	0.44	0.50	6.15	12.40	2.55	1.00	1.60
9	2.42	10.1	0.12	0.13	2.43	4.04	0.55	0.17	
		16.3	0.23	0.23	4.05	7.21	0.94	0.32	1.49
10	0.99	6.15	0.04	0.05	1.11	2.32	0.67	0.21	
		12.8	0.10	0.12	1.83	4.26	1.11	0.41	1.75
11	1.42	9.11	0.05	0.05	1.05	2.71	1.59	0.75	1.60
12	2.85	18.2	0.12	0.16	3.77	8.73	2.80	1.16	1.56
13	0.23	1.62	0.01	0.002	0.03	0.10	0.17	0.08	1.47
		11.4	0.05	0.04	0.19	0.62	1.00	0.57	1.48
14	0.08	2.91	0.01	0.01	0.02	0.06	0.14	0.07	1.35
15	3.73	8.45	0.06	0.08	1.69	3.61	3.61	0.95	1.46

B.6 Estimation of Uncertainties

B.6.1 HO₂ Concentrations

Similar methods for determining uncertainty in [HO₂] is documented in Section A.9.1. The uncertainty can be derived from:

$$[\text{HO}_2] \simeq \sqrt{\frac{J_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}{k_{\text{HO}_2+\text{HO}_2}}} \quad (\text{B.1})$$

The major uncertainties in [H₂O₂] arise from our sample preparation procedure and instruments, and we estimate that it induces about systematic ~20% error in the determined [H₂O₂]. We evaluate the uncertainty in $k_{\text{HO}_2+\text{HO}_2}$ to be ~21% at ambient temperature, and ~23% at high temperature based on the method in JPL documentation.¹⁵ Thus, the resulting uncertainty in the estimated [HO₂] in this work equals ~17%.

B.6.2 Product Concentrations and Ratios of Product Yields

Similar methods for determining uncertainty in product yields is documented in Section A.9.2. In this work, we evaluate the uncertainty in the concentrations of detected products to be ~21%, while the uncertainty in the ratios of product concentrations to be ~25%.

B.6.3 Amount of Oxidized 2-ethoxyethanol and Normalized Product Yields

In order to calculate the amount of 2-EE consumed ($\Delta[2\text{-EE}]$) during the experiments, we add ethylene glycol (EG) into our chamber and measure its oxidation product glycoaldehyde (GA). We start with the rate equations for the loss of 2-EE and EG and the production of GA:

$$\frac{d[2\text{-EE}]}{dt} = -k_{2\text{-EE}+\text{OH}}[2\text{-EE}][\text{OH}] \quad (\text{B.2})$$

$$\frac{d[\text{EG}]}{dt} = -k_{\text{EG}+\text{OH}}[\text{EG}][\text{OH}] = -\frac{d[\text{GA}]}{dt} \quad (\text{B.3})$$

By assuming that the amount of 2-EE and EG oxidized is much smaller than the initial concentrations of the two compounds, we can simplify the equations as:

$$\frac{\Delta[2\text{-EE}]}{\Delta t} \simeq -k_{2\text{-EE}+\text{OH}}[2\text{-EE}]_i[\text{OH}] \quad (\text{B.4})$$

$$\frac{\Delta[\text{EG}]}{\Delta t} = -\frac{\Delta[\text{GA}]}{\Delta t} \simeq -k_{\text{EG}+\text{OH}}[\text{EG}]_i[\text{OH}] \quad (\text{B.5})$$

Rearranging and combining the Equations B.4 and B.5 gives us the expression to estimate $\Delta[2\text{-EE}]$:

$$\Delta[2\text{-EE}] \simeq [2\text{-EE}]_i \cdot \frac{\Delta[\text{GA}]}{[\text{EG}]_i} \cdot \frac{k_{2\text{-EE}+\text{OH}}}{k_{\text{EG}+\text{OH}}} \quad (\text{B.6})$$

Thus, $\Delta[2\text{-EE}]$ is constrained by the following quantities: the ratio between the concentrations of EG and GA, the initial concentration of 2-EE, and the rate coefficients of 2-EE and EG oxidation reaction by OH. We have the uncertainties in the ratios between the concentrations of detected species from the previous section (25%). The major source of uncertainty in $[2\text{-EE}]$ arises from our sample preparation procedure (Section B.2), and the error is likely to be small. We adopt the error in the rate coefficients from their literature values,^{4,16–20} which is $\sim 25\%$ for $k_{2\text{-EE}+\text{OH}}$ and $\sim 18\%$ for $k_{\text{EG}+\text{OH}}$. As a result, we are able to determine the uncertainty in $\Delta[2\text{-EE}]$ to be $\sim 40\%$, and the normalized yield of oxidation products from our measurements, which equals to the concentration of the product divided by $\Delta[2\text{-EE}]$, to be $\sim 45\%$.

Table B.10: Sources of uncertainties for reaction parameters determined in this study. ^a Values at room temperature (294 K). ^b Values at high temperature (309.5 K). ^c Uncertainty in $k_{RO_2+HO_2}$ of 2-EE RO₂ are derived from that of C₂H₅O₂.¹⁵

Quantity	Constraints	Sources of Uncertainty	Value
α_{4a} (k_{4a}/k_4)	$\frac{[2\text{-OH-ethylformate}]}{[3\text{-ROOH}]}$ $\frac{[3\text{-R=O}]}{[3\text{-ROOH}]}$	Fit Fig. 3.2a (13%), $\frac{[2\text{-OH-ethylformate}]}{[3\text{-ROOH}]}$ (25%) Fit Fig. 3.2b (13%), $\frac{[3\text{-R=O}]}{[3\text{-ROOH}]}$ (25%)	$0.896 \pm 0.026^a, 0.936 \pm 0.016^b$
α_{4b} (k_{4b}/k_4)			$0.048 \pm 0.013^a, 0.035 \pm 0.009^b$
α_{4c} ($(k_{4c.1} + k_{4c.2})/k_4$)			$0.056 \pm 0.016^a, 0.029 \pm 0.009^b$
$((k_{4c.1} + k_{4c.2})/k_{4c.3})$	$\frac{[3\text{-R=O}]+[3\text{-OH-R'CHO}]}{[2\text{-OH-ethylformate}]}$	Fit Fig. B.5 (3%), $\frac{[3\text{-R=O}]+[3\text{-OH-R'CHO}]}{[2\text{-OH-ethylformate}]}$ (25%)	0.0954 ± 0.024
Slope Fig 3.3 $\frac{\alpha_{4a}k_{RO_2+HO_2}}{k_{1,6\text{ H-shift,3-RO}_2}}$	$\frac{[3\text{-ROOH}]}{[3\text{-OOH-R'CHO}][HO_2]}$	Fit Fig. 3.2 (2%), $\frac{[3\text{-ROOH}]}{[3\text{-OOH-R'CHO}]}$ (25%), $[HO_2]$ (17%)	$(7.33 \pm 2.21) \times 10^{-11}^a$ $(1.95 \pm 0.59) \times 10^{-11}^b$
$\frac{\alpha_{2\text{-RO}_2}}{\alpha_{3\text{-RO}_2}}$	$\frac{[2\text{-ROOH}]}{[3\text{-ROOH}]} (25\%)$		1.5 ± 0.4
$\alpha_{2\text{-RO}_2} + \alpha_{3\text{-RO}_2}$	Normalized $[2\text{-ROOH}] + [3\text{-ROOH}]$ (45%), α_{4a} (29%)		$0.8 + 0.2/-0.4$
$k_{1,5\text{ H-shift,2-RO}_2}$	Normalized $[2\text{-ROOH}]$ (45%), α_{4a} (29%), $k_{RO_2+HO_2}[HO_2]$ (56%)		$0.13 \pm 0.10^a, 0.54 \pm 0.42^b$
$k_{1,5\text{ H-shift,3-RO}_2}$	Normalized $[3\text{-ROOH}]$ (45%), α_{4a} (29%), $k_{RO_2+HO_2}[HO_2]$ (56%)		$0.13 \pm 0.10^a, 0.59 \pm 0.46^b$
H-shift rate coefficients of 2-OO-3-ROOH and 3-OO-2-ROOH	H-shift rate coefficients of 2- and 3-RO ₂ (77%), $k_{RO_2+HO_2}[HO_2]$ (56%), $\frac{[2\text{-OO-3-ROOH}]_{eq}}{[3\text{-OO-2-ROOH}]_{eq}}$ (27%), Normalized $[3\text{-OOH-R'=O}]$ (56%), $\alpha_{2\text{-RO}_2} + \alpha_{3\text{-RO}_2}$ (53%)		See Table 3.3, Monte Carlo method is applied to derive the difference between plus and minus error.

B.7 Additional Results

B.7.1 GC Peak Assignments

To assign the m/z 191 signal to 3-OOH-R'=O, we use deuterium exchange experiments to eliminate from consideration the exact mass isomers, i.e., the diols 2-ROH and 3-ROH shown in Scheme B.2, which would be produced in reactions of 2-RO₂ and 3-RO₂ with themselves or with each other (through RO₂+RO₂ chemistry). 3-OOH-R'=O has only one readily exchangeable hydrogen, while the diols have two. With addition of D₂O to the GC effluent, analytes with exchangeable H's will undergo H/D exchange with the hydrogen replaced by deuterium, and signals of compounds with n exchangeable H's will shift up by n m/z . Deuteration of GC effluent is achieved by passing dry N₂ through D₂O (99.9%, Cambridge Isotope Laboratories, Inc.) into the flow tube (through which the GC effluent is transmitted to the CIMS) during GC sampling. Figure B.1 shows the gas chromatograms from a HO₂ experiment after deuteration. Consistent with our assignments, the signal of ROOH's and oxo-ROOH's shift up by 2 m/z , and the signal of 2-OH-ethylformate, 3-R=O, and 3-OOH-R'CHO shift up by 1 m/z . The peak at m/z 191 also shifts up by 1 m/z , and no signal at m/z 193 beyond the contribution of the ¹³C isotope is observed.

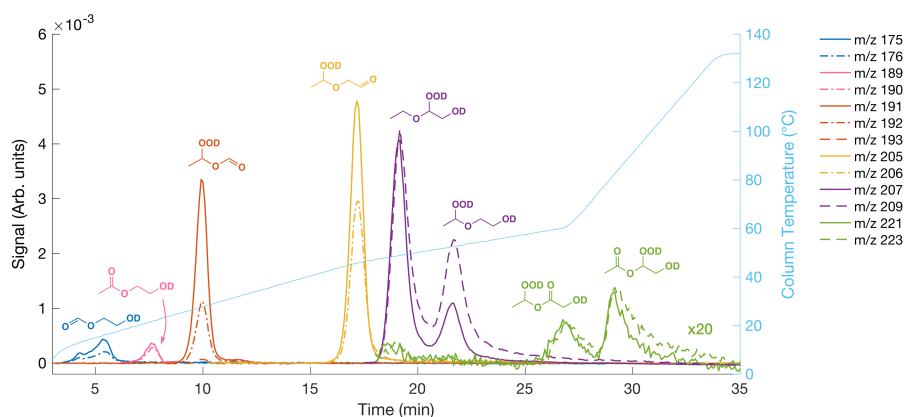


Figure B.1: Gas chromatograms of deuterated oxidation products from a 2-EE HO₂ experiment. Signals for original product m/z are in solid line. $m/z + 1$ signals are in dash-dotted line, and $m/z + 2$ signals are in dashed line. The signals at m/z 221 and m/z 223 are scaled up by a factor of 20.

The assignment of GC peaks at m/z 189 and m/z 221 is facilitated by oxidizing 2-R=O and 3-R=O standards, ethyl glycolate (Sigma Aldrich, 98%) and 2-hydroxyethyl acetate (TCI, >60%), under high [HO₂] condition. The resulted gas chromatograms are shown in Figure B.2(c). Comparing with the peaks at the same m/z from a 2-EE

(Figure B.2(a)) and an EVE experiment (Figure B.2(b)), we are able to identify the 2-R=O and 3-R=O peaks (at m/z 189), as well as the two m/z 221 peaks eluting at higher temperature.

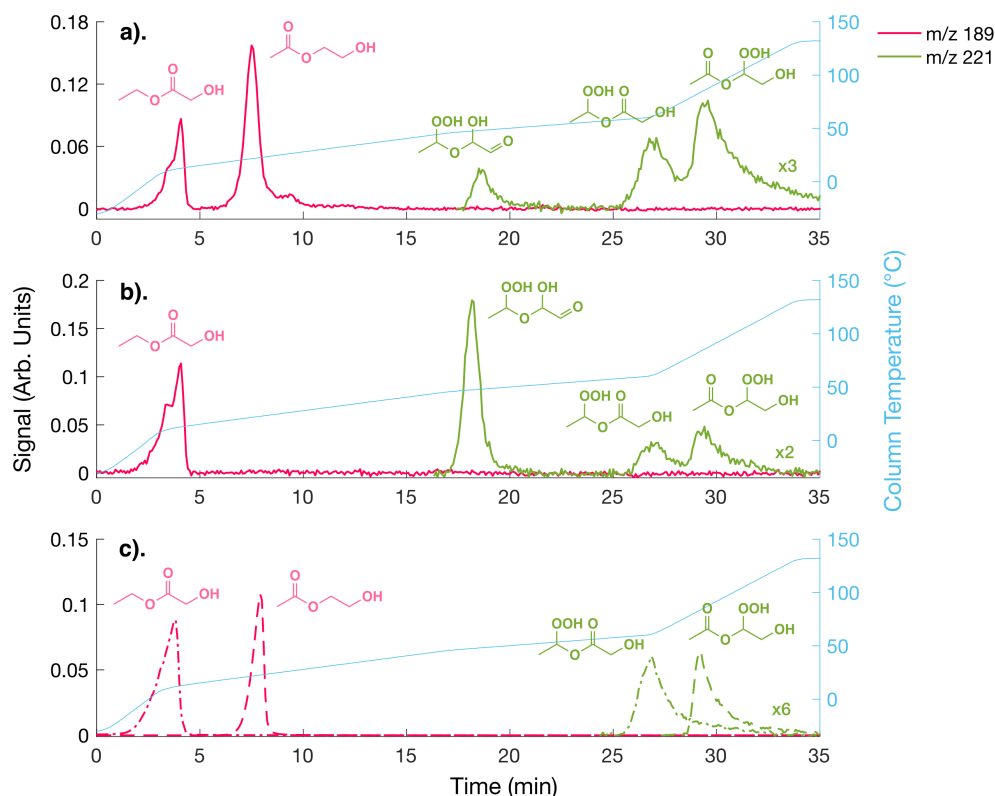


Figure B.2: Gas chromatograms of products at m/z 189 (2-R=O and 3-R=O) and m/z 221 (2-OH-3-OOH-R'CHO, 2-oxo-3-ROOH, and 3-oxo-2-ROOH) from **a).** a 2-EE HO₂ experiment; **b).** an EVE HO₂ experiment, **c).** oxidation of ethyl glycolate (2-R=O, in dash-dotted line) and 2-hydroxyethyl acetate (3-R=O, in dashed line). The m/z 221 signals in the figure are all scaled up by certain factors denoted in the figure. The pink dotted line in **(a)** indicates the m/z 189 signals from the oxidation run prior to the run of GC signals in pink solid line.

From Figure B.2(a) and (b), we notice that the peak assigned to 2-R=O (the first peak) obtain an irregular shape. We further notice that the GC signal of 2-R=O does not increase with illumination, unlike other oxidation products in the system. As shown in the dotted and solid pink line in Figure B.2(a), which represents m/z 189 signals from two consecutive oxidation runs, there is minimal difference in 2-R=O signals between the two runs. Such phenomenon hampers our efforts to measure 2-R=O quantitatively. One explanation is that the signal at m/z 189 may arise from some unknown impurities (or other unrecognized products) that elutes at

similar temperature as 2-R=O, which may account for the irregular peak shape in Figure B.2(a) and (b). Another possibility is that the unusual peak shape indicates peak fronting in chromatography. The compound is likely not trapped efficiently in the column. The observed signal may only correspond to the amount that is adsorbed to the column phase during each GC run, which explains the unchanged signal across runs.

B.7.2 Results from Experiments with NO

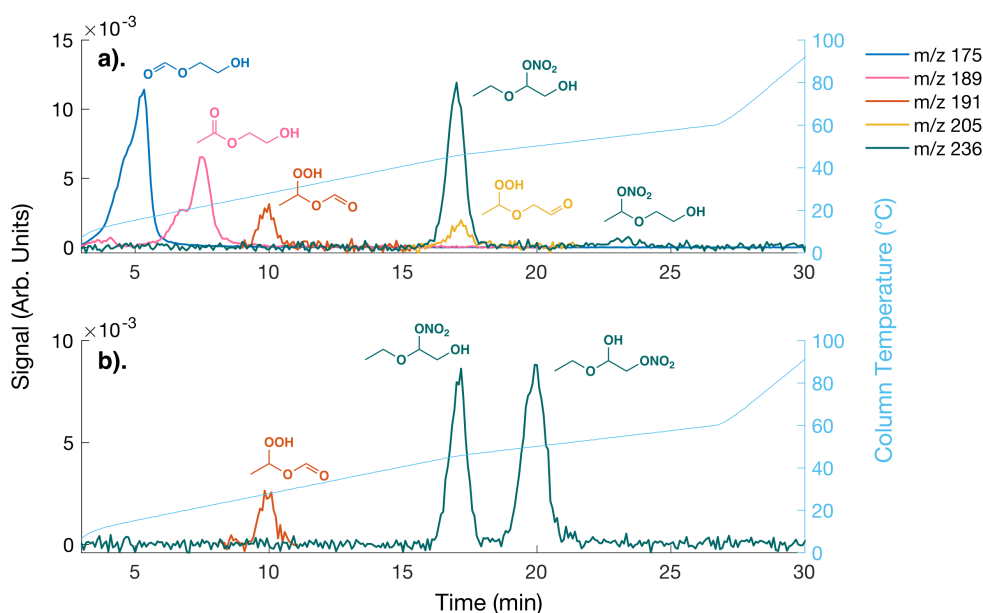


Figure B.3: Gas chromatograms of oxidation products from NO experiments of **a).** 2-EE and **b).** EVE. Major products include: 2-OH-ethylformate (m/z 175), 3-R=O and 3-OH-R'CHO (m/z 189), 3-OOH-R'=O (m/z 191), 3-OOH-R'CHO (m/z 205), and the hydroxynitrates (m/z 236). The signal at m/z 175 is scaled down by a factor of 50, and the signal at m/z 189 is scaled down by a factor of 5.

Shown in Figure B.3 are the gas chromatograms of products formed in oxidation experiments of 2-EE and EVE at high [NO] (~ 500 ppb; $\sim 1.2 \times 10^{13}$ molecules/cm³). These experiments enable us to identify 2-OH-ethylformate (m/z 175), 3-R=O and 3-OH-R'CHO (m/z 189, 3-OH-R'CHO likely corresponds to the unresolved shoulder at slightly lower temperature of the major peak), which are major products from reactions of alkoxy radical 3-RO, and two hydroxynitrates 2-RONO₂ and 3-RONO₂ (m/z 236). Oxidation of EVE differentiates the two nitrate peaks from 2-EE experiments, with 2-RONO₂ eluting at lower temperature and 3-RONO₂ at higher temperature. We also observe products from autooxidation pathways in these experiments, such as 3-OOH-R'CHO (m/z 205) and 3-OOH-R'=O (m/z 191). Given the

short bimolecular lifetime (~ 0.01 s), the product yields of those compounds are low.

In Figure B.3(b), by comparing the gas chromatograms from 2-EE and EVE experiments, we assign the 1,2-hydroxynitrate (2-RONO_2) to the peak that elutes at lower temperature than the 2,1-hydroxynitrate peak. However, such assignment of the hydroxynitrates from EVE experiments is counterintuitive. Since the hydrogen-bonding interaction between the -OH group of 1,2-hydroxynitrate with the column should be stronger than that of the 2,1-hydroxynitrate due to less steric hindrance, we expect that 1,2-hydroxynitrate to elute later than the 2,1-hydroxynitrate. We speculate that the elution of 2,1-hydroxynitrate may be retarded by the presence of the ether oxygen neighboring to the hydroxy group, which might strengthen the interaction between the -OH group and the column surface.

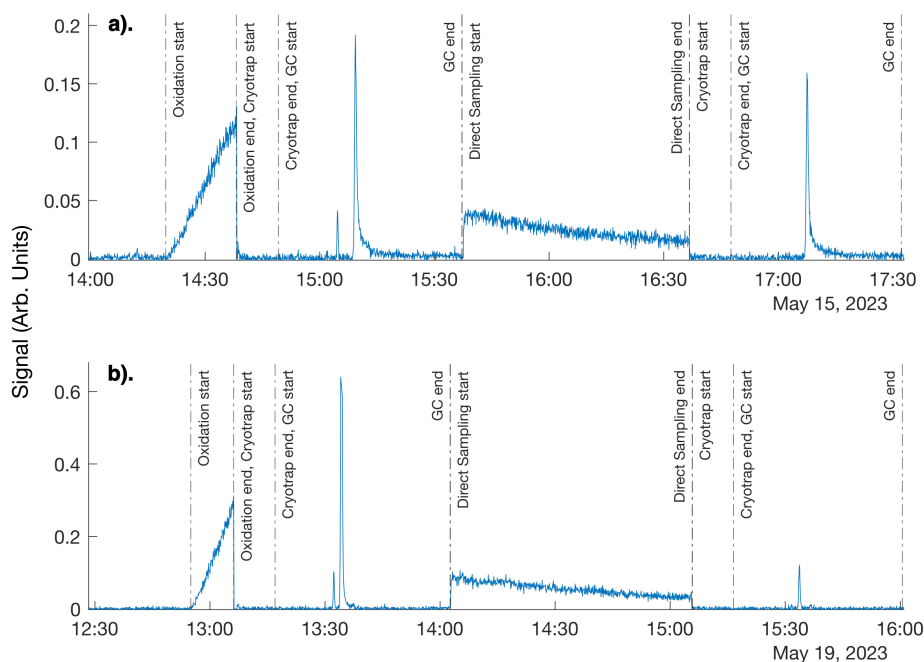
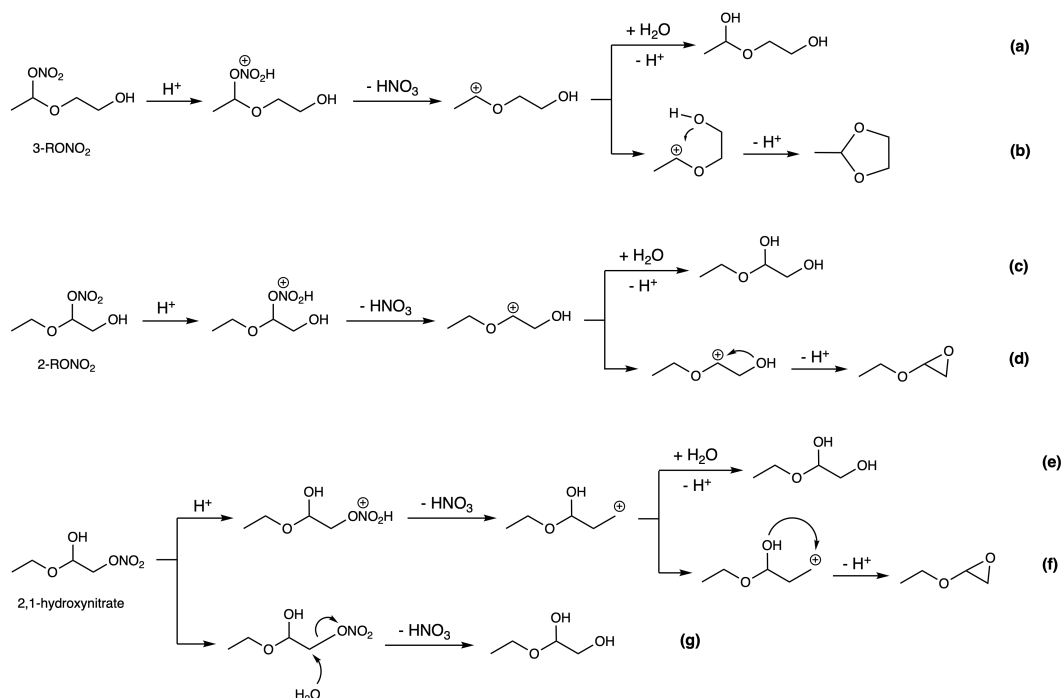


Figure B.4: Time series of m/z 236 signals for **a).** a 2-EE experiment and **b).** an EVE experiment with NO. Important timesteps of GC-CIMS operation are denoted. The nitrate peaks are of different shapes and intensities from those in Figure B.3 since the experiments are run under high sensitivity mode rather than normal mode (see Section B.2), and fragmentation of the analytes at the ion source likely alters the GC signal.

Another unusual phenomenon we observed in the NO experiments is the fast decay of CIMS signals of the hydroxynitrates (m/z 236). Shown in Figure B.4 are the time series of m/z 236 from the NO experiments with 2-EE and EVE. We measure the overall loss rate for the nitrates from 2-EE experiment to be around 0.033 min^{-1} ,

and that from EVE experiment to be 0.037 min^{-1} . The loss of the nitrate signals is likely due to wall deposition, which may result from acid-catalyzed hydrolysis in the condensed phase.^{21,22} We propose the possible hydrolysis mechanisms for the nitrates in Scheme B.4.



Scheme B.4: Speculative hydrolysis mechanisms for hydroxynitrates observed in our experiments.

Shown in Figure B.5 is the relationship between the concentrations of 3-R=O and

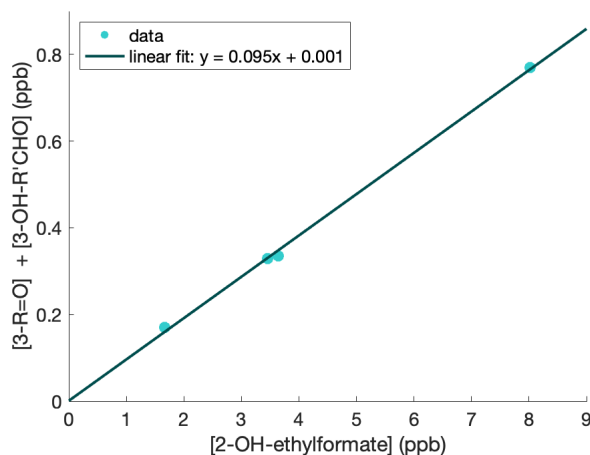


Figure B.5: $([3\text{-R=O}] + [3\text{-OH-R'CHO}])$ vs. $[2\text{-OH-ethylformate}]$ from 2-EE NO experiments and the linear fit result.

3-OH-R'CHO and the concentration of 2-OH-ethylformate from several 2-EE NO experiments. From the linear fitting, we determine that the yield of the two products from 3-RO isomerization relative to that of 2-OH-ethylformate is 0.095 ± 0.024 .

B.7.3 Additional Figures

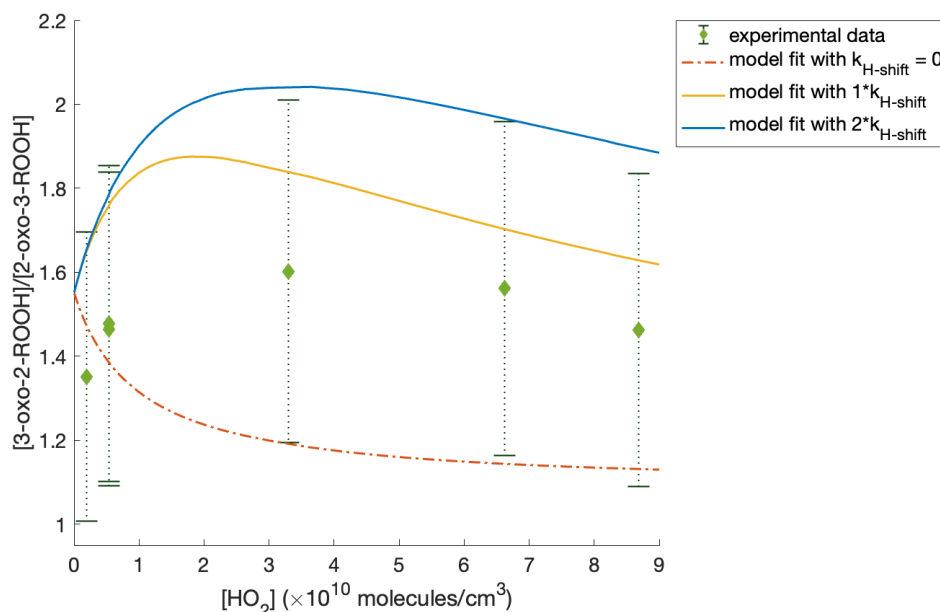


Figure B.6: $[3\text{-oxo-2-ROOH}]/[2\text{-oxo-3-ROOH}]$ vs. $[\text{HO}_2]$ at high temperature (309.5 K). The data (in green markers) are from experiments at 309.5 K. The orange dashed line is the result from model run without the 1,5 H-shift reaction of 2-OO-3-ROH radical, and the solid lines are results from model run with the 1,5 H-shift rate coefficient of 2-OO-3-ROH scaled by 1 and 2 times the calculated rate coefficients.

Shown in Figure B.6 are the experimental and model results of $[3\text{-oxo-2-ROOH}]/[2\text{-oxo-3-ROOH}]$ vs. $[\text{HO}_2]$ at high temperature (309.5 K). The modeled outputs of the ratio between the two products seems to fail to fit well with the experimental results, and thus we refrain from providing an estimate for the 1,5 H-shift rate coefficient of 2-OO-3-ROH at high temperature. Still, at higher 1,5 H-shift rate, the modelled trend of the ratio obtains a similar shape with the trend from experimental results. The modelled results also fit within the error of experimental measurements, which mainly results from the uncertainties in the sensitivities of the compounds. Therefore, the seemingly divergence between the experimental and model results may be explained by the overestimation of the relative instrument sensitivities of 3-oxo-2-ROOH compared to 2-oxo-3-ROOH. The modelled trend of the ratio converges at ~ 1.55 at low $[\text{HO}_2]$, which is slightly higher than that at room temperature (~ 1.43). The difference likely arises from the decrease in the rate coefficients of bimolecular

reaction ($\text{RO}_2 + \text{HO}_2$) at higher temperature.

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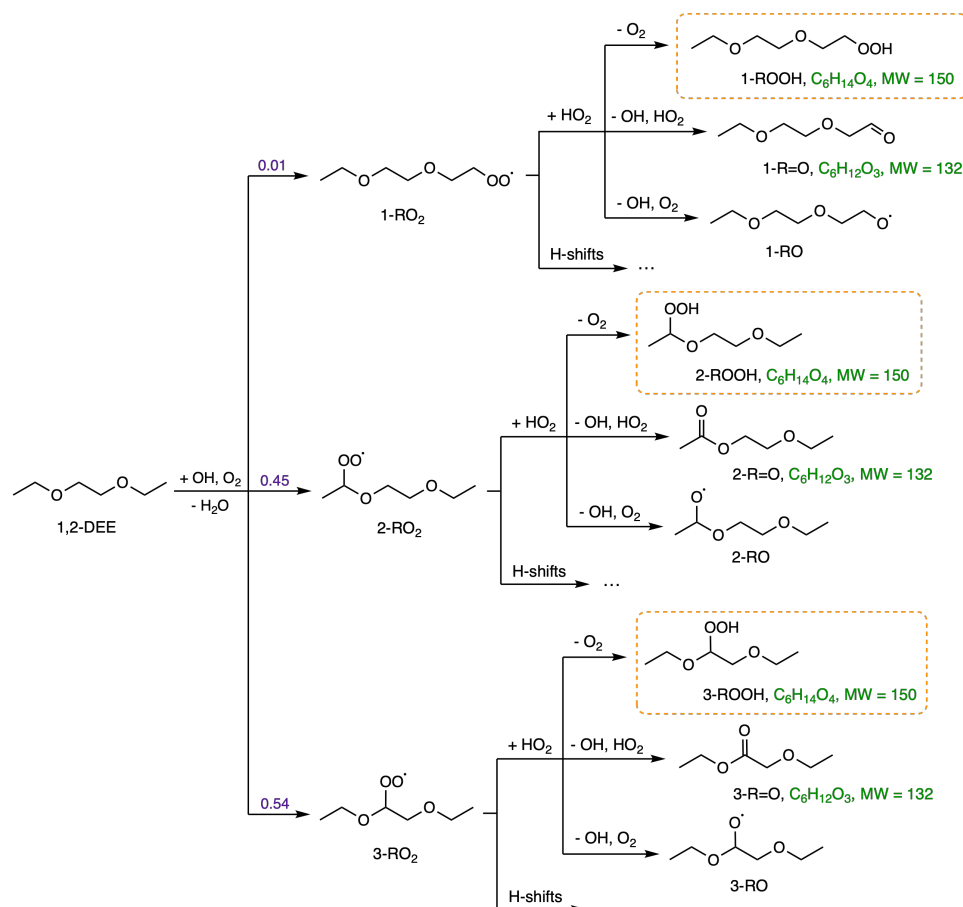
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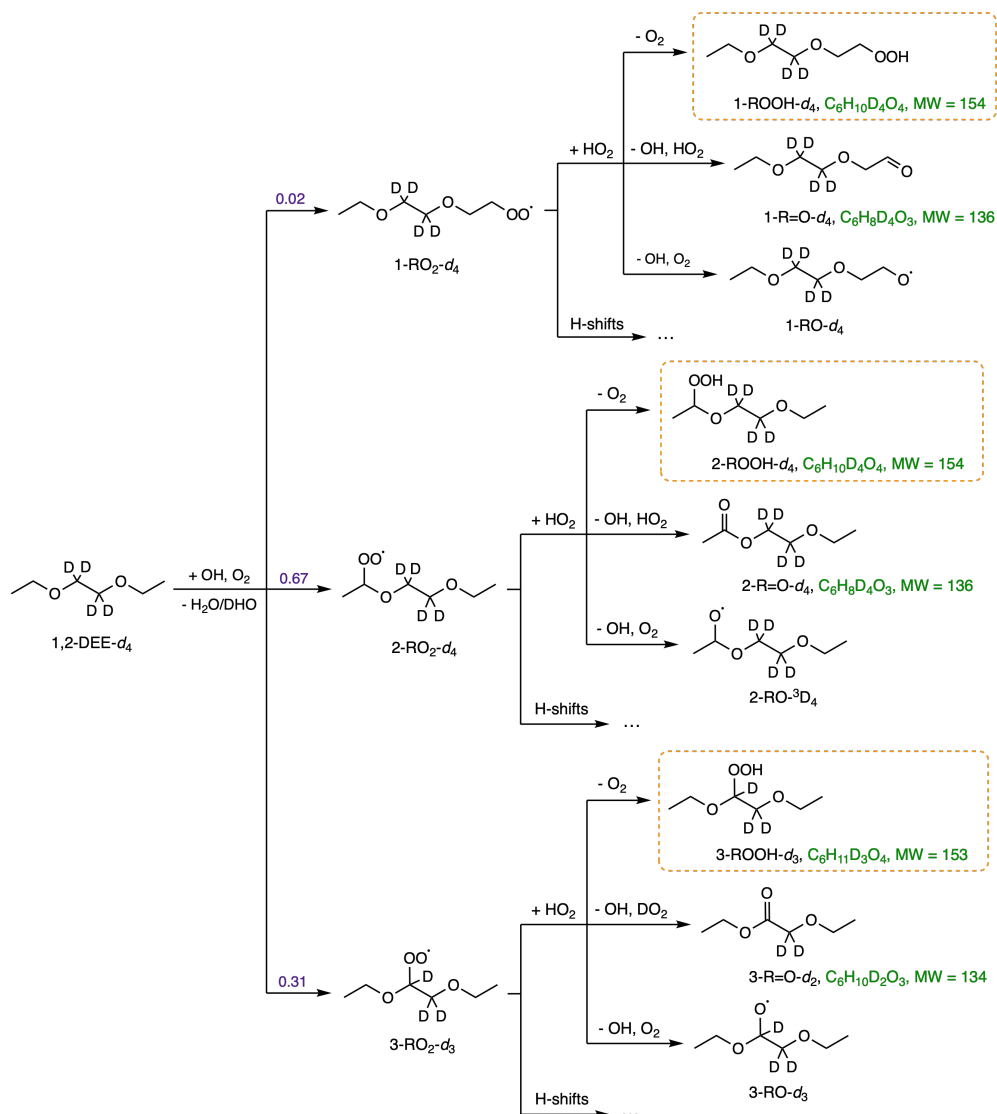
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SUPPLEMENTARY INFORMATION FOR CHAPTER 4

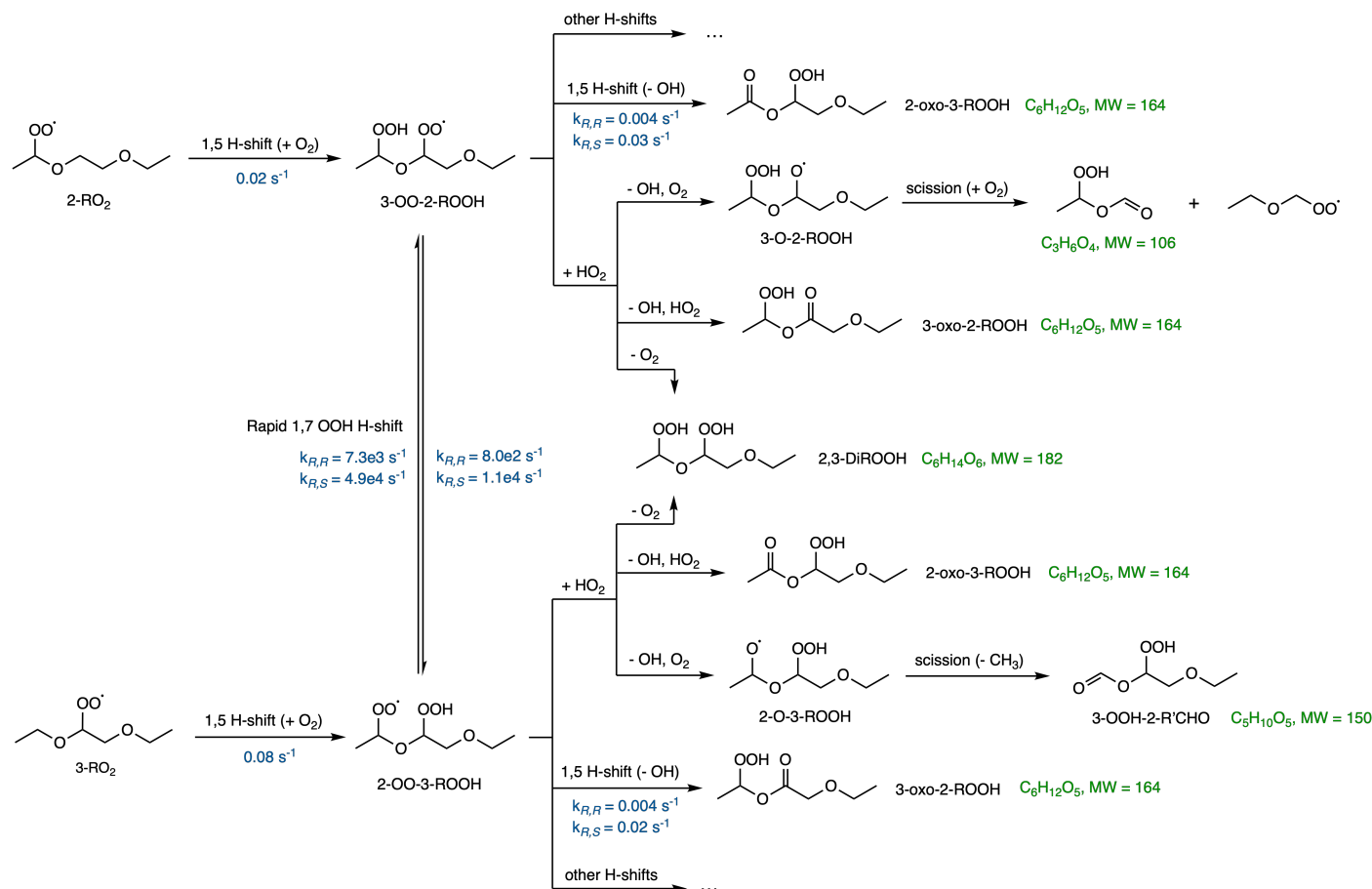
C.1 Additional Oxidation Mechanisms and GC analysis



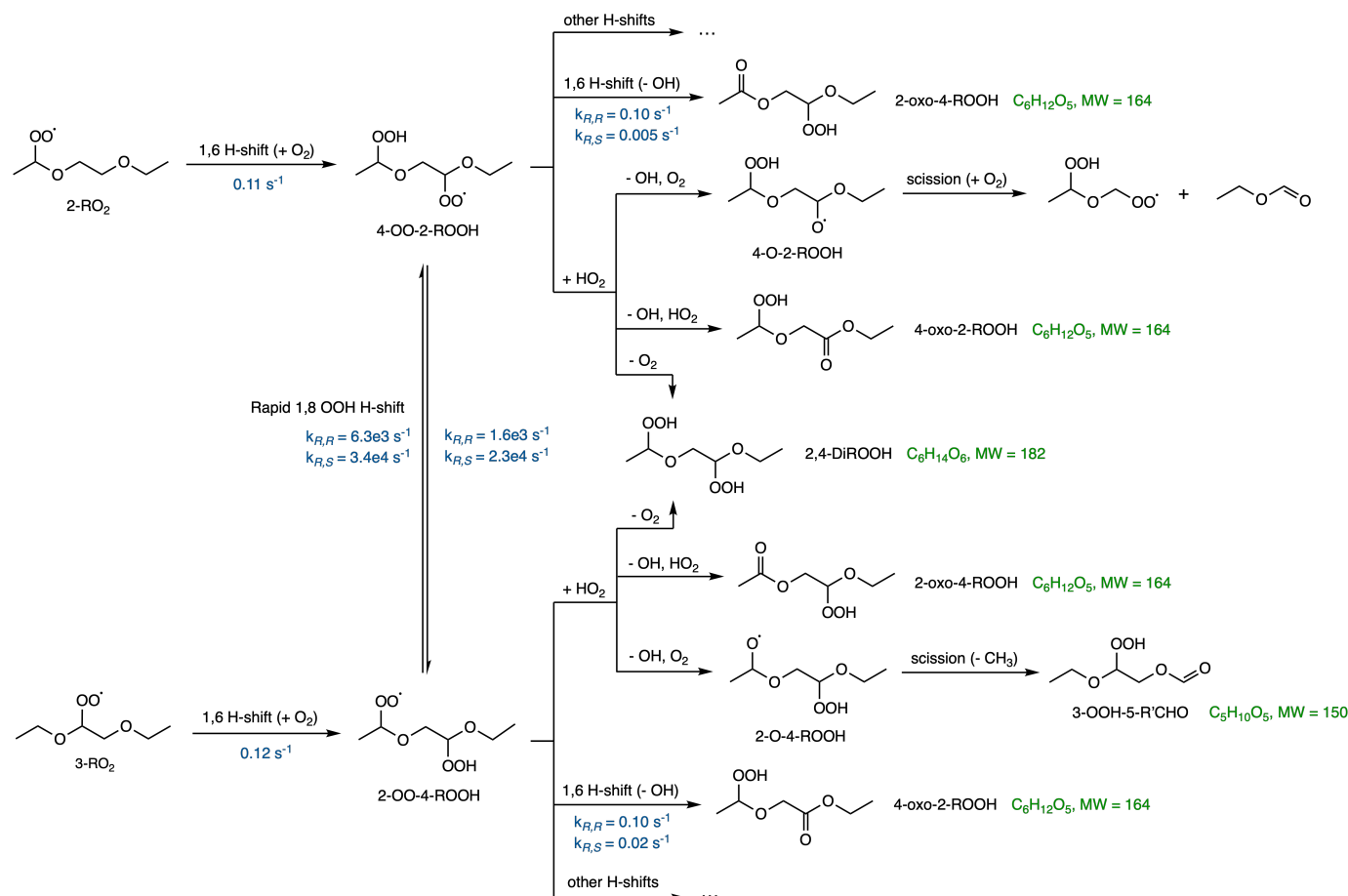
Scheme C.1: Initial step of OH-initiated photo-oxidation of 1,2-DEE. The branching fractions of the initial steps are denoted in purple (derived in Section C.8.1). The subsequent bimolecular reactions of generated RO₂ with HO₂ and respective products are also shown. Further pathways from RO₂ H-shift reactions are shown in Scheme 4.4 in the main text and C.3 to C.4. The molecular masses of major closed-shell products are denoted in green. Products detectable by our instrument are shown in orange boxes.



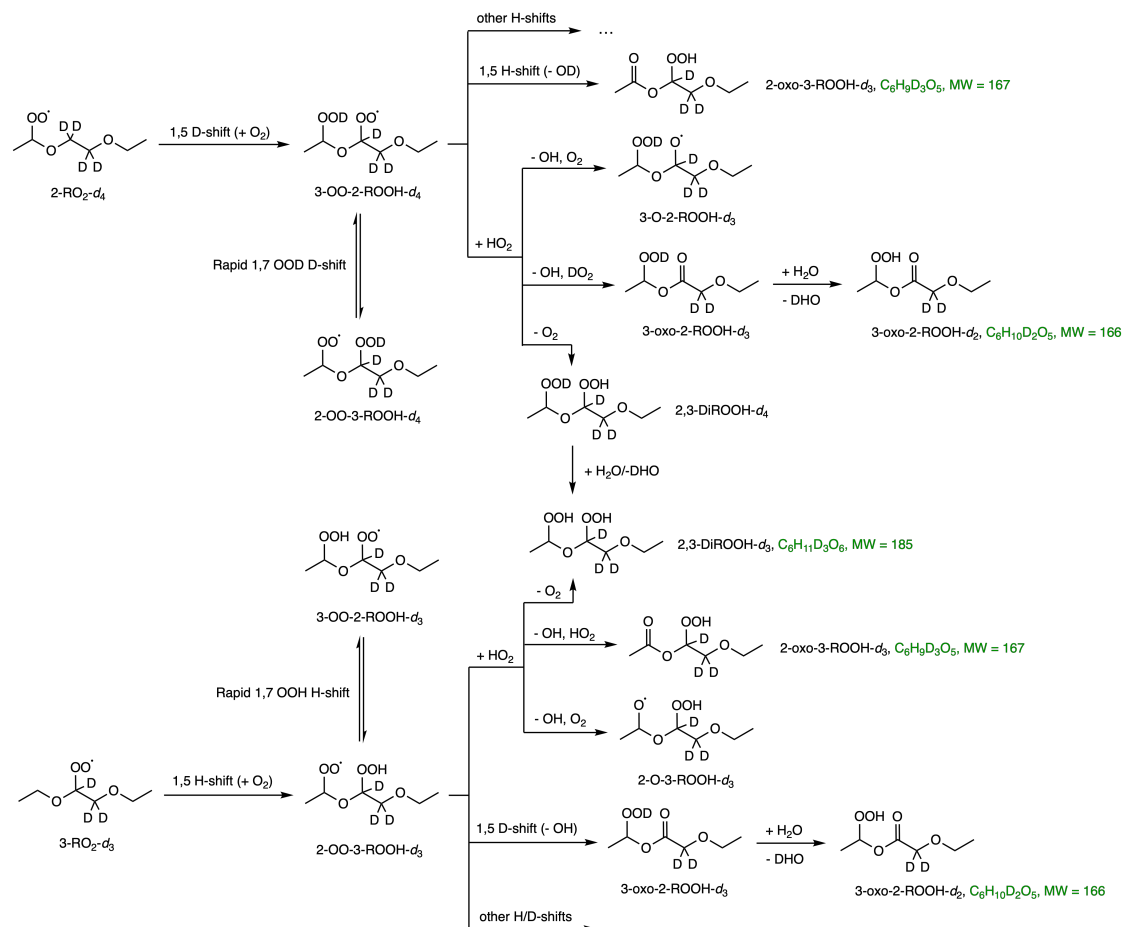
Scheme C.2: Initial step of OH-initiated photo-oxidation of 1,2-DEE (left) and 1,2-DEE- d_4 . The branching fractions of the initial steps are denoted in purple (derived in Section C.8.1). The subsequent bimolecular reactions of generated RO₂ with HO₂ and respective products are also shown. Further pathways from RO₂ H/D-shift reactions are shown in Scheme C.5 to C.7. The molecular masses of major closed-shell products are denoted in green. Products detectable by our instrument are shown in orange boxes.



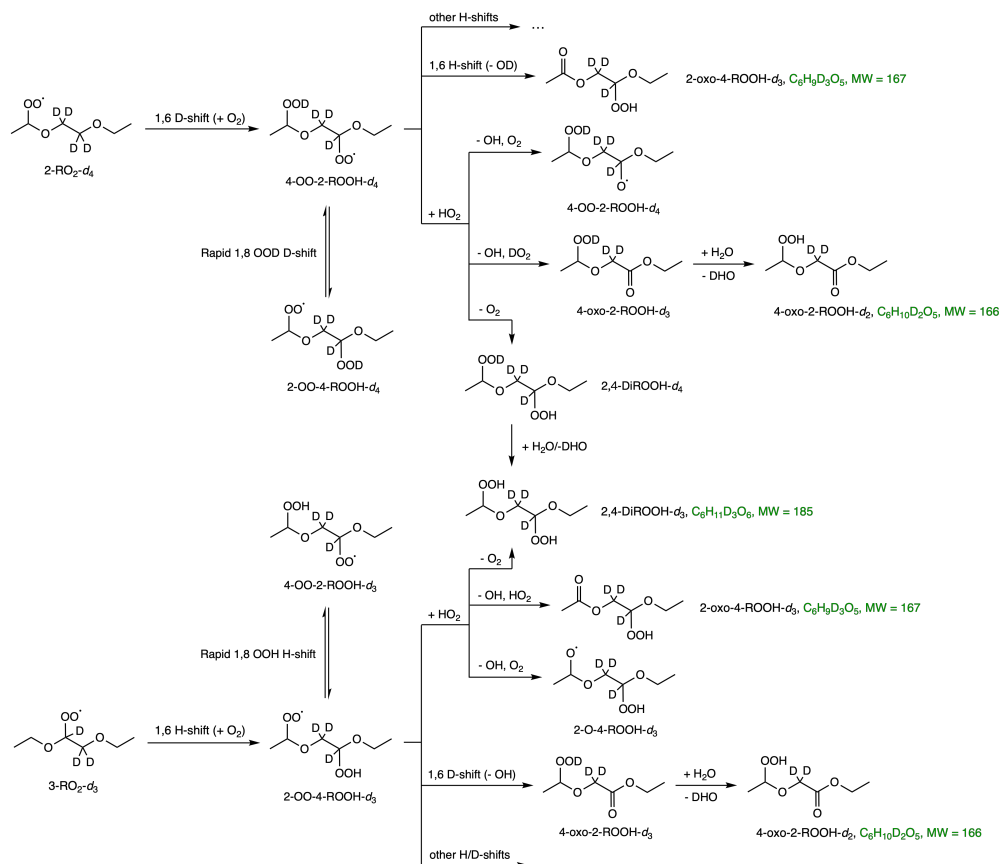
Scheme C.3: Mechanism of 1,2-DEE 2-RO₂ and 3-RO₂ 1,5 H-shift reactions. The H-shift rate coefficients are calculated at 294 K and denoted in blue. Subsequent reactions of generated hydroperoxy RO₂ (2-OO-3-ROOH and 3-OO-2-ROOH), including their bimolecular reaction with HO₂, unimolecular H-shift reactions, and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.



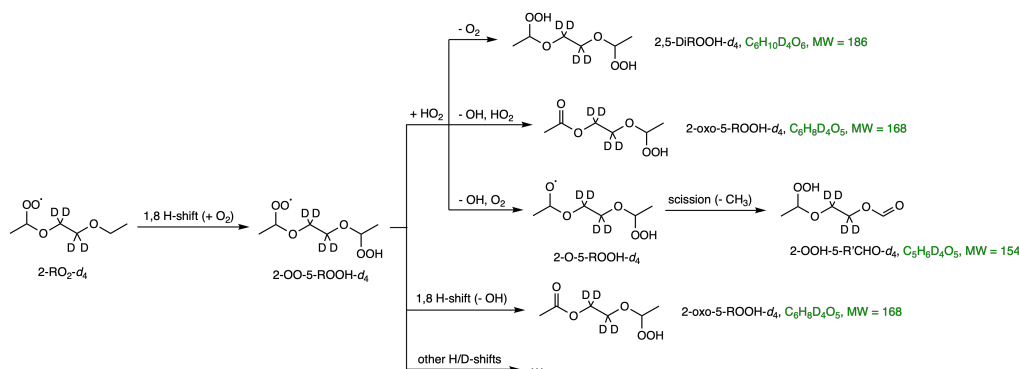
Scheme C.4: Mechanism of 1,2-DEE 2-RO₂ and 3-RO₂ 1,6 H-shift reactions. The H-shift rate coefficients are calculated at 294 K and denoted in blue. Subsequent reactions of generated hydroperoxy RO₂ (2-OO-4-ROOH and 4-OO-2-ROOH), including their bimolecular reaction with HO₂, unimolecular H-shift reactions, and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.



Scheme C.5: Mechanism of 1,2-DEE 2-RO₂-d₄ and 3-RO₂-d₃ 1,5 H/D-shift reactions. Subsequent reactions of generated hydroperoxy RO₂ (deuterated 2-OO-3-ROOH and 3-OO-2-ROOH), including their bimolecular reaction with HO₂, unimolecular H-shift reactions, fast H/D exchange of hydroperoxide deuterium atom ($-\text{OOD} \xrightarrow{\text{H}_2\text{O/-DHO}} -\text{OOH}$), and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.



Scheme C.6: Mechanism of 1,2-DEE 2-RO₂-d₄ and 3-RO₂-d₃ 1,6 H/D-shift reactions. Subsequent reactions of generated hydroperoxy RO₂ (deuterated 2-OO-4-ROOH and 4-OO-2-ROOH), including their bimolecular reaction with HO₂, unimolecular H-shift reactions, fast H/D exchange of hydroperoxide deuterium atom ($-\text{OOD} \xrightarrow{\text{H}_2\text{O}/-\text{DHO}} -\text{OOH}$), and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.



Scheme C.7: Mechanism of 1,2-DEE 2-RO₂-d₄ 1,8 H-shift reactions. Subsequent reactions of generated hydroperoxy RO₂ (2-OO-4-ROOH and 4-OO-2-ROOH), including their bimolecular reaction with HO₂, unimolecular H-shift reactions, and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.

C.1.1 Gas Chromatograms

The following gas chromatograms come from 1,2-DEE oxidation experiment No.12 (Table C.1) and a 1,2-DEE-d₄ oxidation experiment conducted under similar conditions.

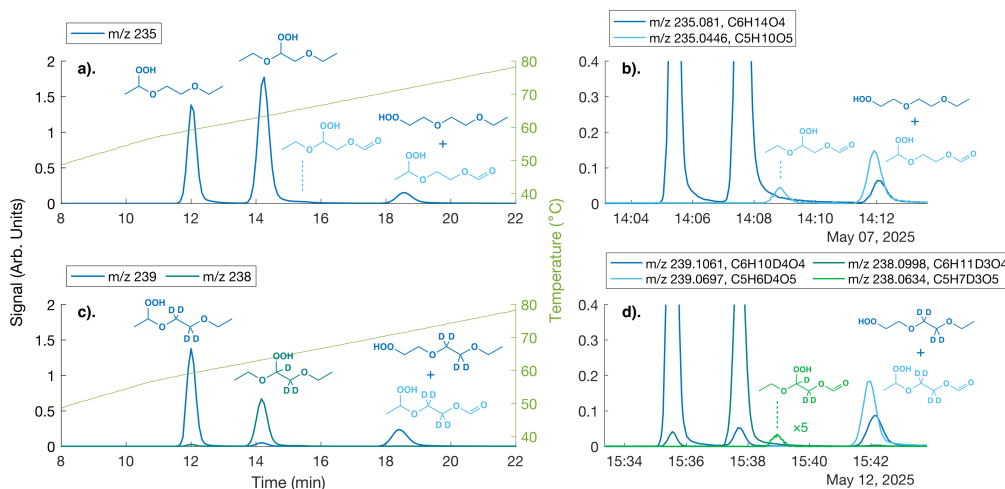


Figure C.1: Gas chromatograms of ROOHs (Scheme C.1 and C.2) and C5 ketohydroperoxides (Scheme 4.4, C.4, C.7). **(a)** GC traces from 1,2-DEE oxidation, **(b)** Zoomed-in view of **(a)** with high-resolution mass spectrometry (HR-MS) data, **(c)** GC traces from 1,2-DEE-d₄ oxidation, **(d)** Zoomed-in view of **(c)** with HR-MS data. Certain signals are scaled up by a factor denoted in the figure. HR-MS analysis are applied to resolve the overlapping GC signals of the ROOHs, 2-OOH-5-R'CHO, and 3-OOH-5-R'CHO (tentatively assigned), and facilitate our quantification of those compounds (Table C.19).

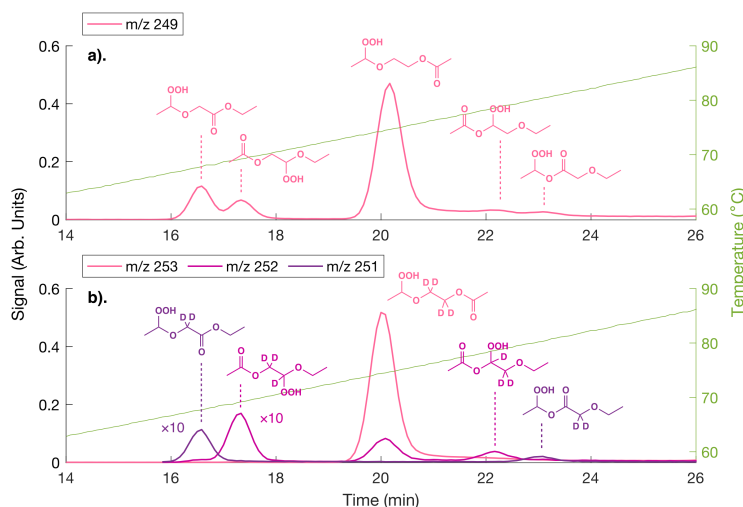


Figure C.2: Gas chromatograms of C6 ketohydroperoxides. **(a)** GC traces from 1,2-DEE oxidation (Scheme 4.4, C.3, C.4), **(b)** GC traces from 1,2-DEE- d_4 oxidation (Scheme C.5, C.6, C.7). Signals for m/z 252 and 251 are scaled up by a factor of 10 as denoted in the figure. The GC peak at m/z 252 eluting at ~20 min, ~2% of the m/z 253 peak, likely corresponds to 2-oxo-5-ROOH formed from the "non-fully deuterated" 1,2-DEE- d_3 due to the 98% isotopic purity of the ethylene glycol- d_4 used in the synthesis (see Section C.2). The assignments of 2-oxo-4-ROOH vs. 2-oxo-3-ROOH (m/z 252 in **(b)**) and 4-oxo-2-ROOH vs. 3-oxo-2-ROOH (m/z 251 in **(b)**) are tentative based on calculated 1,5 and 1,6 H-shift rate coefficients of primary RO_2 (Table C.3), as well as oxidation of authentic standards in Figure C.3. The larger GC peaks are assigned to products from the faster 1,6 H-shifts.

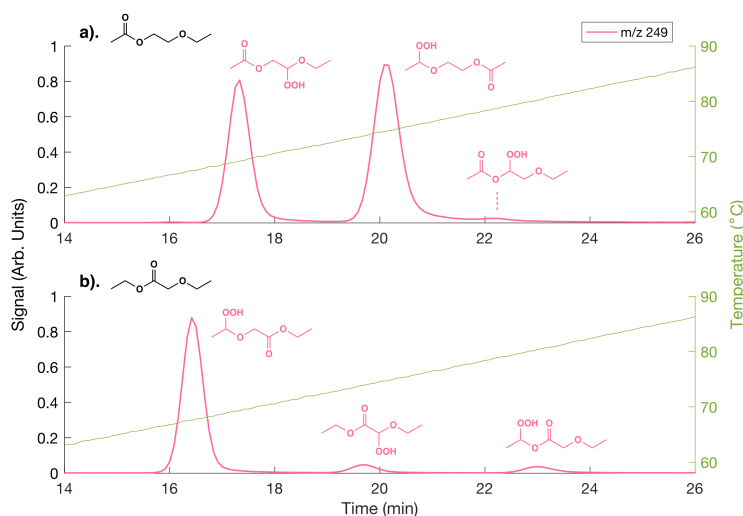


Figure C.3: Gas chromatograms of oxidation of 1,2-DEE 2-R=O and 3-R=O standards at high $[HO_2]$. **(a)** 2-R=O, aka 2-ethoxyethyl acetate (Sigma Aldrich, 98%) **(b)** 3-R=O, aka ethyl ethoxyacetate (TCI, >95%). Peak assignments are made based on structure-activity relationship (SAR) prediction of OH reactions with those compounds^{1,2} and HO_2 reactions with generated RO_2 ,³ and experimental results from 1,2-DEE oxidation.

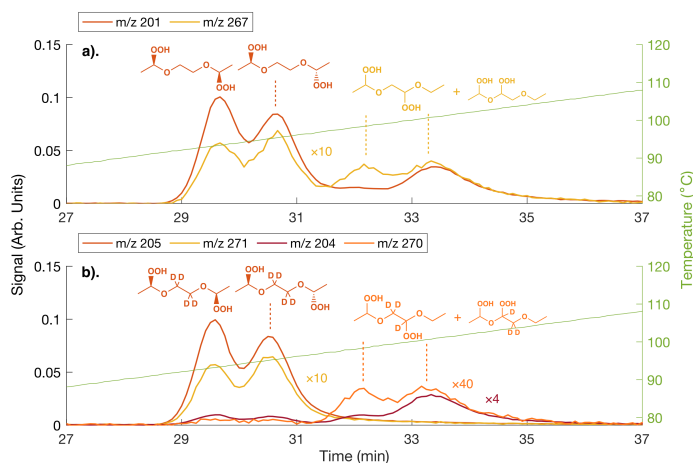


Figure C.4: Gas chromatograms of dihydroperoxides (Scheme 4.4, C.3 to C.7) (a) GC traces from 1,2-DEE oxidation, (b) GC traces from 1,2-DEE- d_4 . Certain signals are scaled up by a factor denoted in the figure. GC signals at m/z = mass neutral + 85 and + 19 of the products are shown. For the four GC peaks detected at m/z 204/270, the two eluting at ~30 min likely correspond to 2,5-DiROOH formed from 1,2-DEE- d_3 as discussed in Figure C.2. Based on calculated 1,5 and 1,6 H-shift rate coefficients of primary RO_2 , the two peaks eluting at ~33 min are attributed primarily to 2,4-DiROOH stereoisomers, with possible minor contributions from 2,3-DiROOH. Assignments of different stereoisomers of 2,5-DiROOH are tentative based on our expectation of the strength of the interaction between the molecule and the column. The (*R,S*) diastereomer likely has stronger intramolecular interactions between the two hydroperoxide groups which weakens the compound's interaction with the column, and thus elute earlier than the (*R,R*) diastereomer.

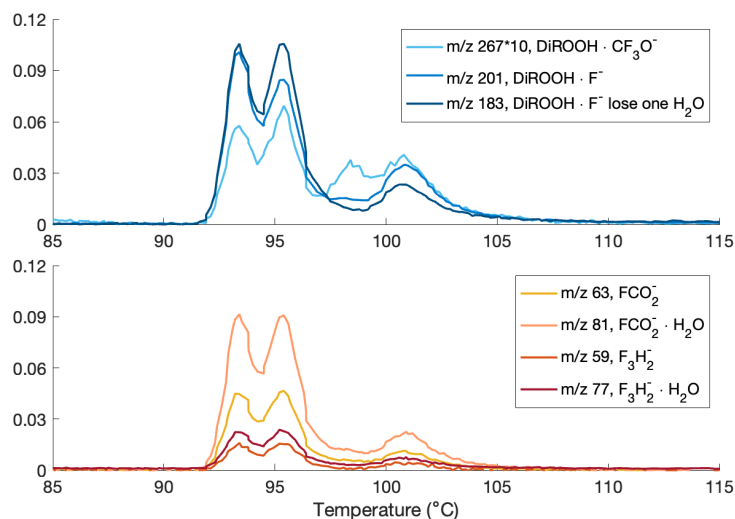
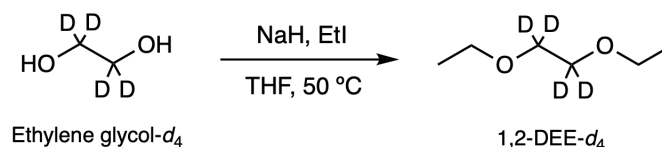


Figure C.5: Gas chromatograms of major product ions of DiROOHs from 1,2-DEE oxidation. The signals of all detected product ions are summed to quantify the overall yields of DiROOHs (Table C.19).

C.2 Synthetic Procedure



Unless otherwise stated, reactions were performed in flame-dried glassware under ambient conditions using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reagents were purchased from commercial sources and used as received. Ethylene glycol (D_4 , 98%) was purchased from Cambridge Isotope Laboratories, Inc., and was stored in a nitrogen filled glovebox after opening. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (250 μm) and visualized by UV fluorescence quenching, potassium permanganate staining, or p-anisaldehyde staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 μm) was used for flash chromatography. Mass spectra were obtained using a Hewlett Packard 5972 GC-MS system with separation on an INNOWAX column (Agilent technologies).

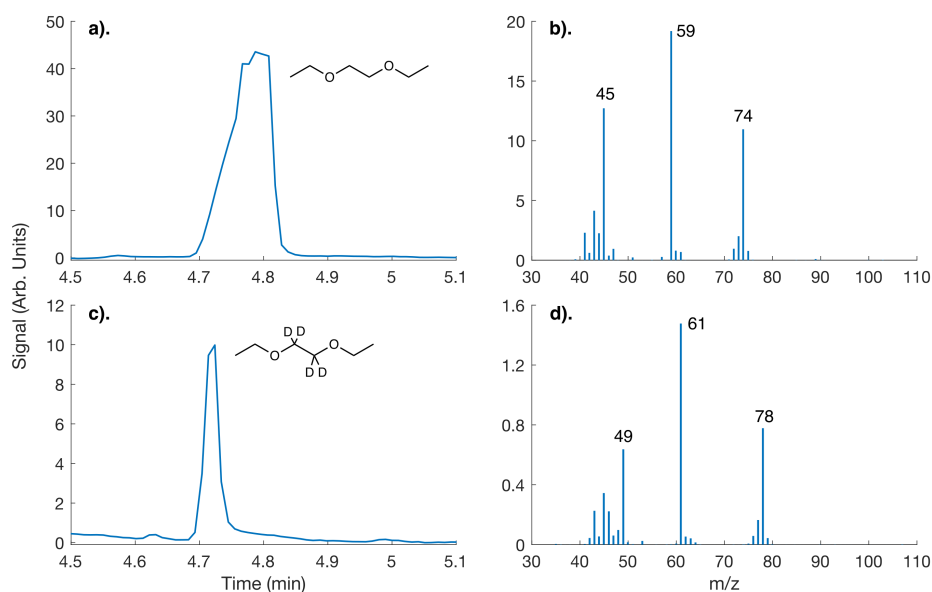


Figure C.6: GC-MS spectra of (a) and (b) 1,2-DEE (authentic standard), (c) and (d) 1,2-DEE- d_4 (synthesized). Both samples are run in dichloromethane (DCM) solution. (a) and (c) present the total ion chromatograms, with comparable retention times for the standard and the synthesized compound. (b) and (d) present the corresponding mass spectra of the GC peak, where the m/z shifts in the major fragment ions confirms successful incorporation of deuterium atoms and the identity of the synthesized compound.

To a flame dried 250 mL three-neck round bottom flask equipped with a reflux condenser was added NaH (818.0 mg, 20.45 mmol, 2.5 equiv) and THF (80 mL, 0.1M). Ethylene glycol- d_4 (EG-D4, 1.0g, 8.18 mmol, 1.0 equiv) was then added dropwise and the reaction mixture was stirred at 23 °C for 30 minutes. Ethyl iodide (EtI, 3.19 g, 20.45 mmol, 2.5 equiv) was then added and the reaction mixture was warmed to 50 °C and stirred at this temperature for 16 h, at which point TLC analysis indicated consumption of EG-D4. Saturated aqueous NH_4Cl solution (50 mL) was slowly added to the reaction mixture, followed by Et_2O (100 mL). The reaction mixture was further diluted with water (100 mL) and the product was extracted with Et_2O (3×100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated to near dryness to afford an ethereal solution containing 1,2-DEE- d_4 as determined by GC/MS analysis (Figure C.6).

C.3 Experimental Conditions

VOCs (1,2-DEE and CH_3OH) are transferred into the chamber through gas-tight 500 cm^3 glass bulbs. The desired mixing ratios were prepared via serial dilution using a vacuum/ N_2 system, with pressure in the bulbs measured by pressure sensors (MKS 1000 and 10 Torr Baratron pressure transducers). Liquid phase reagent (H_2O_2) is added by directly evaporating a known amount of the solution into the chamber.

Table C.1: Experimental conditions. All concentrations are in ppb. All experiments are conducted at ambient temperature of $294 \pm 1\text{K}$.

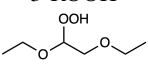
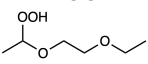
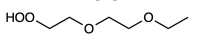
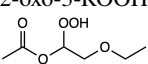
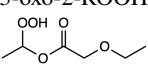
Exp. No.	[1,2-DEE] ₀	[CH ₃ OH] ₀	[H ₂ O ₂] ₀	Bulb type	Bulb #	Oxidation time (min)
1	337	93099	2064	350 nm	8	15
2	313	91054	2060	254 nm	8	1 2
3	429	92956	2110	254 nm	2	8
4	296	91848	2439	350 nm	2	60
5	316	93841	2166	350 nm	8	15 100
6	303	91014	2090	254 nm	1	8 12
7	297	93272	2481	350 nm	1	120 150
8	339	93506	2008	254 nm	4	2 4

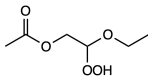
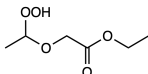
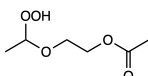
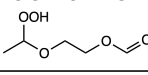
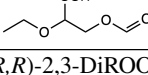
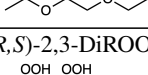
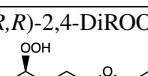
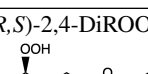
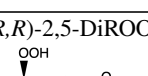
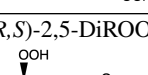
Exp. No.	[1,2-DEE] ₀	[CH ₃ OH] ₀	[H ₂ O ₂] ₀	Bulb type	Bulb #	Oxidation time (min)
9	301	91593	2044	350 nm	4	35 65
10	312	90881	2017	350 nm	2	60 80
11	306	92336	1994	254 nm	2	4 8
12	302	92682	2010	254 nm	1	8 16
13	278	89462	1926	254 nm	8	1 2

C.4 CIMS Calibration

The method of CIMS calibration in this work is the same as that documented in Section A.3. The following table list the CIMS sensitivities of 1,2-DEE oxidation products calibrated based on their calculated ion-molecule collision rates and the measured sensitivity of ethylene glycol (Sigma-Aldrich, 99.8%).

Table C.2: Calculated dipole moments (μ_D), polarizabilities (α), CF₃O[−]-molecule collision rate coefficients (k_c), and CIMS sensitivities for molecules of interests in our system. ^a Normalized relative to that of ethylene glycol. ^b measured sensitivity data and uncertainties

Molecule	m/z	μ_D (D)	α (Å ³)	k_c (10 ^{−9} cm ³ molec ^{−1} s ^{−1})	Relative k_c ^a	Sensitivity (10 ^{−4} cts/pptv)
Ethylene glycol 	147	2.08	5.11	1.90	1	2.50 (± 0.20) ^b
3-ROOH 	235	2.43	14.00	2.02	1.06	2.65 (± 0.21)
2-ROOH 	235	3.32	13.79	2.49	1.31	3.27 (± 0.26)
1-ROOH 	235	3.44	13.82	2.55	1.34	3.35 (± 0.27)
2-oxo-3-ROOH 	249	3.65	13.93	2.61	1.38	3.44 (± 0.28)
3-oxo-2-ROOH 	249	3.34	13.89	2.46	1.30	3.24 (± 0.26)

Molecule	m/z	μ_D (D)	α (Å ³)	k_c (10 ⁻⁹ cm ³ molec ⁻¹ s ⁻¹)	Relative k_c	Sensitivity (10 ⁻⁴ cts/ppbv)
2-oxo-4-ROOH 	249	3.14	13.79	2.35	1.24	3.10 (± 0.25)
4-oxo-2-ROOH 	249	4.01	13.81	2.81	1.48	3.69 (± 0.30)
2-oxo-5-ROOH 	249	3.51	13.64	2.54	1.34	3.34 (± 0.27)
2-OOH-5-R'CHO 	235	3.58	11.81	2.57	1.35	3.38 (± 0.27)
3-OOH-5-R'CHO 	235	2.79	11.94	2.16	1.13	2.84 (± 0.23)
(R,R)-2,3-DiROOH 	267	2.08	15.21	1.82	0.96	2.39 (± 0.19)
(R,S)-2,3-DiROOH 	267	2.78	15.07	2.18	1.15	2.87 (± 0.23)
(R,R)-2,4-DiROOH 	267	2.54	15.05	2.05	1.08	2.70 (± 0.22)
(R,S)-2,4-DiROOH 	267	2.46	15.08	2.22	1.17	2.92 (± 0.23)
(R,R)-2,5-DiROOH 	267	3.77	14.95	2.64	1.39	3.47 (± 0.28)
(R,S)-2,5-DiROOH 	267	3.56	14.88	2.57	1.35	3.38 (± 0.27)

C.5 Computational Results

C.5.1 1,2-DEE RO₂ H-shift Rate Coefficients

The RO₂ H/D-shift rate coefficients $k(T)$ were calculated with a Multi-Conformer Transition State Theory (MC-TST) approach,^{4,5} using Equation C.1. Calculation results for first- and second-generation peroxy radical products at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory are shown in Table C.3 and Table C.4 respectively.

$$k_{MC}(T) = \kappa \frac{k_B T}{h} \frac{\sum_i^{\text{TS}} \exp\left(\frac{-\Delta E_i}{k_B T}\right) Q_{\text{TS},i}}{\sum_j^{\text{R}} \exp\left(\frac{-\Delta E_j}{k_B T}\right) Q_{\text{R},j}} \exp\left(\frac{-\Delta^\ddagger E_0}{k_B T}\right) \quad (\text{C.1})$$

Results calculated with lowest-conformer transition state theory (Equation C.2) are also shown for comparison.

$$k_{LC}(T) = \kappa \frac{k_B T}{h} \frac{Q_{\text{TS},0}}{Q_{\text{R},0}} \exp\left(\frac{-\Delta^\ddagger E_0}{k_B T}\right) \quad (\text{C.2})$$

where $Q_{\text{TS},0}$ and $Q_{\text{R},0}$ are the lowest-conformer partition function of the transition state and reactant respectively.

The minor second-generation peroxy radical products 2-OO-3-ROOH and 3-OO-2-ROOH are connected by an H-scrambling reaction pathway, an H-shift where the abstraction site is a hydroperoxyl group. The 2-OO-4-ROOH and 4-OO-2-ROOH isomers are connected in the same manner, via another H-scrambling pathway. Previous work,⁶ suggests that H-scrambling rate coefficients calculated based on F12 energetics may be unreliable. For this reason, we report here rate coefficients calculated for these reactions at the ω B97X-D/aug-cc-pVTZ level of theory, in Table C.5. The rate coefficients calculated for H-scrambling reactions are much larger than those of competing H-shifts, so that we assume an equilibrium is established between the isomers connected by these pathways as soon as either of them is formed from O₂-addition. This means that the reaction pathways directly available to one of the connected RO₂ isomers are readily available to the other, and vice-versa. Thus, the rate coefficients for these cases (shown in Table C.4) were calculated assuming that the reactant is a merged-well system, where the conformers of the higher-energy RO₂ isomer are thermally accessible to the lower-energy isomer. In other words, the sum in the denominator of Equation C.1 is over all conformers of both RO₂, and the reaction energy barrier $\Delta^\ddagger E_0$ is the zero-point corrected energy difference between

the lowest-conformer of the TS and the lowest-conformer of the lowest-energy RO₂ reactant isomer.

Table C.3: Reaction energy barriers ($\Delta^\ddagger E_0$) calculated as the zero-point corrected energy difference between the lowest-conformer of the TS and reactant, multi- and lowest-conformer TST rate coefficients (k_{MC} and k_{LC}), multi- and lowest-conformer ratio of partition functions ($Q_{TS/R,MC}$ and $Q_{TS/R,LC}$), and Eckart tunneling factor (κ), calculated at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory and 298.15 K, for first-generation RO₂ H/D-shift reactions. α -OR and β -OR notation indicate the H-shift abstraction site.

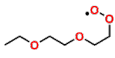
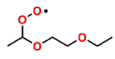
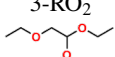
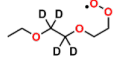
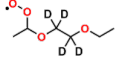
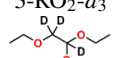
T = 298.15 K; ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ							
Reactant	Reaction	$\Delta^\ddagger E_0$ [kcal mol ⁻¹]	k_{MC} [s ⁻¹]	$Q_{TS/R}$	k_{LC} [s ⁻¹]	$Q_{TS/R,LC}$	κ
 1-RO ₂	1,6 H-shift	21.68	2.36×10^{-3}	0.0253	7.11×10^{-3}	0.0762	116.2
	1,7 H-shift	19.27	2.53×10^{-2}	0.0095	7.77×10^{-2}	0.0293	56.4
	1,9 H-shift	18.55	1.39×10^{-2}	0.0013	8.53×10^{-2}	0.0080	67.9
 2-RO ₂	1,5 H-shift	20.50	3.18×10^{-2}	0.0928	5.99×10^{-2}	0.1746	58.5
	1,6 H-shift	18.76	1.49×10^{-1}	0.0219	5.36×10^{-1}	0.0786	62.3
	1,8 H-shift	16.85	7.03×10^{-1}	0.0052	2.99	0.0220	49.1
 3-RO ₂	1,5 H-shift	19.87	1.08×10^{-1}	0.1102	3.60×10^{-1}	0.3687	57.3
	1,6 H-shift (α -OR)	18.55	1.52×10^{-1}	0.0126	7.59×10^{-1}	0.0631	76.3
	1,6 H-shift (β -OR)	25.42	6.84×10^{-6}	0.0550	1.37×10^{-5}	0.1102	85.9
	1,7 H-shift	24.97	2.06×10^{-6}	0.0143	6.12×10^{-6}	0.0426	46.7
 1-RO ₂ -d ₄	1,6 D-shift	22.73	4.76×10^{-5}	0.0246	1.40×10^{-4}	0.0723	14.3
	1,7 D-shift	20.30	7.03×10^{-4}	0.0090	2.12×10^{-3}	0.0269	9.7
	1,9 H-shift	18.46	1.58×10^{-2}	0.0013	9.70×10^{-2}	0.0078	67.9
 2-RO ₂ -d ₄	1,5 D-shift	21.61	6.77×10^{-4}	0.0873	1.31×10^{-3}	0.1693	8.6
	1,6 D-shift	19.84	3.73×10^{-3}	0.0205	1.36×10^{-2}	0.0749	10.2
	1,8 H-shift	16.82	7.31×10^{-1}	0.0051	3.15	0.0219	49.0
 3-RO ₂ -d ₃	1,5 H-shift	19.83	1.38×10^{-1}	0.1326	3.80×10^{-1}	0.3642	57.3
	1,6 H-shift (α -OR)	18.47	2.07×10^{-1}	0.0152	8.45×10^{-1}	0.0620	76.2
	1,6 H-shift (β -OR)	25.38	8.82×10^{-6}	0.0663	1.45×10^{-5}	0.1091	86.0
	1,7 H-shift	24.93	2.75×10^{-6}	0.0177	6.56×10^{-6}	0.0422	46.7

Table C.4: Reaction energy barriers ($\Delta^\ddagger E_0$) calculated as the zero-point corrected energy difference between the lowest-conformer of the TS and reactant, multi- and lowest-conformer TST rate coefficients (k_{MC} and k_{LC}), multi- and lowest-conformer ratio of partition functions ($Q_{TS/R,MC}$ and $Q_{TS/R,LC}$), and Eckart tunneling factor (κ), calculated at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory and 298.15 K, for second-generation RO₂ H-shift reactions assuming established equilibria between 3-OO-2-ROOH and 2-OO-3-ROOH and between 4-OO-2-ROOH and 2-OO-4-ROOH via H-scrambling reactions (see Table C.5).

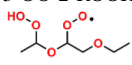
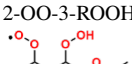
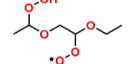
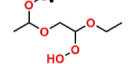
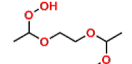
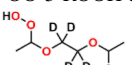
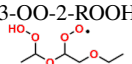
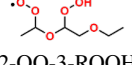
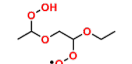
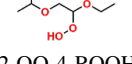
T = 298.15 K; ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ							
Reactant	Reaction	$\Delta^\ddagger E_0$ [kcal mol ⁻¹]	k_{MC} [s ⁻¹]	$Q_{TS/R}$	k_{LC} [s ⁻¹]	$Q_{TS/R,LC}$	κ
3-OO-2-ROOH 	(R,R) 1,5 H-shift (α -OOH)	23.90	5.62×10^{-3}	2.2108	1.77×10^{-3}	0.6982	135.5
	(R,R) 1,6 H-shift (ζ -OOH)	20.55	5.45×10^{-2}	0.1590	2.26×10^{-2}	0.0660	63.7
	(R,S) 1,5 H-shift (α -OOH)	22.54	3.65×10^{-2}	0.6284	5.70×10^{-3}	0.0982	312.1
	(R,S) 1,6 H-shift (ζ -OOH)	19.88	1.05×10^{-1}	0.1004	1.11×10^{-1}	0.1061	63.1
2-OO-3-ROOH 	(R,R) 1,5 H-shift (α -OOH)	22.84	5.95×10^{-3}	0.3470	3.86×10^{-3}	0.2254	151.2
	(R,R) 1,6 H-shift (β -OOH)	21.23	4.39×10^{-2}	0.2592	7.20×10^{-2}	0.4249	99.6
	(R,R) 1,8 H-shift (δ -OOH)	18.46	5.28×10^{-1}	0.0736	6.50×10^{-1}	0.0905	39.3
	(R,S) 1,5 H-shift (α -OOH)	23.25	2.23×10^{-2}	1.5233	9.50×10^{-3}	0.6478	260.9
	(R,S) 1,6 H-shift (β -OOH)	22.90	5.55×10^{-3}	0.5635	3.97×10^{-3}	0.4032	97.1
	(R,S) 1,8 H-shift (δ -OOH)	19.13	1.11×10^{-1}	0.0480	2.02×10^{-1}	0.0873	39.3
4-OO-2-ROOH 	(R,R) 1,5 H-shift (ζ -OOH)	20.02	8.74×10^{-2}	0.0848	2.42×10^{-1}	0.2350	78.9
	(R,R) 1,6 H-shift (α -OOH)	21.71	1.34×10^{-1}	0.2509	3.70×10^{-1}	0.6921	702.7
	(R,S) 1,5 H-shift (ζ -OOH)	19.71	6.66×10^{-2}	0.0505	2.03×10^{-1}	0.1538	59.7
	(R,S) 1,6 H-shift (α -OOH)	22.50	6.45×10^{-3}	0.0935	2.38×10^{-2}	0.3446	343.2
2-OO-4-ROOH 	(R,R) 1,5 H-shift (β -OOH)	22.09	8.73×10^{-3}	0.4850	4.25×10^{-3}	0.2365	44.8
	(R,R) 1,6 H-shift (α -OOH)	21.31	1.29×10^{-1}	0.1383	6.17×10^{-1}	0.6619	624.7
	(R,R) 1,8 H-shift (γ -OOH)	20.61	1.95×10^{-2}	0.0736	4.85×10^{-2}	0.1816	54.9
	(R,S) 1,5 H-shift (β -OOH)	21.62	1.42×10^{-2}	0.1822	3.52×10^{-2}	0.4502	88.6
	(R,S) 1,6 H-shift (α -OOH)	22.25	1.98×10^{-2}	0.1662	3.77×10^{-2}	0.3156	389.5
	(R,S) 1,8 H-shift (γ -OOH)	19.95	2.35×10^{-2}	0.0285	1.04×10^{-1}	0.1266	56.0
2-OO-5-ROOH 	(R,R) 1,5 H-shift (δ -OOH)	21.03	7.88×10^{-3}	0.0997	1.01×10^{-2}	0.1273	33.0
	(R,R) 1,6 H-shift (γ -OOH)	20.30	1.55×10^{-2}	0.0553	3.63×10^{-2}	0.1296	34.3
	(R,R) 1,8 H-shift (α -OOH)	20.09	5.49×10^{-3}	0.0171	2.97×10^{-2}	0.0922	27.5
	(R,S) 1,5 H-shift (δ -OOH)	20.57	1.47×10^{-2}	0.0519	2.86×10^{-2}	0.1006	54.4
	(R,S) 1,6 H-shift (γ -OOH)	19.49	6.55×10^{-2}	0.0279	1.52×10^{-1}	0.0648	72.5
	(R,S) 1,8 H-shift (α -OOH)	20.80	1.17×10^{-3}	0.0118	3.81×10^{-3}	0.0383	28.3
2-OO-5-ROOH- <i>d</i> ₄ 	(R,R) 1,5 D-shift (δ -OOH)	22.16	2.29×10^{-4}	0.0988	2.86×10^{-4}	0.1233	6.6
	(R,R) 1,6 D-shift (γ -OOH)	21.40	5.39×10^{-4}	0.0541	1.22×10^{-3}	0.1221	7.8
	(R,R) 1,8 H-shift (α -OOH)	20.09	5.80×10^{-3}	0.0179	2.99×10^{-2}	0.0920	27.5
	(R,S) 1,5 D-shift (δ -OOH)	21.67	2.90×10^{-4}	0.0510	5.44×10^{-4}	0.0957	7.0
	(R,S) 1,6 D-shift (γ -OOH)	20.57	1.36×10^{-3}	0.0261	3.14×10^{-3}	0.0603	10.1
	(R,S) 1,8 H-shift (α -OOH)	20.78	1.20×10^{-3}	0.0116	3.96×10^{-3}	0.0382	28.2

Table C.5: Reaction energy barriers ($\Delta^\ddagger E_0$) calculated as the zero-point corrected energy difference between the lowest-conformer of the TS and reactant, multi- and lowest-conformer TST rate coefficients (k_{MC} and k_{LC}), multi- and lowest-conformer ratio of partition functions ($Q_{TS/R,MC}$ and $Q_{TS/R,LC}$), and Eckart tunneling factor (κ), calculated at the ω B97X-D/aug-cc-pVTZ level of theory and 298.15 K, for second-generation RO₂ H-scrambling (OOH H-shift) reactions.

T = 298.15 K; ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ							
Reactant	Reaction	$\Delta^\ddagger E_0$ [kcal mol ⁻¹]	k_{MC} [s ⁻¹]	$Q_{TS/R}$	k_{LC} [s ⁻¹]	$Q_{TS/R,LC}$	κ
 3-OO-2-ROOH	(R,R) 1,7 H-shift (-OOH)	15.41	9.95×10^2	0.2845	6.90×10^2	0.1972	111.1
	(R,S) 1,7 H-shift (-OOH)	14.30	1.30×10^4	0.4764	5.37×10^3	0.1964	133.7
 2-OO-3-ROOH	(R,R) 1,7 H-shift (-OOH)	13.63	8.49×10^3	0.1209	3.09×10^4	0.4400	111.1
	(R,S) 1,7 H-shift (-OOH)	12.02	5.56×10^4	0.0435	9.37×10^4	0.0734	133.7
 4-OO-2-ROOH	(R,R) 1,8 H-shift (-OOH)	14.52	1.95×10^3	0.0717	7.58×10^3	0.2781	193.7
	(R,S) 1,8 H-shift (-OOH)	12.95	2.63×10^4	0.0878	4.55×10^4	0.1517	150.4
 2-OO-4-ROOH	(R,R) 1,8 H-shift (-OOH)	13.48	7.19×10^3	0.0453	5.27×10^4	0.3323	193.7
	(R,S) 1,8 H-shift (-OOH)	11.28	3.73×10^4	0.0074	1.17×10^5	0.0233	150.4

C.5.2 Temperature Dependence of RO₂ H-shift Rate Coefficients

The temperature dependence of H/D-shift rate coefficients was obtained from calculated MC-TST results over the 250-350 K temperature range, fitted with a modified Arrhenius expression:

$$k(T) = A \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot \exp\left(\frac{-B}{RT^3}\right) \quad (\text{C.3})$$

Fitted modified Arrhenius expression parameters A , E_a , and B are shown in Tables C.6 and C.7.

Table C.6: Rate coefficients calculated with MC-TST at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory, at 294 and 298.15 K, for first-generation RO₂ H/D-shift reactions. Modified Arrhenius expression parameters A , E_a , and B (Equation C.3) fitted with calculated rate coefficients over the 250-350 K temperature range. α -OR and β -OR notation indicate the H-shift abstraction site.

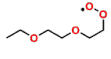
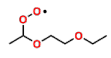
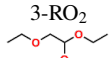
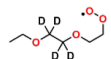
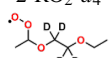
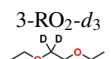
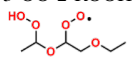
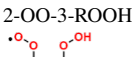
Reactant	Reaction	k (294.00 K) [s ⁻¹]	k (298.15 K) [s ⁻¹]	A [s ⁻¹]	E_a [kcal mol ⁻¹]	B [kcal K ² mol ⁻¹]
 1-RO ₂	1,6 H-shift	1.67×10 ⁻³	2.36×10 ⁻³	1.69×10 ¹⁰	19.13	-1.42×10 ⁵
	1,7 H-shift	1.85×10 ⁻²	2.53×10 ⁻²	6.47×10 ⁹	16.84	-1.14×10 ⁵
	1,9 H-shift	1.05×10 ⁻²	1.39×10 ⁻²	1.01×10 ⁹	16.26	-1.28×10 ⁵
 2-RO ₂	1,5 H-shift	2.27×10 ⁻²	3.18×10 ⁻²	4.06×10 ¹¹	19.76	-1.68×10 ⁵
	1,6 H-shift	1.11×10 ⁻¹	1.49×10 ⁻¹	2.16×10 ¹⁰	16.66	-1.28×10 ⁵
	1,8 H-shift	5.50×10 ⁻¹	7.03×10 ⁻¹	3.12×10 ⁹	14.56	-1.24×10 ⁵
 3-RO ₂	1,5 H-shift	7.82×10 ⁻²	1.08×10 ⁻¹	2.42×10 ¹¹	18.54	-1.50×10 ⁵
	1,6 H-shift (α -OR)	1.15×10 ⁻¹	1.52×10 ⁻¹	1.75×10 ¹⁰	16.78	-1.50×10 ⁵
	1,6 H-shift (β -OR)	4.53×10 ⁻⁶	6.84×10 ⁻⁶	6.00×10 ¹⁰	23.19	-1.29×10 ⁵
	1,7 H-shift	1.30×10 ⁻⁶	2.06×10 ⁻⁶	7.79×10 ⁹	22.25	-8.89×10 ⁴
 1-RO ₂ -d ₄	1,6 D-shift	3.10×10 ⁻⁵	4.76×10 ⁻⁵	9.19×10 ¹⁰	22.30	-1.28×10 ⁵
	1,7 D-shift	4.78×10 ⁻⁴	7.03×10 ⁻⁴	1.44×10 ¹⁰	19.07	-8.05×10 ⁴
	1,9 H-shift	1.19×10 ⁻²	1.58×10 ⁻²	8.36×10 ⁸	15.96	-1.19×10 ⁵
 2-RO ₂ -d ₄	1,5 D-shift	4.43×10 ⁻⁴	6.77×10 ⁻⁴	3.53×10 ¹¹	21.17	-9.70×10 ⁴
	1,6 D-shift	2.57×10 ⁻³	3.73×10 ⁻³	4.05×10 ¹⁰	18.82	-9.23×10 ⁴
	1,8 H-shift	5.37×10 ⁻¹	7.31×10 ⁻¹	4.07×10 ⁹	14.81	-1.34×10 ⁵
 3-RO ₂ -d ₃	1,5 H-shift	1.00×10 ⁻¹	1.38×10 ⁻¹	4.19×10 ¹¹	18.73	-1.51×10 ⁵
	1,6 H-shift (α -OR)	1.56×10 ⁻¹	2.07×10 ⁻¹	2.73×10 ¹⁰	16.84	-1.48×10 ⁵
	1,6 H-shift (β -OR)	5.58×10 ⁻⁶	8.82×10 ⁻⁶	4.54×10 ¹⁰	22.54	-9.82×10 ⁴
	1,7 H-shift	1.73×10 ⁻⁶	2.75×10 ⁻⁶	4.72×10 ¹⁰	23.66	-1.35×10 ⁵

Table C.7: Rate coefficients calculated with MC-TST at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory, at 294 and 298.15 K, for second-generation RO₂ H-shift reactions. Modified Arrhenius expression parameters A , E_a , and B (Equation C.3) fitted with calculated rate coefficients over the 250-350 K temperature range.

Reactant	Reaction	k (294.00 K) [s ⁻¹]	k (298.15 K) [s ⁻¹]	A [s ⁻¹]	E_a [kcal mol ⁻¹]	B [kcal K ² mol ⁻¹]
 3-OO-2-ROOH	(<i>R,R</i>) 1,5 H-shift (α -OOH)	3.90×10 ⁻³	5.62×10 ⁻³	1.06×10 ¹³	23.49	-2.36×10 ⁵
	(<i>R,R</i>) 1,6 H-shift (ζ -OOH)	3.86×10 ⁻²	5.45×10 ⁻²	3.53×10 ¹¹	18.99	-1.34×10 ⁵
	(<i>R,S</i>) 1,5 H-shift (α -OOH)	2.68×10 ⁻²	3.65×10 ⁻²	4.66×10 ¹²	22.43	-2.83×10 ⁵
	(<i>R,S</i>) 1,6 H-shift (ζ -OOH)	7.69×10 ⁻²	1.05×10 ⁻¹	2.46×10 ¹⁰	16.61	-9.79×10 ⁴
 2-OO-3-ROOH	(<i>R,R</i>) 1,5 H-shift (α -OOH)	4.18×10 ⁻³	5.95×10 ⁻³	6.61×10 ¹²	23.28	-2.45×10 ⁵
	(<i>R,R</i>) 1,6 H-shift (β -OOH)	3.12×10 ⁻²	4.39×10 ⁻²	1.53×10 ¹¹	18.46	-1.19×10 ⁵
	(<i>R,R</i>) 1,8 H-shift (δ -OOH)	3.87×10 ⁻¹	5.28×10 ⁻¹	6.25×10 ¹⁰	16.11	-8.95×10 ⁴
	(<i>R,S</i>) 1,5 H-shift (α -OOH)	1.62×10 ⁻²	2.23×10 ⁻²	8.73×10 ¹²	23.14	-2.87×10 ⁵
	(<i>R,S</i>) 1,6 H-shift (β -OOH)	3.80×10 ⁻³	5.55×10 ⁻³	5.71×10 ¹¹	20.71	-1.42×10 ⁵
	(<i>R,S</i>) 1,8 H-shift (δ -OOH)	8.12×10 ⁻²	1.11×10 ⁻¹	1.53×10 ¹⁰	16.16	-8.52×10 ⁴

Reactant	Reaction	k (294.00 K) [s ⁻¹]	k (298.15 K) [s ⁻¹]	A [s ⁻¹]	E_a [kcal mol ⁻¹]	B [kcal K ² mol ⁻¹]
4-OO-2-ROOH 	(<i>R,R</i>) 1,5 H-shift (ζ -OOH)	6.39×10^{-2}	8.74×10^{-2}	6.82×10^{10}	17.69	-1.30×10^5
	(<i>R,R</i>) 1,6 H-shift (α -OOH)	1.04×10^{-1}	1.34×10^{-1}	9.07×10^{10}	18.84	-2.40×10^5
	(<i>R,S</i>) 1,5 H-shift (ζ -OOH)	4.99×10^{-2}	6.66×10^{-2}	6.00×10^9	16.31	-1.22×10^5
	(<i>R,S</i>) 1,6 H-shift (α -OOH)	4.91×10^{-3}	6.45×10^{-3}	1.61×10^{11}	21.65	-3.00×10^5
2-OO-4-ROOH 	((<i>R,R</i>) 1,5 H-shift (β -OOH)	5.88×10^{-3}	8.73×10^{-3}	7.14×10^{11}	20.17	-1.06×10^5
	(<i>R,R</i>) 1,6 H-shift (α -OOH)	1.01×10^{-1}	1.29×10^{-1}	4.35×10^{10}	18.53	-2.49×10^5
	(<i>R,R</i>) 1,8 H-shift (γ -OOH)	1.39×10^{-2}	1.95×10^{-2}	2.90×10^{10}	17.73	-9.98×10^4
	(<i>R,S</i>) 1,5 H-shift (β -OOH)	1.02×10^{-2}	1.42×10^{-2}	2.96×10^{11}	20.20	-1.81×10^5
	(<i>R,S</i>) 1,6 H-shift (α -OOH)	1.51×10^{-2}	1.98×10^{-2}	7.30×10^{10}	19.98	-2.52×10^5
	(<i>R,S</i>) 1,8 H-shift (γ -OOH)	1.71×10^{-2}	2.35×10^{-2}	9.27×10^9	17.11	-1.14×10^5
2-OO-5-ROOH 	(<i>R,R</i>) 1,5 H-shift (δ -OOH)	5.37×10^{-3}	7.88×10^{-3}	4.87×10^{11}	20.18	-1.18×10^5
	(<i>R,R</i>) 1,6 H-shift (γ -OOH)	1.08×10^{-2}	1.55×10^{-2}	1.02×10^{11}	18.61	-1.00×10^5
	(<i>R,R</i>) 1,8 H-shift (α -OOH)	3.78×10^{-3}	5.49×10^{-3}	1.99×10^{11}	19.90	-1.24×10^5
	(<i>R,S</i>) 1,5 H-shift (δ -OOH)	1.05×10^{-2}	1.47×10^{-2}	1.50×10^{12}	21.49	-2.12×10^5
	(<i>R,S</i>) 1,6 H-shift (γ -OOH)	4.79×10^{-2}	6.55×10^{-2}	3.16×10^{11}	19.43	-1.89×10^5
	(<i>R,S</i>) 1,8 H-shift (α -OOH)	8.08×10^{-4}	1.17×10^{-3}	9.76×10^{11}	22.68	-2.07×10^5
2-OO-5-ROOH- <i>d</i> ₄ 	(<i>R,R</i>) 1,5 D-shift (δ -OOH)	1.45×10^{-4}	2.29×10^{-4}	1.27×10^{12}	22.53	-9.43×10^4
	(<i>R,R</i>) 1,6 D-shift (γ -OOH)	3.50×10^{-4}	5.39×10^{-4}	1.44×10^{11}	20.43	-6.58×10^4
	(<i>R,R</i>) 1,8 H-shift (α -OOH)	3.99×10^{-3}	5.80×10^{-3}	2.19×10^{11}	19.96	-1.28×10^5
	(<i>R,S</i>) 1,5 D-shift (δ -OOH)	1.85×10^{-4}	2.90×10^{-4}	1.44×10^{12}	22.67	-1.12×10^5
	(<i>R,S</i>) 1,6 D-shift (γ -OOH)	9.05×10^{-4}	1.36×10^{-3}	2.50×10^{11}	20.62	-1.03×10^5
	(<i>R,S</i>) 1,8 H-shift (α -OOH)	8.29×10^{-4}	1.20×10^{-3}	6.93×10^{11}	22.33	-1.95×10^5

C.5.3 Octane- and Ethoxypentane-derived RO₂ H-shift Rate Coefficients

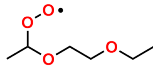
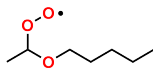
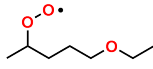
H-shift reaction rate coefficients for three additional peroxy radicals, one derived from octane (OCT 2-RO₂) and two derived from ethoxypentane (EP 2-RO₂ and EP 7-RO₂), were calculated with the same methods as the ones used for DEE RO₂ H-shifts. Calculation results for these systems are shown in Table C.8. Results for DEE 2-RO₂ are included for comparison.

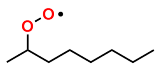
Analysis of the calculation results for RO₂ H-shift reactions in Figure C.7 suggests that the difference in selectivity observed for ether- and hydrocarbon-derived RO₂ is not due to entropic factors, given that the ratio of partition functions $Q_{TS/R,MC}$ (third term in Equation C.1) decreases with increasing span in a similar fashion in all systems. In fact, there is a slight increase in $Q_{TS/R,MC}$ when going from a 1,7 to a 1,8 span in OCT 2-RO₂. The increase in entropic penalty due to the loss of many internal rotors in the transition state of the longer-span pathway (as seen from the lowest-conformer ratio of partition functions $Q_{TS/R,LC}$) is partly counteracted by an increase in conformational entropy, likely due to a relaxation in angle and/or torsional ring-strain. This indicates that the selectivity differences among systems are controlled by differences in reaction energy barrier heights. Here, we explore how inductive, stereoelectronic, and steric effects impact this selectivity.

Previous studies^{7,8} suggested that the altered intramolecular H-shift selectivity ob-

served when different (endocyclic) functional groups are present in the ring-like transition states may be partly due to geometrical factors and stereoelectronic constraints. As endocyclic bond lengths and angles differ with substitution at the substrate's backbone, the H-shift spans at which optimal orbital interactions are possible may also change. In the case of RO₂ H-shifts, optimal overlap between the singly-occupied molecular orbital (SOMO) and the σ_{CH} orbital, required for the reaction to take place, occur with a O—H—C angle of $\sim 180^\circ$ and a C—O—O—H dihedral angle of $\sim 90^\circ$. As the H-shift span increases from 1,4 to 1,8, geometrical constraints imposed by (angle) ring-strain relax, so that the reacting functional groups can more easily orient themselves to maximize the overlap between the SOMO and σ_{CH} orbital. As seen from Table C.9, the O—H—C angle and the C—O—O—H dihedral angle in the TS deviate less from their optimum as the H-shift span increases. However, the trends are very similar for ether and hydrocarbon-derived RO₂. We conclude, therefore, that stereoelectronic effects due to differing geometrical constraints are not significant enough to explain why the selectivity towards the 1,8 H-shift is so large for DEE 2-RO₂ in comparison to OCT 2-RO₂.

Table C.8: Reaction energy barriers ($\Delta^\ddagger E_0$) calculated as the zero-point corrected energy difference between the lowest-conformer of the TS and reactant, multi- and lowest-conformer TST rate coefficients (k_{MC} and k_{LC}), multi- and lowest-conformer ratio of partition functions ($Q_{\text{TS/R,MC}}$ and $Q_{\text{TS/R,LC}}$), and Eckart tunneling factor (κ), calculated at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory and 298.15 K, for H-shift reactions available to OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, and EP 7-RO₂.

T = 298.15 K; ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ							
Reactant	Reaction	$\Delta^\ddagger E_0$ [kcal mol ⁻¹]	k_{MC} [s ⁻¹]	$\frac{\sum Q_{\text{TS}}}{\sum Q_{\text{R}}}$	k_{LC} [s ⁻¹]	$\frac{Q_{\text{TS}}}{Q_{\text{R}}}$	κ
	1,5 H-shift	20.50	2.93×10^{-2}	0.0853	5.99×10^{-2}	0.1746	58.5
	1,6 H-shift	18.76	1.47×10^{-1}	0.0215	5.36×10^{-1}	0.0786	62.3
	1,8 H-shift	16.85	6.94×10^{-1}	0.0051	2.99	0.0220	49.1
	1,5 H-shift	19.07	1.37×10^{-1}	0.0541	1.94×10^{-1}	0.0768	38.5
	1,6 H-shift	21.25	1.28×10^{-3}	0.0124	4.58×10^{-3}	0.0447	62.3
	1,7 H-shift	20.28	4.49×10^{-3}	0.0094	9.27×10^{-3}	0.0193	56.2
	1,8 H-shift	20.21	1.23×10^{-3}	0.0038	5.74×10^{-3}	0.0177	34.1
	1,4 H-shift	33.18	4.22×10^{-9}	0.1926	5.65×10^{-9}	0.2579	7328.8
	1,5 H-shift	23.79	9.28×10^{-5}	0.0894	7.45×10^{-5}	0.0718	46.1
	1,6 H-shift	19.17	5.83×10^{-2}	0.0230	1.78×10^{-1}	0.0699	45.7
	1,8 H-shift	20.07	4.23×10^{-3}	0.0045	1.36×10^{-2}	0.0144	78.4

Reactant	Reaction	$\Delta^\ddagger E_0$ [kcal mol ⁻¹]	k_{MC} [s ⁻¹]	$\frac{\sum Q_{TS}}{\sum Q_R}$	k_{LC} [s ⁻¹]	$\frac{Q_{TS}}{Q_R}$	κ
	1,4 H-shift	32.76	1.47×10^{-8}	0.2727	2.04×10^{-8}	0.3790	8857.6
	1,5 H-shift	22.13	1.59×10^{-3}	0.0940	2.73×10^{-3}	0.1615	45.7
	1,6 H-shift	21.83	8.71×10^{-4}	0.0278	2.58×10^{-3}	0.0824	50.6
	1,7 H-shift	21.45	5.24×10^{-4}	0.0084	1.32×10^{-3}	0.0213	53.2
	1,8 H-shift	23.62	3.50×10^{-5}	0.0090	5.19×10^{-5}	0.0134	129.0

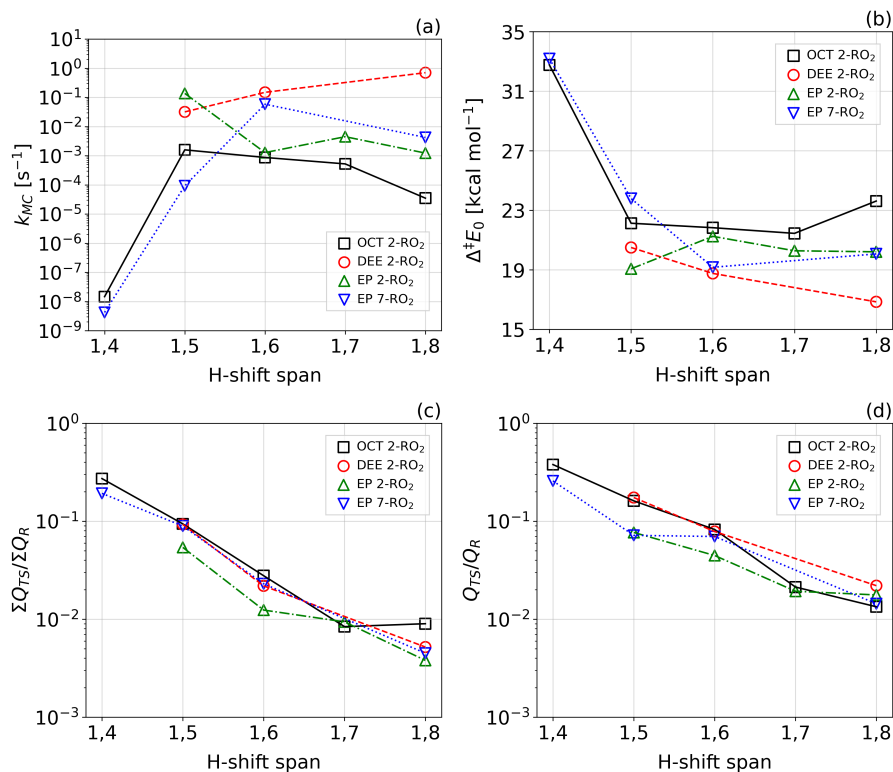
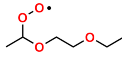
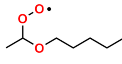
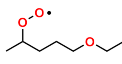
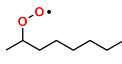
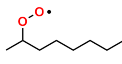
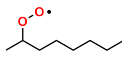


Figure C.7: Calculation results for H-shift reactions available to OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, and EP 7-RO₂, at the ROCCSD(T)-F12a/VDZ-F12 // ω B97X-D/aug-cc-pVTZ level of theory and 298.15 K. (a) Multi-conformer reaction rate coefficients k_{MC} ; (b) Reaction energy barriers $\Delta^\ddagger E_0$ calculated as the zero-point corrected energy difference between the lowest-conformer of the TS and reactant; (c) Multi-conformer ratio of partition functions $Q_{TS/R,MC}$ (third term in Equation C.1); (d) Lowest-conformer ratio of partition functions $Q_{TS/R,LC}$.

Table C.9: Angles ($\angle$) and dihedral angles (ϕ) related to the proper overlap between n_O and σ_{CH}^* or σ_{CH} orbitals, in optimized geometries calculated at the ω B97X-D/aug-cc-pVTZ level of theory, for OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, and EP 7-RO₂ H-shift transition states.

System	Species	$\angle$ O--H--C	ϕ C-O-O--H	ϕ C-O-C--H
DEE 2-RO ₂ 	1,5 H-shift TS	146.2°	-49.5°	33.8°
	1,6 H-shift TS	158.6°	-72.1°	72.4°
	1,8 H-shift TS	176.9°	82.4°	-81.9°
EP 2-RO ₂ 	1,5 H-shift TS	145.9°	-50.1°	34.9°
	1,6 H-shift TS	159.0°	-72.3°	—
	1,7 H-shift TS	168.2°	82.0°	—
EP 7-RO ₂ 	1,8 H-shift TS	176.6°	-96.1°	—
	1,4 H-shift TS	133.4°	-34.6°	—
	1,5 H-shift TS	152.6°	-53.7°	—
OCT 7-RO ₂ 	1,6 H-shift TS	161.2°	-75.5°	-65.5°
	1,8 H-shift TS	173.7°	-100.1°	-62.9°
	1,4 H-shift TS	133.5°	-34.4°	—
OCT 7-RO ₂ 	1,5 H-shift TS	152.6°	-52.9°	—
	1,6 H-shift TS	161.9°	-75.7°	—
	1,7 H-shift TS	169.2°	-88.5°	—
OCT 7-RO ₂ 	1,8 H-shift TS	171.9°	95.8°	—

C.5.4 Local Electrophilicity Indices

The effect of induction by distal oxyl groups on H-shift energy barriers was probed with site-selective differences in a local electrophilicity index $\Delta\omega^+$.^{9,10} To the extent that polar effects affect H-shift transition states' relative stability, the intramolecular attack of an electrophilic radical center (such as the peroxy group in RO₂) should be selective towards abstraction sites leading to more nucleophilic radical products (i.e. in reactions with more negative $\Delta\omega^+$ values), as per the principle of polarity-match.^{11,12} This index difference $\Delta\omega^+$ is calculated from the global electrophilicity index ω and the condensed Fukui function for nucleophilic attack $f^+(X)$ at the radical-center X. The former is obtained as follows:¹³

$$\omega = \frac{\mu^2}{2\eta} \quad (C.4)$$

where μ is the electronic chemical potential and η is the absolute chemical hardness of the species,^{14,15} which are in turn calculated with Equations C.5 and C.6:

$$\mu = -\chi = \frac{-(I + A)}{2} \quad (C.5)$$

$$\eta = I - A \quad (C.6)$$

where E is the electronic energy and N is the number of electrons in the radical. The structure of the H-shift products (QOOH) were obtained by redrawing the geometry of the reactant's lowest-energy conformer, removing a hydrogen atom from the abstraction site and replacing the peroxy group by a hydroperoxy group, and re-optimizing the geometry at the same level of theory.

The Fukui function for nucleophilic attack f^+ is a local measure of the electrophilic power of a given attack site in a molecule, and describes the local change in electron density as a response to the addition of electrons to the system.¹⁶ The best attack sites will see the largest relative increase in electron density upon interaction with a nucleophile, and will therefore display a larger value of f^+ . Using the finite differences approximation,¹⁷ the Fukui function $f^+(X)$ condensed onto the radical center X is calculated as the local electron density difference between the anionic ($N + 1$) and the neutral (N) form of the species,

$$f^+(X) = \rho_{N+1}(X) - \rho_N(X) \quad (C.7)$$

$$\rho(X) = -q(X) \quad (C.8)$$

where $q(X)$ is the partial charge at the radical center X , calculated with natural population analysis.¹⁸ Finally, the local electrophilicity index ω^+ for RO_2 reactants and H-shift products is calculated as,⁹

$$\omega^+ = \omega f^+(X) \quad (C.9)$$

and the corresponding site-specific difference in this index is calculated as:

$$\Delta\omega^+ = \omega^+(\text{product}) - \omega^+(\text{reactant}) \quad (C.10)$$

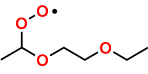
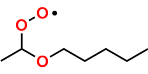
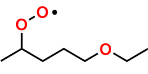
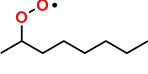
An analogous measure $\Delta\omega^k$,¹⁰ using the natural spin density $\rho_s(X)$ at the radical center X instead of the Fukui function $f^+(X)$ as a local descriptor,¹⁹ was also calculated:

$$\omega^k = \omega \rho_s(X) \quad (C.11)$$

$$\Delta\omega^k = \omega^k(\text{product}) - \omega^k(\text{reactant}) \quad (C.12)$$

The observed trends in $\Delta\omega^+$ and $\Delta\omega^k$ were very similar. The results from these calculations are shown in Figure C.8 and Table C.10.

Table C.10: Vertical ionization potential (I), vertical electron affinity (A), global electrophilicity index (ω), Fukui function for nucleophilic attack $f^+(X)$ condensed onto the radical center X, spin density ($\rho_s(X)$) at the radical X, Fukui function-based local electrophilicity index (ω^+), Spin density-based local electrophilicity index (ω^k), and site-specific differences in local electrophilicity indices $\Delta\omega^+ = \omega^+(\text{QOOH}) - \omega^+(\text{RO}_2)$ and $\Delta\omega^k = \omega^k(\text{QOOH}) - \omega^k(\text{RO}_2)$, calculated at the $\omega\text{B97X-D/ aug-cc-pVTZ}$ level of theory and using natural population analysis, for OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, EP 7-RO₂, and their respective 1, n H-shift products (1, n QOOH).

System	Species	I [eV]	A [eV]	ω [eV]	f^+X	ρ_sX	ω [eV]	ω^k [eV]	$\Delta\omega$ [eV]	$\Delta\omega^k$ [eV]
 DEE 2-RO ₂	RO ₂	10.24	0.35	1.42	0.58	0.69	0.82	0.98	—	—
	1,5 QOOH	7.58	-0.19	0.88	0.54	0.84	0.47	0.73	-0.34	-0.24
	1,6 QOOH	7.54	-0.12	0.90	0.63	0.86	0.57	0.77	-0.25	-0.21
	1,8 QOOH	7.11	-0.69	0.66	0.48	0.85	0.32	0.56	-0.50	-0.41
 EP 2-RO ₂	RO ₂	10.32	0.54	1.51	0.59	0.70	0.88	1.06	—	—
	1,5 QOOH	7.13	-0.41	0.75	0.56	0.84	0.42	0.63	-0.47	-0.43
	1,6 QOOH	7.58	-0.29	0.84	0.63	0.94	0.53	0.80	-0.35	-0.26
	1,7 QOOH	7.32	-0.53	0.73	0.56	0.95	0.41	0.69	-0.48	-0.36
 EP 7-RO ₂	RO ₂	10.33	0.42	1.46	0.57	0.69	0.84	1.01	—	—
	1,4 QOOH	7.86	0.08	1.01	0.61	0.94	0.62	0.96	-0.22	-0.05
	1,5 QOOH	7.54	-0.37	0.81	0.59	0.95	0.48	0.77	-0.36	-0.24
	1,6 QOOH	6.76	-0.73	0.61	0.47	0.85	0.28	0.52	-0.55	-0.49
 OCT 7-RO ₂	RO ₂	10.31	0.44	1.46	0.57	0.69	0.84	1.01	—	—
	1,4 QOOH	7.91	0.13	1.04	0.63	0.94	0.65	0.97	-0.19	-0.04
	1,5 QOOH	7.30	-0.52	0.73	0.59	0.95	0.43	0.70	-0.41	-0.32
	1,6 QOOH	7.25	-0.54	0.72	0.60	0.95	0.43	0.68	-0.41	-0.33
	1,7 QOOH	7.28	-0.59	0.71	0.60	0.95	0.43	0.67	-0.41	-0.34
	1,8 QOOH	7.38	-0.66	0.70	0.58	0.95	0.41	0.66	-0.43	-0.35

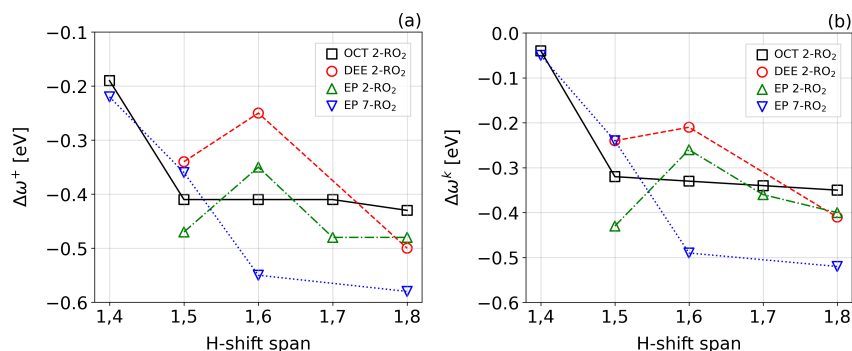


Figure C.8: (a) Site-specific differences in condensed Fukui function-based local electrophilicity indices $\Delta\omega^+ = \omega^+(\text{QOOH}) - \omega^+(\text{RO}_2)$ and in (b) Spin density-based local electrophilicity indices $\Delta\omega^k = \omega^k(\text{QOOH}) - \omega^k(\text{RO}_2)$, calculated with natural population analysis at the $\omega\text{B97X-D/ aug-cc-pVTZ}$ level of theory, for H-shift reactions available to OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, and EP 7-RO₂.

C.5.5 Non-Covalent Interaction Analysis

The impact of steric effects on H-shift selectivity was probed with non-covalent interaction (NCI) analysis,^{20,21} using the Multiwfn v3.8 software.^{22,23} The reduced density gradient (RDG) $s(\rho)$ is an unitless quantity, calculated from the ratio between the electron density ρ and its gradient $\nabla\rho$, useful for identifying regions where non-covalent interactions take place, as well as assessing their strength.

$$s(\rho) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}} \quad (\text{C.13})$$

Close to critical points, such as bond critical points or ring critical points as defined by the theory of atoms in molecules,²⁴ the density gradient $\nabla\rho$ approaches zero (and therefore so does the reduced gradient). Regions in space associated with weaker, non-covalent interactions, however, display small electron densities ρ in addition to small $s(\rho)$. Moreover, the second-order derivative of the electron density ($\nabla^2\rho$) can be used to characterize the nature of these interactions. More specifically, the sign of the second-largest eigenvalue of $\nabla^2\rho$ (λ_2) at a given point indicates if the interaction is attractive or repulsive. While the largest eigenvalue λ_3 is associated with the internuclear axis (between e.g. two interacting fragments) and is positive for all weak interactions, λ_2 is associated with the plane orthogonal to the internuclear axis and is negative for attractive interactions, such as H-bonds or van der Waals interactions, and positive for repulsive interactions, such as steric clashes.

Plots of $s(\rho)$ versus $\text{sign}(\lambda_2)\rho$ calculated for various H-shift transition states of 1,2-DEE RO₂ at the ω B97X-D/aug-cc-pVTZ level of theory and using a high quality grid, are shown in Figures C.9-C.12 as examples. Visual interpretation of RDG plots is mostly qualitative: troughs dipping below $s(\rho) \sim 0.5$ represent NCI interactions. Larger, deeper troughs, towards more positive/negative values of $\text{sign}(\lambda_2)\rho$ are associated with stronger repulsive/attractive interactions. For all systems, the decrease in transition state (angle) ring-strain with increasing H-shift span (from 1,4 to 1,6) is clearly seen from a shift in repulsive NCI troughs towards less positive values of $\text{sign}(\lambda_2)\rho$. Less obvious, but still apparent, is an increase in the size of attractive and repulsive NCI troughs for longer-span H-shift transition states (compared to a 1,6 span TS), consistent with the appearance of transannular interactions. That being said, analysis of relative steric strain by comparing RDG plots for 1,8 H-shift transition states across different RO₂ is challenging with this qualitative view.

A quantitative NCI analysis, based on an index calculated from electron density

integrals over NCI regions,²¹ was also used here:

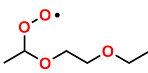
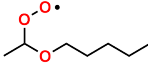
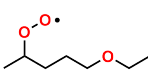
$$q_{\text{bind}} = q_{\text{rep}} - q_{\text{att}} \quad (\text{C.14})$$

$$q_{\text{rep}} = \int_{\Omega_{\text{NCI}}} \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad \lambda_2(\mathbf{r}) > 0 \quad (\text{C.15})$$

$$q_{\text{att}} = \int_{\Omega_{\text{NCI}}} \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad \lambda_2(\mathbf{r}) < 0 \quad (\text{C.16})$$

where the q_{rep} and q_{att} indices describe repulsive and attractive contributions, respectively, to the overall NCI interaction index q_{bind} . This index has been shown to closely reflect the potential energy curves of H-bonded complexes as the interacting fragments move relative to each other.²¹ A density exponential value of 4/3, a grid size of 0.1 bohr, and a cutoff $s(\rho)$ value of 0.6 for defining NCI domains were used in the calculations. A summary of calculated NCI indices for OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, EP 7-RO₂, and their respective H-shift transition states is shown in Table C.11. Details of calculated NCI domain isosurfaces, volumes and q_{bind} indices for all systems can be found at [\[link here\]](#).

Table C.11: Non-covalent interaction (NCI) indices based on electron density integrals over all domains contained within a reduced density gradient $s(\rho) < 0.6$ isosurface for attractive (q_{att}), repulsive (q_{rep}), and overall ($q_{\text{bind}} = q_{\text{rep}} - q_{\text{att}}$) interactions. Calculated were done at the ω B97X-D/aug-cc-pVTZ level of theory with a grid spacing of 0.1 bohr and an electron density exponent of 4/3, for OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, EP 7-RO₂, and their respective 1, n H-shift transition states. Activation NCI indices calculated as $\Delta^\ddagger q = q(\text{TS}) - q(\text{RO}_2)$.

System	Species	q_{att} [a.u.]	q_{rep} [a.u.]	q_{bind} [a.u.]	$\Delta^\ddagger q_{\text{att}}$ [a.u.]	$\Delta^\ddagger q_{\text{rep}}$ [a.u.]	$\Delta^\ddagger q_{\text{bind}}$ [a.u.]
	RO ₂	0.0008	0.0016	0.0008	—	—	—
	1,5 H-shift TS	0.0000	0.0064	0.0064	-0.0008	0.0048	0.0056
	1,6 H-shift TS	0.0000	0.0028	0.0028	-0.0008	0.0012	0.0020
	1,8 H-shift TS	0.0011	0.0059	0.0048	0.0003	0.0043	0.0040
	RO ₂	0.0008	0.0025	0.0017	—	—	—
	1,5 H-shift TS	0.0011	0.0086	0.0075	0.0004	0.0062	0.0058
	1,6 H-shift TS	0.0004	0.0040	0.0036	-0.0004	0.0015	0.0019
	1,7 H-shift TS	0.0019	0.0077	0.0058	0.0011	0.0052	0.0041
	1,8 H-shift TS	0.0017	0.0062	0.0045	0.0009	0.0037	0.0028
	RO ₂	0.0005	0.0014	0.0009	—	—	—
	1,4 H-shift TS	0.0013	0.0098	0.0084	0.0008	0.0084	0.0076
	1,5 H-shift TS	0.0019	0.0102	0.0083	0.0013	0.0088	0.0074
	1,6 H-shift TS	0.0002	0.0023	0.0021	-0.0003	0.0009	0.0012
	1,8 H-shift TS	0.0025	0.0060	0.0036	0.0019	0.0046	0.0027

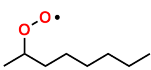
System	Species	q_{att} [a.u.]	q_{rep} [a.u.]	q_{bind} [a.u.]	$\Delta^{\ddagger} q_{\text{att}}$ [a.u.]	$\Delta^{\ddagger} q_{\text{rep}}$ [a.u.]	$\Delta^{\ddagger} q_{\text{bind}}$ [a.u.]
	RO ₂	0.0003	0.0009	0.0006	—	—	—
	1,4 H-shift TS	0.0000	0.0084	0.0084	-0.0003	0.0076	0.0078
	1,5 H-shift TS	0.0001	0.0064	0.0063	-0.0001	0.0056	0.0057
	1,6 H-shift TS	0.0000	0.0016	0.0016	-0.0003	0.0008	0.0010
	1,7 H-shift TS	0.0030	0.0080	0.0050	0.0027	0.0071	0.0044
	1,8 H-shift TS	0.0035	0.0094	0.0059	0.0032	0.0085	0.0053

Table C.12: NCI domain volumes and indices at $s(\rho) < 0.6$ for DEE 2-RO₂.

Domain	1	2	3	4	5	total
q_{att} [a.u.]	0.000000	0.000003	0.000799	0.000000	0.000030	0.000832
q_{rep} [a.u.]	0.000036	0.000248	0.000974	0.000044	0.000305	0.001607
q_{bind} [a.u.]	0.000036	0.000245	0.000175	0.000044	0.000274	0.000775
$V_{\lambda_2 < 0}$ [bohr ³]	0.000	0.002	0.425	0.000	0.023	0.450
$V_{\lambda_2 > 0}$ [bohr ³]	0.015	0.136	0.561	0.009	0.167	0.888

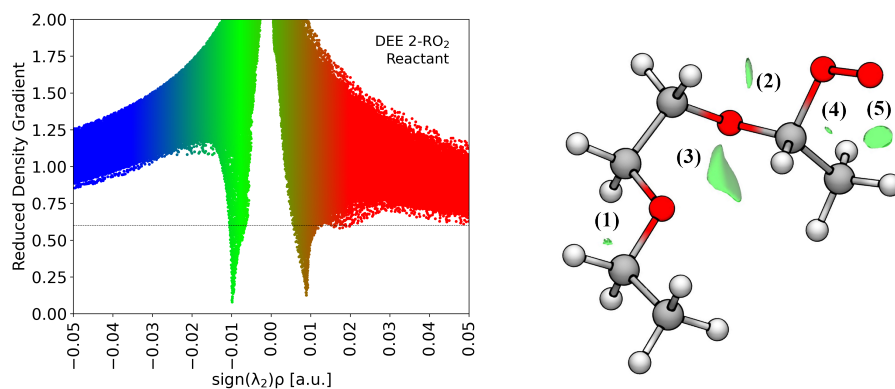


Figure C.9: RDG plot (left) and NCI domains at $s(\rho) < 0.6$ for DEE 2-RO₂ (right).

Table C.13: NCI domain volumes and indices at $s(\rho) < 0.6$ for DEE 2-RO₂ 1,5 H-shift TS.

Domain	1	2	total
q_{att} [a.u.]	0.000000	0.000000	0.000000
q_{rep} [a.u.]	0.006246	0.000123	0.006369
q_{bind} [a.u.]	0.006246	0.000123	0.006369
$V_{\lambda_2 < 0}$ [bohr ³]	0.000	0.000	0.000
$V_{\lambda_2 > 0}$ [bohr ³]	0.874	0.007	0.881

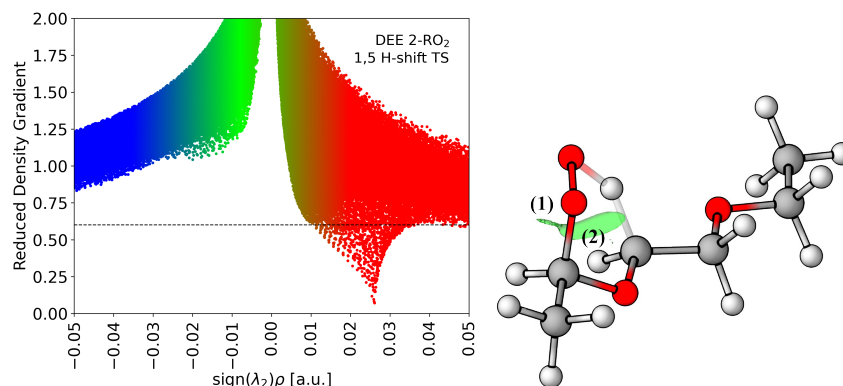


Figure C.10: RDG plot (left) and NCI domains at $s(\rho) < 0.6$ for DEE 2-RO₂ 1,5 H-shift TS (right).

Table C.14: NCI domain volumes and indices at $s(\rho) < 0.6$ for DEE 2-RO₂ 1,6 H-shift TS.

Domain	1	2	3	4	total
q_{att} [a.u.]	0.000000	0.000000	0.000000	0.000000	0.000000
q_{rep} [a.u.]	0.000313	0.000330	0.002109	0.000059	0.002811
q_{bind} [a.u.]	0.000313	0.000330	0.002109	0.000059	0.002811
$V_{\lambda_2 < 0}$ [bohr ³]	0.000	0.000	0.000	0.000	0.000
$V_{\lambda_2 > 0}$ [bohr ³]	0.113	0.064	0.774	0.023	0.974

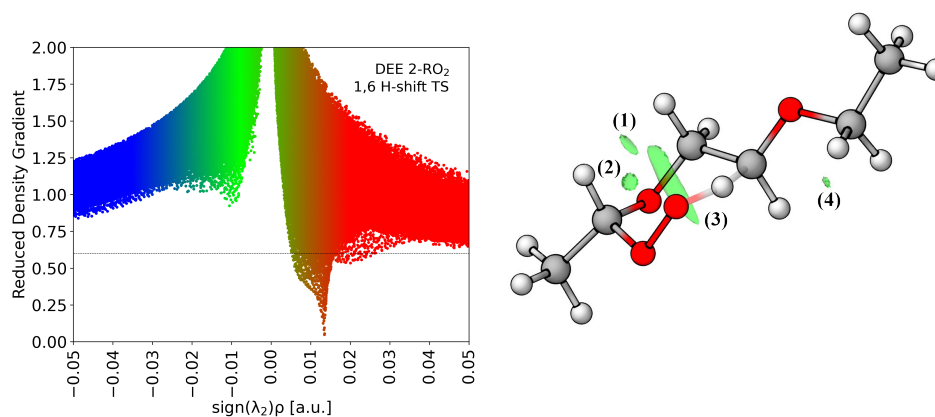
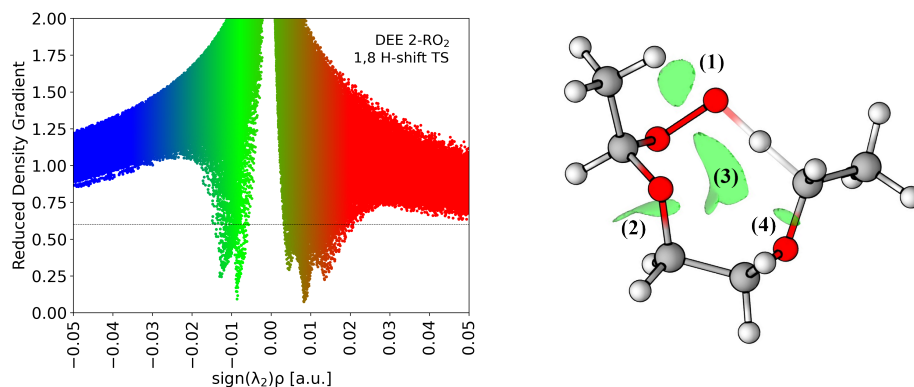


Figure C.11: RDG plot (left) and NCI domains at $s(\rho) < 0.6$ for DEE 2-RO₂ 1,6 H-shift TS (right).

Table C.15: NCI domain volumes and indices at $s(\rho) < 0.6$ for DEE 2-RO₂ 1,8 H-shift TS.

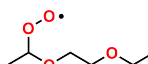
Domain	1	2	3	4	total
q_{att} [a.u.]	0.000593	0.000222	0.000289	0.000000	0.001104
q_{rep} [a.u.]	0.001302	0.001306	0.002722	0.000588	0.005918
q_{bind} [a.u.]	0.000708	0.001084	0.002434	0.000588	0.004815
$V_{\lambda_2 < 0}$ [bohr ³]	0.240	0.107	0.180	0.000	0.527
$V_{\lambda_2 > 0}$ [bohr ³]	0.370	0.425	1.714	0.186	2.695

**Figure C.12:** RDG plot (left) and NCI domains at $s(\rho) < 0.6$ for DEE 2-RO₂ 1,8 H-shift TS (right).

C.5.6 Natural Steric Analysis

Natural steric analysis^{25,26} was also used to assess the impact of steric effects on H-shift selectivity. The quantity selected for this analysis was the total steric exchange energy, calculated from the energy difference between natural localized molecular orbitals (NLMO) and their respective pre-orthogonalization (PNLMO) counterparts. Results from these calculations are shown in Table C.16.

Table C.16: Total natural localized molecular orbital (NLMO) steric energy from natural steric analysis for α and β NLMOs ($E_{\text{steric}}(\alpha)$ and $E_{\text{steric}}(\beta)$), and spin-averaged value (E_{steric}), calculated at the ω B97X-D/aug-cc-pVTZ level of theory, for OCT 2-RO₂, DEE 2-RO₂, EP 2-RO₂, EP 7-RO₂, and their respective 1, n H-shift transition states. Activation steric energy calculated as $\Delta^\ddagger E_{\text{steric}} = E_{\text{steric}}(\text{TS}) - E_{\text{steric}}(\text{RO}_2)$.

System	Species	$E_{\text{steric}}(\alpha)$ [kcal mol ⁻¹]	$E_{\text{steric}}(\beta)$ [kcal mol ⁻¹]	E_{steric} [kcal mol ⁻¹]	$\Delta^\ddagger E_{\text{steric}}$ [kcal mol ⁻¹]
DEE 2-RO ₂	RO ₂	185	177	362	—
	1,5 H-shift TS	226	198	424	62.2
	1,6 H-shift TS	220	193	412	50.0
	1,8 H-shift TS	228	199	427	65.1

System	Species	$E_{\text{steric}}(\alpha)$ [kcal mol ⁻¹]	$E_{\text{steric}}(\beta)$ [kcal mol ⁻¹]	E_{steric} [kcal mol ⁻¹]	$\Delta^\ddagger E_{\text{steric}}$ [kcal mol ⁻¹]
EP 2-RO ₂	RO ₂	203	194	397	—
	1,5 H-shift TS	253	225	477	80.5
	1,6 H-shift TS	248	215	463	65.8
	1,7 H-shift TS	252	215	467	69.6
	1,8 H-shift TS	249	214	464	66.7
EP 7-RO ₂	RO ₂	202	194	396	—
	1,4 H-shift TS	254	219	473	76.7
	1,5 H-shift TS	255	215	470	74.1
	1,6 H-shift TS	241	211	452	56.2
	1,8 H-shift TS	245	217	462	65.8
OCT 7-RO ₂	RO ₂	221	212	433	—
	1,4 H-shift TS	270	236	507	73.7
	1,5 H-shift TS	272	234	505	72.1
	1,6 H-shift TS	262	228	490	56.7
	1,7 H-shift TS	269	233	501	68.1
	1,8 H-shift TS	278	244	522	89

C.5.7 Generalized Anomeric Effects

As discussed in the manuscript, some effect is working to counteract the inductive C–H deactivation by β -oxyl substitution in 1,6 H-shift reactions. The reaction energy barrier of this pathway is slightly higher for EP 2-RO₂ and EP 7-RO₂, compared to OCT 2-RO₂ and DEE 2-RO₂ respectively. We hypothesize that this counteracting effect is due to the fact that the β -oxyl group is endocyclic in the ring-like transition state, providing it with some degree of stabilization that an analogous exocyclic group would not. Differences in transannular strain, invoked to explain the energy barrier trends in 1,8 H-shifts, cannot account for this relative stabilization because this type of interactions should be minimal in 1,6 H-shift transition states. This is in agreement with the natural steric analysis and NCI analysis calculations done here. Furthermore, while we show that smaller transannular strain is part of the explanation why DEE 2-RO₂ is selective towards the 1,8 H-shift pathway in comparison to OCT 2-RO₂, it cannot fully explain why the 1,8 H-shift energy barrier is lower for DEE 2-RO₂ than it is for EP 7-RO₂ (see Tables C.11 and C.16).

We speculate on possible explanations for these inconsistencies. The effect is apparently related to the replacement of a β -peroxyl methylene group by an oxygen atom. In the same way that a σ -withdrawing group can make abstraction sites in β -positions less nucleophilic, it can also make a β -peroxyl group more electrophilic,

and therefore a better H atom acceptor. Consequently, RO₂ with electronegative heteroatoms at β -peroxyl positions (DEE 2-RO₂ and EP 2-RO₂) become more reactive towards intramolecular H-shifts *overall*. However, this hypothesis is not supported by the calculated local electrophilicity indices (Table C.10). While ω^+ is larger for EP 2-RO₂ than it is for EP 7-RO₂ and OCT 2-RO₂, it has the smallest value for DEE 2-RO₂ among RO₂ reactants. Another effect that could possibly be affecting the reaction barrier heights is hyperconjugation between a lone-pair on the ether oxygen and the σ_{CO}^* orbital on the alkylperoxyl group, analogous to what happens in the generalized anomeric effect.²⁷

The generalized anomeric effect is a well-known factor controlling the reaction thermodynamics and kinetics of compounds such as acetals, often rationalized in terms of hyperconjugative interactions between the p-type lone-pair orbital (n_{O}) on an oxygen atom and the σ_{CO}^* orbital on a vicinal C–O bond.^{28–30} We argue that this type of interaction acts to enhance H-shift reaction rates in α -oxyl peroxyl radicals, such as DEE 2-RO₂ and EP 2-RO₂, which we shall discuss from the perspective of spin-orbitals occupied by β -spin electrons, as shown in Scheme 4.5. In the reactant, the vacant p-type spin-orbital on the peroxyl group’s terminal O atom interacts with a filled spin-orbital on the adjacent O atom, resulting in a bonding π_{OO} spin-orbital. At the H-shift transition state, a three-center σ bonding spin-orbital (σ_{3c}) is formed, such that the π_{OO} spin-orbital is replaced by a non-bonding n_{O} spin-orbital. Given a proper alignment between functional groups, both π_{OO} and n_{O} orbitals can interact via hyperconjugation with the σ_{CO}^* orbital on the vicinal C–O bond. However, since non-bonding orbitals are, in general, better electron donors than bonding orbitals, a $n_{\text{O}} \rightarrow \sigma_{\text{CO}}^*$ interaction is stronger than a $\pi_{\text{OO}} \rightarrow \sigma_{\text{CO}}^*$ interaction and the anomeric effect stabilizes the transition state to a greater extent than it does the reactant, lowering the reaction energy barrier. An analogous enhancement in hyperconjugation can also assist H-shift reactions in hydrocarbon-derived RO₂, but to a much lesser extent, because σ_{CC}^* orbitals are poor electron acceptors. Due to electronegativity differences, the (bonding) σ_{CO} orbital is polarized towards the O atom, while the (anti-bonding) σ_{CO}^* is polarized towards the C atom. As a consequence, the overlap between donor and acceptor orbitals is larger for $n_{\text{O}} \rightarrow \sigma_{\text{CO}}^*$ than it is for $n_{\text{O}} \rightarrow \sigma_{\text{CC}}^*$.

Our hypothesis is supported by second-order perturbation theory analysis of NBO donor-acceptor interactions. For β -spin electrons, the calculated change in the $\pi_{\text{OO}}/n_{\text{O}} \rightarrow \sigma_{\text{CX}}^*$ (X = O, C) interaction energy ($E_{(2)}$) between the 1,6 H-shift

transition state and the RO₂ reactant, for instance, is 7.3 and 4.1 kcal/mol for DEE 2-RO₂ and EP 2-RO₂ respectively (X = O), while it is 3.3 and 2.6 kcal/mol for EP 7-RO₂ and OCT 2-RO₂ respectively (X = C). The greater change observed for DEE 2-RO₂ is associated with the fact that the peroxy group in the reactant is aligned at (almost) an antiperiplanar conformation relative to the C–O bond, optimizing the $\pi_{\text{OO}} \rightarrow \sigma_{\text{CC}}^*$ interaction instead. Comparison of interaction energies calculated for α -spin-orbitals reveals that, also for them, $n_{\text{O}} \rightarrow \sigma_{\text{CX}}^*$ hyperconjugation is enhanced at the transition state. Perhaps this is due to an increase in the energy of the donor orbital once the β electron density increases in the same space. A more rigorous analysis of this effect, considering the total change in $E_{(2)}$ for the interaction of the donor orbital with the antibonding orbital on the vicinal C–H and C–CH₃ bonds ($\pi_{\text{OO}}/n_{\text{O}} \rightarrow \sigma_{\text{CC}}^*$ and $\pi_{\text{OO}}/n_{\text{O}} \rightarrow \sigma_{\text{CH}}^*$) as well, for both α and β electrons, indicate a more pronounced difference in TS stabilization. The total change in $\pi_{\text{OO}}/n_{\text{O}} \rightarrow \sigma_{\text{CX}}^*$ interaction energy between the 1,6 H-shift transition state and the RO₂ reactant is 14.0 and 9.2 kcal/mol for DEE 2-RO₂ and EP 2-RO₂ respectively (X = O, C, and H), while it is 5.9 and 6.1 kcal/mol for EP 7-RO₂ and OCT 2-RO₂ respectively (X = C, C, and H).

C.5.8 Intramolecular H-bond in 2-OO-5-ROOH radical

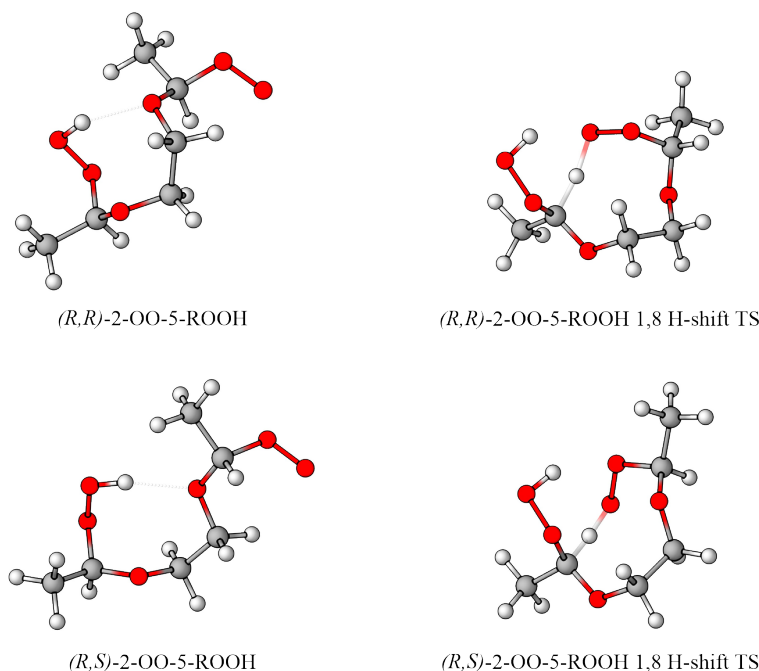


Figure C.13: Molecular structure of lowest conformers of (R,S)/(R,R)-2-OO-5-ROOH and their respective 1,8 H-shift transition states, optimized at the ω B97X-D/aug-cc-pVTZ level of theory. Faded bonds are partially broken. Color code: Gray = C; Red = O; White = H.

C.6 Box Model Implementation

We implement in the photochemical box model a photo-oxidation mechanism of 1,2-DEE, including the reactions of major peroxy radicals, formation of the first-generation closed-shell products, and important secondary reactions of those products. The full mechanism in .txt is available at: doi.org/10.22002/h46t8-rc655. The reaction kinetics involving formation of key oxidation products discussed in this work are listed in Table C.17.

Table C.17: Major bimolecular and unimolecular reactions and respective rate constants. All rate constants are evaluated at 294 K and 993 hPa. ^a Calculated based on Calvert et al.³¹ ^b Calculated based on Jenkin et al.³ ^c Branching ratios of bimolecular reactions, rate coefficients of RO₂ H-shift reactions, and equilibrium constants of equilibrium reactions come from derivations in this work.

Bimolecular Reaction	Rate Constant ($\times 10^{-11} \frac{\text{cm}^3}{\text{molecule}\cdot\text{s}}$)	Branching Ratio ^c (α)
1,2-DEE + OH $\rightarrow$ 1-RO ₂	5.86 ^a	0.01
$\rightarrow$ 2-RO ₂		0.45
$\rightarrow$ 3-RO ₂		0.54
1-RO ₂ + HO ₂ $\rightarrow$ 1-ROOH + O ₂	1.96 ^b	0.96
2-RO ₂ + HO ₂ $\rightarrow$ 2-ROOH + O ₂	1.96 ^b	0.79
3-RO ₂ + HO ₂ $\rightarrow$ 3-ROOH + O ₂	1.96 ^b	0.51
2-OO-5-ROOH + HO ₂ $\rightarrow$ 2,5-DiROOH + O ₂	2.10 ^b	0.65
$\rightarrow$ 2-oxo-5-ROOH + OH + HO ₂		0.26
$\rightarrow$ 2-O-5-ROOH + OH + O ₂		0.09
2-OO-4-ROOH + HO ₂ $\rightarrow$ 2,4-DiROOH + O ₂	2.10 ^b	0.80
$\rightarrow$ 2-oxo-4-ROOH + OH + HO ₂		0.10
$\rightarrow$ 2-O-4-ROOH + OH + O ₂		0.10
4-OO-2-ROOH + HO ₂ $\rightarrow$ 2,4-DiROOH + O ₂	2.10 ^b	0.64
$\rightarrow$ 4-oxo-2-ROOH + OH + HO ₂		0.13
$\rightarrow$ 4-O-2-ROOH + OH + O ₂		0.23
Unimolecular Reaction	Rate Constant ^c (s ⁻¹)	
Sum of 1-RO ₂ H-shift reactions	0.085	
2-RO ₂ $\xrightarrow{\text{O}_2}$ 2-OO-5-ROOH (1,8 H-shift)	1.17	
Average of 2-RO ₂ and 3-RO ₂ 1,6 H-shifts	0.18	
Average of 2-RO ₂ and 3-RO ₂ 1,5 H-shifts	0.06	
(R,R)-2-OO-5-ROOH $\rightarrow$ 2-oxo-5-ROOH + OH (1,8 H-shift)	0.027	
(R,S)-2-OO-5-ROOH $\rightarrow$ 2-oxo-5-ROOH + OH (1,8 H-shift)	0.007	
2-OO-5-ROOH 1,5 + 1,6 H-shifts	0.12	
2-OO-4-ROOH $\rightarrow$ 4-oxo-2-ROOH + OH (1,6 H-shift)	0.058	
4-OO-2-ROOH $\rightarrow$ 2-oxo-4-ROOH + OH (1,6 H-shift)	0.029	
Chemical Equilibrium	Equilibrium constant ^c	
2-OO-4-ROOH $\rightleftharpoons$ 4-OO-2-ROOH	$\frac{5}{6}$	

Major secondary reactions of first-generation closed-shell products include their reactions with OH and photolysis. The reaction kinetics of the OH reactions are directly adopted from Master Chemical Mechanism (MCM).³² For compounds that lack information regarding their OH reactions, the kinetics of structurally similar compounds are used.

The photolytic properties of many functionalized oxidation products (hydroperoxides, aldehydes, and ketohydroperoxides) we examined in this study have so far been understudied. The photolysis rate coefficients of organic hydroperoxides are expected to be close to that of H₂O₂, given the similar absorption cross sections for H₂O₂ and organic hydroperoxides in the 200-350 nm range.³³ The photolysis rate coefficients of H₂O₂ in our chamber are measured in previous studies to be $1.7 \times 10^{-6} \text{ s}^{-1}$ under eight 350 nm bulbs and $2.7 \times 10^{-4} \text{ s}^{-1}$ under eight 254 nm bulbs.^{34,35} These rates are applied to all hydroperoxides in the box model. For ketohydroperoxides, their photolysis rates are estimated assuming additivity of the absorption cross sections of carbonyls and hydroperoxides.³³ Due to lack of knowledge of potential influences on the cross section by the interaction between the functional groups,³⁶ our estimated photolysis rates of the multifunctional products can be off. Our estimation of the photolysis rate coefficients are in Table C.18.

Table C.18: Estimated photolysis reaction rate coefficients of relevant compound classes in the system.

Molecules	Wavelength	
	254 nm	350 nm
H₂O₂ and hydroperoxides	$2.7 (\pm 0.4) \times 10^{-4} \text{ s}^{-1}$	$1.7 (\pm 0.2) \times 10^{-6} \text{ s}^{-1}$
Ketohydroperoxides	$3.0 (\pm 0.4) \times 10^{-4} \text{ s}^{-1}$	$1.9 (\pm 0.2) \times 10^{-6} \text{ s}^{-1}$

Overall, we estimate that secondary chemistry of the oxidation products accounts for ~8% loss in their measured concentrations. Since our analysis in this study is derived from ratios between concentrations of oxidation products with similar secondary chemistry, the influence of secondary chemistry on our analysis of the key reaction parameters is much smaller.

C.7 Experimental Results

C.7.1 Table of Results

Table C.19: Experimental results with all data corrected. All concentrations are in ppb. HO₂ concentrations are determined by the box model. ^a Here we assume that the remaining two GC peaks in Figure C.4 all refer to 2,4-DiROOH. This assumption is further discussed in Section C.8.3

Exp. No.	[HO ₂]	[1-ROOH]	[2-ROOH]	[3-ROOH]	[2-oxo-5-ROOH]	[4-oxo-2-ROOH]	[2-oxo-4-ROOH]	[3-oxo-2-ROOH] + [2-oxo-3-ROOH]
1	0.18	0.009	0.04	0.15	0.13	0.08	0.04	0.01
2	2.33	0.08	1.55	2.18	0.53	0.07	0.05	0.05
		0.15	3.04	4.37	1.00	0.13	0.11	0.08
3	1.33	0.39	5.13	9.43	2.87	0.48	0.35	0.25
4	0.10	0.02	0.06	0.23	0.36	0.25	0.12	0.04
5	0.19	0.008	0.04	0.14	0.15	0.09	0.05	0.02
		0.05	0.26	0.91	1.16	0.65	0.33	0.14
6	1.01	0.22	2.72	5.41	2.04	0.41	0.28	0.17
		0.28	3.80	7.38	2.80	0.58	0.39	0.23
7	0.07	0.01	0.04	0.15	0.31	0.23	0.10	0.03
		0.01	0.05	0.18	0.37	0.29	0.12	0.04
8	1.86	0.17	2.68	4.18	1.09	0.17	0.12	0.10
		0.32	5.17	8.06	2.11	0.34	0.26	0.18
9	0.13	0.02	0.08	0.28	0.28	0.19	0.08	0.04
		0.03	0.14	0.50	0.58	0.36	0.17	0.07
10	0.09	0.02	0.06	0.22	0.29	0.20	0.09	0.04
		0.02	0.07	0.27	0.35	0.25	0.11	0.4
11	1.36	0.21	3.13	5.43	1.66	0.28	0.20	0.16
		0.39	6.32	10.9	3.23	0.59	0.43	0.27
12	0.99	0.09	1.21	2.48	0.89	0.18	0.12	0.09
		0.18	2.35	4.64	1.82	0.36	0.26	0.15

Exp. No.	[HO ₂]	[1-ROOH]	[2-ROOH]	[3-ROOH]	[2-oxo-5-ROOH]	[4-oxo-2-ROOH]	[2-oxo-4-ROOH]	[3-oxo-2-ROOH] + [2-oxo-3-ROOH]
13	2.27	0.10	1.94	2.85	0.65	0.10	0.07	0.05
		0.21	3.93	5.73	1.27	0.20	0.16	0.11

Exp. No.	[HO ₂]	[2-OOH-5-R'CHO]	[3-OOH-5-R'CHO]	[(R,S)-2,5-DiROOH]	[(R,R)-2,5-DiROOH]	[2,4-DiROOH] ^a
1	0.18	0.03	0.01	0.10	0.10	0.14
2	2.33	0.16	0.05	0.63	0.64	0.60
		0.30	0.09	1.28	1.27	1.29
3	1.33	0.94	0.27	3.50	3.40	3.40
4	0.10	0.04	0.02	0.20	0.18	0.25
5	0.19	0.03	0.01	0.11	0.10	0.14
		0.18	0.08	0.89	0.83	1.12
6	1.01	0.56	0.19	2.24	2.21	2.33
		0.73	0.26	3.25	3.23	3.42
7	0.07	0.03	0.01	0.14	0.12	0.17
		0.04	0.02	0.18	0.16	0.22
8	1.86	0.38	0.09	1.28	1.26	1.42
		0.76	0.23	2.42	2.37	2.82
9	0.13	0.06	0.02	0.18	0.17	0.23
		0.10	0.03	0.36	0.34	0.48
10	0.09	0.04	0.02	0.16	0.15	0.19
		0.05	0.02	0.21	0.19	0.25
11	1.36	0.49	0.16	1.88	1.91	2.11
		1.09	0.32	3.91	3.96	3.91
12	0.99	0.23	0.09	1.06	1.04	1.17
		0.46	0.17	2.05	1.99	2.31
13	2.27	0.20	0.06	0.80	0.82	0.83
		0.43	0.13	1.60	1.56	1.67

C.7.2 Vapor Wall Loss

Vapor wall loss refers to the partitioning of gas-phase organic products onto chamber walls, thereby removing them from the system. The vapor wall loss of major oxidation products are quantified by measuring their decay after irradiation. We then correct the yields of the oxidation products using the estimated wall loss rate. The wall loss rate is estimated by fitting the dark decay of the compounds of interests, which gives $9.38 \times 10^{-6} \text{ s}^{-1}$ for ROOH's, $3.30 \times 10^{-5} \text{ s}^{-1}$ for ketohydroperoxides, and $4.95 \times 10^{-5} \text{ s}^{-1}$ for dihydroperoxides.

The observed vapor wall loss rate for dihydroperoxides are smaller than our expectation, since those compounds are expected to have very low volatility and would readily partition into the condensed phase.³⁷ The potential underestimation is likely due to the short equilibrium timescale for low-volatility vapor between the gas-phase and the wall-phase.^{38,39} Smaller the vapor-wall equilibrium timescale of a compound, earlier the wall loss process starts to affect its detectable gas phase concentration. The compound likely already approaches gas-wall equilibrium during the oxidation period, which would result in a smaller decay observed after oxidation. The potential underestimation of wall loss of dihydroperoxides can lead to biases in our estimations of some parameters. For example, overestimation in the slope in Figure 4.2 and 4.3 would lead to underestimation of 1,8 H-shift rate coefficient of 2-RO₂ and overestimation of 1,8 H-shift rate coefficient of 2-OO-5-ROOH.

C.7.3 GC Transmission Efficiency

A certain portion of the reaction products can be lost by decomposition and/or reaction with the column surface as they are traveling through the column. The GC transmission efficiencies of the products are evaluated by comparing their measured concentrations when sampled directly from the chamber with those when sampled from GC. Losses are often greater for compounds eluting at higher temperature. In our experiments, we observe no noticeable loss for products eluting at lower temperatures (<80 °C), i.e. the hydroperoxides and ketohydroperoxides. For dihydroperoxides eluting at >100 °C, we observe a GC transmission rate at ~80-90%, which is accounted for when quantifying the yields of those products.

C.8 Additional Results and Discussion

C.8.1 α_{RO_2} and α_{ROOH}

The branching fractions of respective simple RO_2 (α_{RO_2}) during the initiation step and the branching fractions to the formation of respective ROOH (α_{ROOH}) from bimolecular reactions $\text{RO}_2 + \text{HO}_2$ (Scheme C.1 and C.2) can be derived by analyzing the variation in the yields of ROOH s as a function of $[\text{HO}_2]$. Similar methods are also applied in our previous studies and are described in detailed in Section . Briefly, using 2- ROOH and 1- ROOH as an example, the ratio between the yields of simple hydroperoxides can be written as:

$$\begin{aligned} \frac{[2\text{-ROOH}]}{[1\text{-ROOH}]} &= \frac{\alpha_{2\text{-ROOH}}[2\text{-RO}_2]_{ss}}{\alpha_{1\text{-ROOH}}[1\text{-RO}_2]_{ss}} \\ &= \frac{\alpha_{2\text{-ROOH}}}{\alpha_{1\text{-ROOH}}} \cdot \frac{\alpha_{2\text{-RO}_2}}{\alpha_{1\text{-RO}_2}} \cdot \frac{k_{1\text{-RO}_2+\text{HO}_2}[\text{HO}_2] + k_{\text{H-shifts},1\text{-RO}_2}}{k_{2\text{-RO}_2+\text{HO}_2}[\text{HO}_2] + k_{\text{H-shifts},2\text{-RO}_2}} \end{aligned} \quad (\text{C.17})$$

Based on Equation C.17, the yield of simple hydroperoxides in the system is mainly governed by the following parameters: 1) the branching ratio of simple RO_2 in the initiation step, 2) the branching ratio of $\text{RO}_2 + \text{HO}_2$ reaction to ROOH formation, and 3) the unimolecular H-shift reaction rate coefficients of RO_2 . When $[\text{HO}_2]$ is sufficiently high that the RO_2 bimolecular reaction rates vastly exceed their H-shift reaction rates, ideally, the ratio of the yields of ROOH s should equal to the ratio of branching fractions of the ROOH formation pathways $((\alpha_{2\text{-RO}_2} \cdot \alpha_{2\text{-ROOH}})/(\alpha_{1\text{-RO}_2} \cdot \alpha_{1\text{-ROOH}}))$ in Equation C.17). As $[\text{HO}_2]$ decreases, the H-shift reactions become more significant in influencing the ratio of the product yields. We use box model simulations to facilitate our estimation of those parameters to produce the best model fit to experimental data.

We first estimate the branching ratio of simple RO_2 in the initiation step (α_{RO_2}) based on observed yields of relevant oxidation products. The branching fraction to formation of 1- RO_2 ($\alpha_{1\text{-RO}_2}$) is estimated by comparing the yield of 1- ROOH to that of all oxidation products in the system, given that 1- ROOH is the dominant oxidation product from 1- RO_2 pathway. From this analysis, $\alpha_{1\text{-RO}_2}$ is estimated to be 0.01 (1%). The branching fraction of 2- RO_2 ($\alpha_{2\text{-RO}_2}$) is estimated by comparing the yields of 2- ROOH and all products from 2- RO_2 1,8 H-shift – its major autooxidation pathway – to the total yield of oxidation products, which gives $\alpha_{2\text{-RO}_2} = 0.45$. The remaining $\alpha_{3\text{-RO}_2}$ is thereby derived by calculating $1 - \alpha_{1\text{-RO}_2} - \alpha_{2\text{-RO}_2}$, which equals 0.54. The branching fractions of RO_2 from oxidation of 1,2- DEE-d_4 are derived by comparing the yields of deuterated ROOH with those of their non-deuterated

counterparts (Scheme C.2, Figure C.1). We observe that the abstraction of a D atom from the methylene site between the two oxygen atoms ($\alpha_{3\text{-RO}_2\text{-d}_3}$) is about a factor of 2.6 slower than the abstraction of an H atom ($\alpha_{3\text{-RO}_2}$).

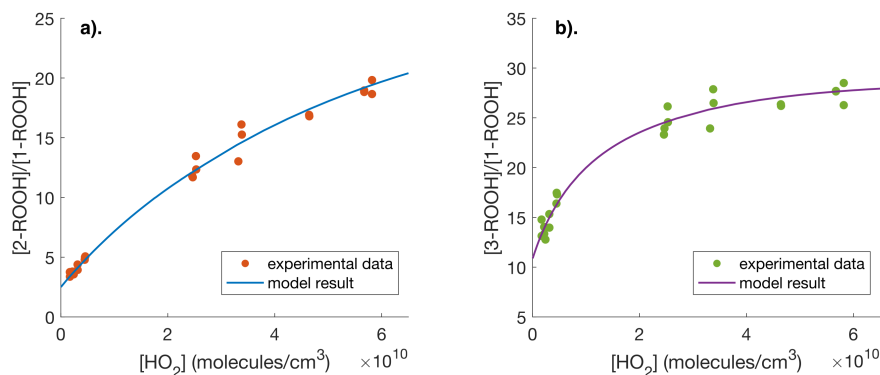
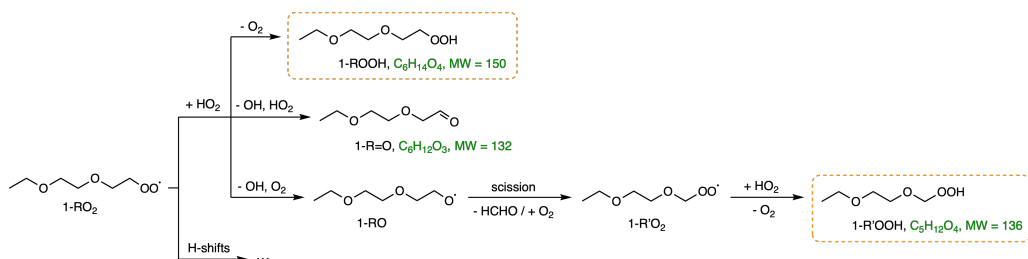


Figure C.14: (a) $[2\text{-ROOH}]/[1\text{-ROOH}]$ vs. $[\text{HO}_2]$, and (b) $[3\text{-ROOH}]/[1\text{-ROOH}]$ vs. $[\text{HO}_2]$. The solid lines represent the optimized model fit to the data. In box model simulation here, we use $k_{\text{H-shifts, 1-RO}_2} = 0.085 \text{ s}^{-1}$, $k_{\text{H-shifts, 2-RO}_2} = 1.4 \text{ s}^{-1}$, and $k_{\text{H-shifts, 3-RO}_2} = 0.25 \text{ s}^{-1}$.

With the derived α_{RO_2} , we estimate α_{ROOH} and the total H-shift rate coefficients of involved RO_2 ($k_{\text{H-shifts, RO}_2}$) based on the variation of $[2\text{-ROOH}]/[1\text{-ROOH}]$ and $[3\text{-ROOH}]/[1\text{-ROOH}]$ as a function of $[\text{HO}_2]$, which is shown in Figure C.14. The resulted reaction parameters from the best fit of the model to the experimental data are in Table C.17. Here we assume that $\alpha_{1\text{-ROOH}} = 0.96$ based on our observation of reaction products from $1\text{-RO}_2 + \text{HO}_2$ reaction (Scheme C.8). We detect low yield of $1\text{-R}'\text{OOH}$ in Scheme C.8 at $\sim 4\%$ of the yield of 1-ROOH in our experiments. The simple assumption that 1-ROOH and $1\text{-R}'\text{OOH}$ are the only products from $1\text{-RO}_2 + \text{HO}_2$ reaction may lead to a slight overestimation of $\alpha_{1\text{-ROOH}}$, leading to overestimation of $\alpha_{2\text{-ROOH}}$, $\alpha_{3\text{-ROOH}}$, and 2-RO_2 and 3-RO_2 H-shift rates. However, the observed yields of relevant reaction products and previous studies suggest



Scheme C.8: Proposed mechanism of 1,2-DEE $1\text{-RO}_2 + \text{HO}_2$ reactions. The molecular masses of major closed-shell products are denoted in green. The products detected by our instrument are shown in orange boxes.

that $\alpha_{1\text{-ROOH}}$ is likely >0.9 ,³ and thus our assumption here should not contribute significantly to the overall uncertainty in our estimated reaction parameters.

C.8.2 2-OO-5-ROOH Reactions

Shown in Figure C.15 is experimental and modeled results of the variations in the yields of various oxidation products from 2-OO-5-ROOH reactions as a function of $[\text{HO}_2]$. Those relationships are used to derived reaction parameters of 2-OO-5-ROOH bimolecular and unimolecular reactions (Scheme 4.4), which are shown in Table 4.3 and Table C.17.

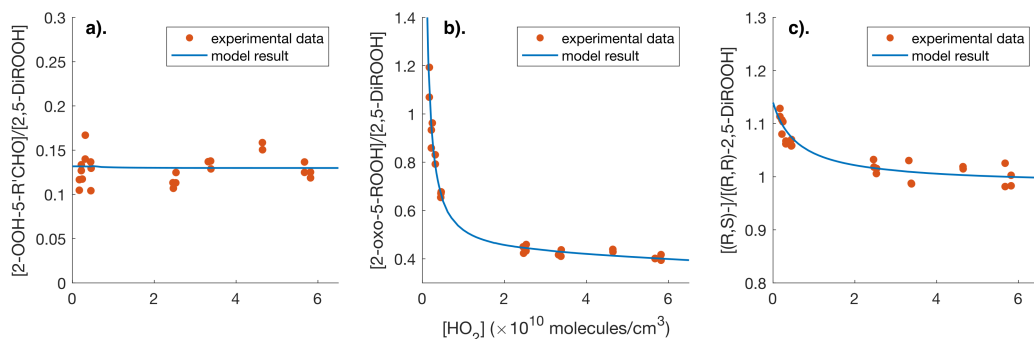


Figure C.15: Yields of various oxidation products from 2-OO-5-ROOH vs. $[\text{HO}_2]$. (a) $[2\text{-OOH-5-R'CHO}]/[2,5\text{-DiROOH}]$, (b) $[2\text{-oxo-5-ROOH}]/[2,5\text{-DiROOH}]$, (c) $[(R,S)\text{-}2,5\text{-DiROOH}]/[(R,R)\text{-}2,5\text{-DiROOH}]$. Model results are based on derived parameters shown in Table C.17.

The ratios of $[2\text{-OOH-5-R'CHO}]/[2,5\text{-DiROOH}]$ and $[2\text{-oxo-5-ROOH}]/[2,5\text{-DiROOH}]$ (Figure C.15a and b), as discussed in the main text, are used to estimate the branching fractions of three channels of bimolecular reaction $2\text{-OO-5-ROOH} + \text{HO}_2$ (Scheme 4.4), as well as the 1,8 H-shift rate coefficient of 2-OO-5-ROOH. Since we do not observe products from other possible reaction pathways of 2-O-5-ROOH (e.g. alkoxy radical isomerization), we assume the scission pathway that leads to formation of 2-OOH-5'CHO the only product derived from 2-O-5-ROOH. The variation in $[2\text{-OOH-5-R'CHO}]/[2,5\text{-DiROOH}]$ at varied $[\text{HO}_2]$ is small, since both products are produced through reaction $2\text{-OO-5-ROOH} + \text{HO}_2$ and the ratio is largely determined by the ratio between the branching fractions $\alpha_{2\text{-O-5-ROOH}}/\alpha_{2,5\text{-DiROOH}}$. In contrast, with the decrease of $[\text{HO}_2]$, the yield of 2-oxo-5-ROOH increases compared to that of 2,5-DiROOH as 1,8 H-shift reaction of 2-OO-5-ROOH becomes more important in the formation of 2-oxo-5-ROOH.

Figure C.15c shows the ratios between the yields of the two diastereomers of 2,5-DiROOH based on our tentative peak assignment in Figure 4.1 and C.4. The

stereoisomer-specific 1,8 H-shift rate coefficient of 2-OO-5-ROOH can be derived by comparing the yields of the two diastereomers as a function of HO_2 concentrations. The stereoisomer with higher H-shift rate coefficient should produce less corresponding dihydroperoxides at lower HO_2 level. If the tentative peak assignment in Figure 4.1 is incorrect, our analysis of (*R,S*) and (*R,R*) diastereomers would be reversed. By fitting the experimental data by box model simulation, we estimate the 1,8 H-shift rate coefficient of (*R,R*)-2-OO-5-ROOH to be $0.027 \pm 0.017 \text{ s}^{-1}$, and that of the (*R,S*) isomer to be $0.007 \pm 0.004 \text{ s}^{-1}$. Although our estimates do not fully agree with the theoretical predictions (Table C.7), they capture the trend that the H-shift rate of the (*R,R*) isomer is ~ 4 times that of the (*R,S*) isomer.

To estimate the rate coefficients of H-shift processes other than the 1,8 H-shift of 2-OO-5-ROOH, i.e. its 1,5 and 1,6 H-shift, we again look at the ratio between the yields of 2-ROOH and direct oxidation products from 2-OO-5-ROOH. The linear relationship between the ratio and $[\text{HO}_2]$ shows an intercept of ~ 0.06 . This non-zero intercept likely attributes to 1,5 and 1,6 H-shift reactions of 2-OO-5-ROOH, which reduce the overall yield of its oxidation products from bimolecular and 1,8 H-shift reactions. From the intercept, we estimate the sum of 1,5 and 1,6 H-shift rate coefficients of 2-OO-5-ROOH through box model simulation, as shown in Figure C.16. By fitting the experimental data with different 2-OO-5-ROOH 1,5 + 1,6 H-shift rate coefficients, we estimate that the combined rate of these shifts is $\sim 0.12 \text{ s}^{-1}$, which is within a factor of 5 of the theoretical values of those H-shifts (Table C.7).

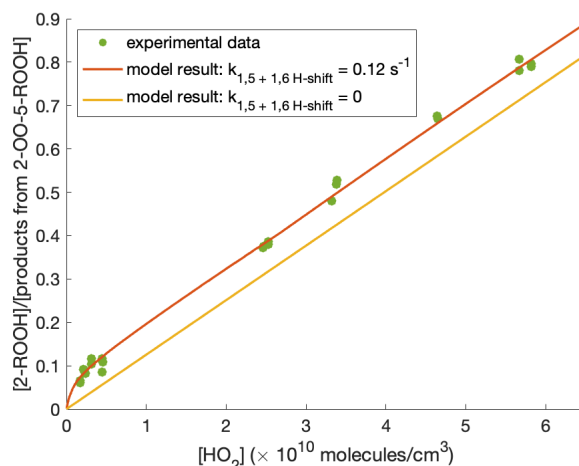


Figure C.16: $[2\text{-ROOH}]/([2\text{-oxo-5-ROOH}] + [2\text{-OOH-5-R'CHO}] + [2,5\text{-DiROOH}])$ vs. $[\text{HO}_2]$ at ambient temperature (294K), with model results of this relationship at different 1,5 + 1,6 H-shift rate coefficients of 2-OO-5-ROOH.

C.8.3 1,5 and 1,6 H-shifts of 2- and 3-RO₂

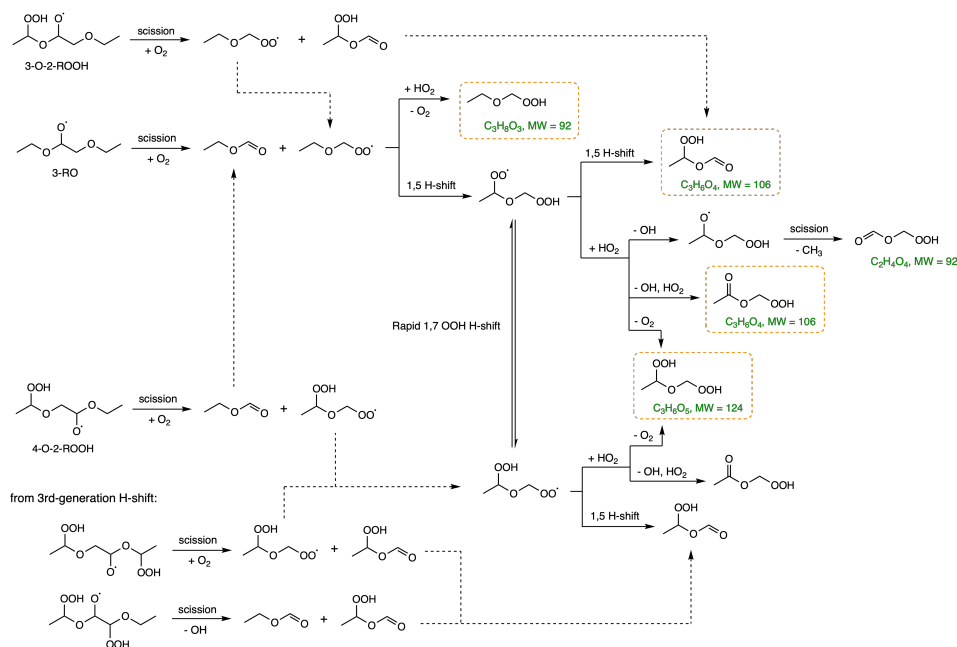
Due to the rapid OOH H-scrambling reaction between the hydroperoxy RO₂ formed via 1,5/1,6 H-shift reactions of 2-RO₂ and 3-RO₂ (Scheme C.3 and C.4), we are unable to distinguish the oxidation products from 1,5/1,6 H-shift of each individual RO₂. Therefore, our estimated rate coefficients of the H-shift reactions represent an average of the process for both RO₂ species. We start with discussion of estimation of the average 1,6 H-shift rates, as the reaction products from 1,6 H-shift pathways have higher yields and thus are better resolved. Note that here we attribute the last two DiROOH GC peaks in Figure C.4 all to 2,4-DiROOH as denoted in Table C.19, since we are unable to distinguish 2,3-DiROOH from 2,4-DiROOH under our chromatographic conditions and we assume based on computational results that the 1,5 H-shifts are much slower than the 1,6 H-shifts. Given that it is possible that 2,3-DiROOH co-elute with 2,4-DiROOH, our following estimation of 1,6 H-shifts should be regarded as an upper limit. We also refrain from conducting stereoselective analyses for the reaction processes discussed below, as the current peak assignments remain uncertain.

Similar to our estimation of the 2-RO₂ 1,8 H-shift rate coefficient, we compare the rates of the bimolecular pathway of both RO₂ with their unimolecular pathway:

$$\begin{aligned}
 & \frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[\text{all products from 2-RO}_2 \text{ and 3-RO}_2 \text{ 1,6 H-shifts}]} \\
 &= \frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[2,4\text{-DiROOH}] + [2\text{-oxo-4-ROOH}] + [4\text{-oxo-2-ROOH}] + [3\text{-OOH-5-R'CHO}] + [4\text{-O-2-ROOH}]} \\
 &= \frac{k_{\text{RO}_2+\text{HO}_2}[2\text{-RO}_2][\text{HO}_2] + k_{\text{RO}_2+\text{HO}_2}[3\text{-RO}_2][\text{HO}_2]}{k_{1,6 \text{ H-shifts, 2-RO}_2 \text{ \& 3-RO}_2}([2\text{-RO}_2] + [3\text{-RO}_2])} \\
 &= \frac{k_{\text{RO}_2+\text{HO}_2}}{k_{1,6 \text{ H-shifts, 2-RO}_2 \text{ \& 3-RO}_2}}[\text{HO}_2]
 \end{aligned} \tag{C.18}$$

From Equation C.18, we should observe a linear relationship between the yields of simple ROOHs divided by their branching fractions from RO₂+HO₂ reaction and the total yields of all oxidation products from the 1,6 H-shift pathways (Scheme C.4). The only unknown quantity from the expression is the yield of the alkoxy radical 4-O-2-ROOH, which likely undergoes scission reaction forming a variety of C3 products (Scheme C.9). However, the C3 products from 1,2-DEE oxidation can arise through a variety of pathways, making it particularly challenging to resolve individual contributions of each pathway, which is not the focus of this study. Thus, we resort to estimate the branching fractions of 2-OO-4-ROOH+HO₂ and 4-OO-2-ROOH+HO₂ reactions, which also enables us to derive the yield of 4-O-2-ROOH.

Similar to the approach discussed in the main text and the previous section, we an-



Scheme C.9: Proposed formation pathways of C₃ products from 1,2-DEE oxidation. The molecular masses of major closed-shell products are denoted in green. Products detected by our instrument are shown in orange boxes.

analyze the following ratios of oxidation product yields to estimate the branching ratios: $[3\text{-OOH-5-R'CHO}]/[2,4\text{-DiROOH}]$, $([2\text{-oxo-4-ROOH}]+[4\text{-oxo-2-ROOH}])/[2,4\text{-DiROOH}]$, and $[4\text{-oxo-2-ROOH}]/[2\text{-oxo-4-ROOH}]$, as shown in Figure C.18. The first two ratios are used to estimate the average values of key reaction parameters of 2-OO-4-ROOH and 4-OO-2-ROOH bimolecular and unimolecular reactions, the latter one is used to determine the equilibrium constant of $2\text{-OO-4-ROOH} \rightleftharpoons 4\text{-OO-2-ROOH}$ and differentiate the performance of 2-OO-4-ROOH and 4-OO-2-ROOH

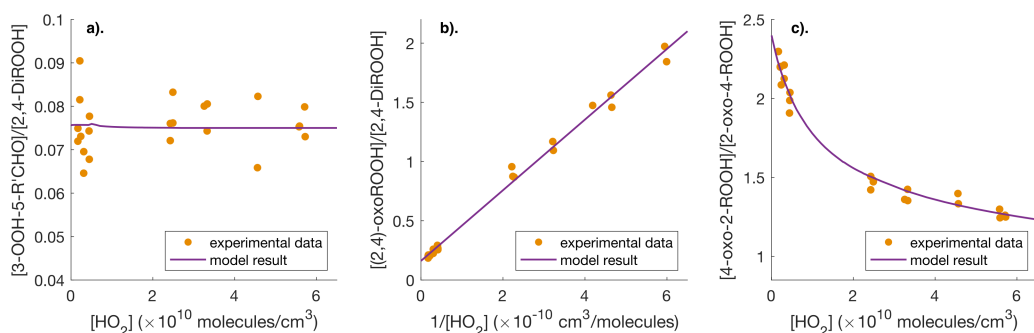
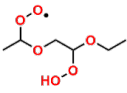
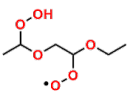


Figure C.18: Yields of various oxidation products from 2-OO-4-ROOH and 4-OO-2-ROOH vs. $[\text{HO}_2]$. (a) $[3\text{-OOH-5-R'CHO}]/[2,4\text{-DiROOH}]$, (b) $([2\text{-oxo-4-ROOH}]+[4\text{-oxo-2-ROOH}])/[2,4\text{-DiROOH}]$, (c) $[4\text{-oxo-2-ROOH}]/[2\text{-oxo-4-ROOH}]$. Model results are based on derived parameters shown in Table C.17 and C.20.

reactions. Our estimates of key reaction parameters are shown in Table C.17 and C.20, including the branching fractions of 2-OO-4-ROOH and 4-OO-2-ROOH + HO₂ reactions, equilibrium constant of 2-OO-4-ROOH $\rightleftharpoons$ 4-OO-2-ROOH, and the rate coefficients of 1,6 H-shift reactions of 2-OO-4-ROOH and 4-OO-2-ROOH.

Table C.20: Estimates of key reaction parameters involving 2-OO-4-ROOH and 4-OO-2-ROOH. ^a Chemical equilibrium of 2-OO-4-ROOH $\rightleftharpoons$ 4-OO-2-ROOH. ^b Branching fractions of bimolecular reactions with HO₂ ^c Rate coefficients of H-shift reactions.

2-OO-4-ROOH	$f_{2\text{-OO-4-ROOH}}$ ^a	$\alpha_{2,4\text{-DiROOH}}$ ^b	$\alpha_{2\text{-oxo-4-ROOH}}$ ^b	$\alpha_{2\text{-O-4-ROOH}}$ ^b	$k_{1,6\text{ H-shift}} (\text{s}^{-1})$ ^c
	$\frac{6}{11}$	0.80	0.10	0.10	0.058
4-OO-2-ROOH	$f_{4\text{-OO-2-ROOH}}$ ^a	$\alpha_{2,4\text{-DiROOH}}$ ^b	$\alpha_{4\text{-oxo-2-ROOH}}$ ^b	$\alpha_{4\text{-O-2-ROOH}}$ ^b	$k_{1,6\text{ H-shift}} (\text{s}^{-1})$ ^c
	$\frac{5}{11}$	0.64	0.13	0.23	0.029

With the derived branching fractions of 2-OO-4-ROOH and 4-OO-2-ROOH + HO₂ reactions, Equation C.18 can be rewritten as:

$$\begin{aligned}
 & \frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[2,4\text{-DiROOH}] + [2\text{-oxo-4-ROOH}] + [4\text{-oxo-2-ROOH}] + [3\text{-OOH-5-R'CHO}] + [4\text{-O-2-ROOH}]} \\
 &= \frac{[2\text{-ROOH}]/\alpha_{2\text{-ROOH}} + [3\text{-ROOH}]/\alpha_{3\text{-ROOH}}}{[2,4\text{-DiROOH}](1 + \frac{f_{4\text{-OO-2-ROOH}}\alpha_{4\text{-O-2-ROOH}}}{\alpha_{2,4\text{-DiROOH, average}}}) + [2\text{-oxo-4-ROOH}] + [4\text{-oxo-2-ROOH}] + [3\text{-OOH-5-R'CHO}]} \\
 &= \frac{k_{\text{RO}_2+\text{HO}_2}}{k_{1,6\text{ H-shifts, 2-RO}_2 \text{ \& } 3\text{-RO}_2}} [\text{HO}_2]
 \end{aligned} \tag{C.19}$$

Based on Equation C.19, a linear relationship is observed with a slope of $(1.10 \pm 0.35) \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1}$ as shown in Figure C.19. The average of the rate coefficients of 2-RO₂ and 3-RO₂ 1,6 H-shift reactions are thus estimated to be $\sim 0.18 \pm 0.11 \text{ s}^{-1}$.

We met difficulties when quantifying the yields of products derived from the 1,5 H-shifts of 2-RO₂ and 3-RO₂, as these reactions likely proceed much more slowly than other H-shift processes (Table C.17). To estimate the average 1,5 H-shift rate coefficients of 2-RO₂ and 3-RO₂, we compared the yields of 2-ROOH and 3-ROOH with those of 2-oxo-3-ROOH and 3-oxo-2-ROOH, which are the only resolvable products from the 1,5 H-shifts. With box model simulation, as shown in Figure C.20, we estimate the rate coefficients to be $\sim 0.06 \text{ s}^{-1}$.

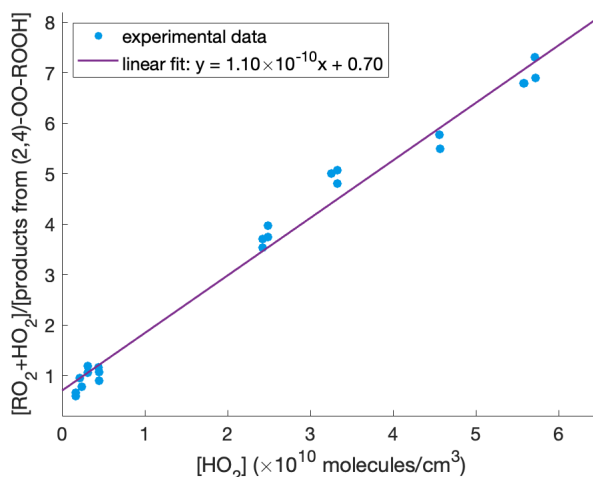


Figure C.19: $k_{\text{RO}_2+\text{HO}_2}$ vs. $k_{1,6}$ H-shift, 2-RO₂ & 3-RO₂ at ambient temperature (294 K), and the result from linear regression fit ($R^2 = 0.985$).

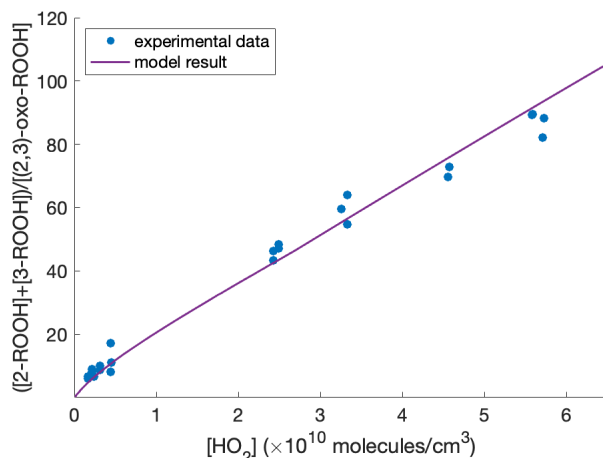


Figure C.20: $([2\text{-ROOH}]+[3\text{-ROOH}])/([2\text{-oxo-3-ROOH}]+[3\text{-oxo-2-ROOH}])$ vs. $[\text{HO}_2]$. Model result are based on parameters shown in Table C.17. Here for 2-OO-3-ROOH and 3-OO-2-ROOH + HO₂ reactions, we assume they have the same reaction parameters as 2-OO-4-ROOH and 4-OO-2-ROOH + HO₂ reactions, respectively.

C.9 Estimation of Uncertainties

The major source of uncertainties in our derived branching fractions and rate coefficients includes: the estimated experimental $[\text{HO}_2]$ ($\sim 16\%$), measured concentrations of reaction products ($\sim 22\%$), and estimated rate coefficients of RO_2+HO_2 reactions ($\sim 52\%$). Details regarding derivation of those error are described in Section A.9. A detailed uncertainty analysis of major reaction parameters derived in this study is in Table C.21.

Table C.21: Sources of uncertainties for reaction parameters determined in this study. ^a Uncertainty in $k_{RO_2+HO_2}$ are derived from that of $k_{C_2H_5O_2+HO_2}$ based on method in JPL documentation.⁴⁰

Quantity	Constraints	Sources of Uncertainty	Value
$\alpha_1\text{-RO}_2$	$\frac{[1\text{-ROOH}]}{[\text{all oxidation products}]} (28\%)$		0.01 ± 0.003
$\alpha_2\text{-RO}_2$	$\frac{[2\text{-ROOH}] + [\text{all products from } 2\text{-OO-5-ROOH}]}{[\text{all oxidation products}]} (28\%)$		0.45 ± 0.14
$\alpha_3\text{-RO}_2$	$1 - \alpha_2\text{-RO}_2 - \alpha_3\text{-RO}_2$		0.54 ± 0.15
$\alpha_1\text{-ROOH}$	$\frac{[1\text{-R'OOH}]}{[1\text{-ROOH}]} (28\%)$		$0.96 + 0.04 / - 0.27$
$\alpha_2\text{-ROOH}$	$\frac{[2\text{-ROOH}]}{[1\text{-ROOH}]} (28\%), \frac{\alpha_2\text{-RO}_2}{\alpha_1\text{-RO}_2 \cdot \alpha_1\text{-ROOH}} (28\%)$		$0.79 + 0.21 / - 0.31$
$\alpha_3\text{-ROOH}$	$\frac{[3\text{-ROOH}]}{[1\text{-ROOH}]} (28\%), \frac{\alpha_3\text{-RO}_2}{\alpha_1\text{-RO}_2 \cdot \alpha_1\text{-ROOH}} (28\%)$		0.51 ± 0.20
Slope Fig. 4.2 ($\frac{\alpha_2\text{-ROOH} \cdot k_{2\text{-RO}_2+HO_2}}{k_{1,8\text{ H-shift, } 2\text{-RO}_2}}$)	slope fit Fig. 4.2 (1.0%), $\frac{[2\text{-ROOH}]}{[\text{all products from } 2\text{-OO-5-ROOH}]} (28\%), [\text{HO}_2] (16\%)$		$(1.32 \pm 0.43) \times 10^{-11}$
$k_{1,8\text{ H-shift, } 2\text{-RO}_2}$	$\alpha_2\text{-ROOH} k_{2\text{-RO}_2+HO_2} / (\text{slope Fig. 4.2})$	slope Fig. 4.2 (32%), $\alpha_2\text{-ROOH} (39\%),$ $k_{RO_2+HO_2} (52\%)^a$	1.17 ± 0.85
Slope Fig. 4.3 ($\frac{k_{1,5\text{ H-shift, } 2\text{-OO-5-ROOH}}{\alpha_{2,5\text{-DiROOH}} \cdot k_{2\text{-OO-5-ROOH}+HO_2}}$)	slope fit Fig. 4.3 (2.9%), $\frac{[2\text{-oxo-5-ROOH}]}{[2,5\text{-DiROOH}]} (28\%), [\text{HO}_2] (16\%)$		$(1.24 \pm 0.40) \times 10^9$
Intercept Fig. 4.3 ($\frac{\alpha_{2\text{-oxo-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}$)	intercept fit Fig. 4.3 (2.6%), $\frac{[2\text{-oxo-5-ROOH}]}{[2,5\text{-DiROOH}]} (28\%)$		0.39 ± 0.11
$\frac{\alpha_{2\text{-O-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}$	$\frac{[2\text{-OOH-R'CHO}]}{[2,5\text{-DiROOH}]} (28\%)$		0.14 ± 0.04
$\alpha_{2,5\text{-DiROOH}}$	$\frac{1}{1 + \frac{\alpha_{2\text{-oxo-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}} + \frac{\alpha_{2\text{-O-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}}$		0.65 ± 0.09

Quantity	Constraints	Sources of Uncertainty	Value
$\alpha_{2\text{-oxo-5-ROOH}}$	$\alpha_{2,5\text{-DiROOH}} \times \frac{\alpha_{2\text{-oxo-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}$	$\alpha_{2,5\text{-ROOH}}$ (14%), $\frac{\alpha_{2\text{-oxo-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}$ (28%)	0.26 ± 0.07
$\alpha_{2\text{-O-5-ROOH}}$	$\alpha_{2,5\text{-DiROOH}} \times \frac{\alpha_{2\text{-O-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}$	$\alpha_{2,5\text{-DiROOH}}$ (14%), $\frac{\alpha_{2\text{-O-5-ROOH}}}{\alpha_{2,5\text{-DiROOH}}}$ (28%)	0.09 ± 0.02
$k_{1,8\text{ H-shift, 2-OO-5-ROOH}}$	(slope Fig. 4.3) $\times \alpha_{2,5\text{-DiROOH}} k_{2\text{-OO-5-ROOH}+\text{HO}_2}$	slope Fig. 4.3b (32%), $\alpha_{2,5\text{-DiROOH}}$ (14%), $k_{\text{RO}_2+\text{HO}_2}$ (52%)	0.017 ± 0.011
Slope Fig. C.18b ($\frac{k_{1,6\text{ H-shift, (2,4)-OOROOH average}}}{\alpha_{2,4\text{-DiROOH, average}} \cdot k_{(2,4)\text{-OOROOH}+\text{HO}_2}}$)	slope fit Fig. C.18b (1.8%), $\frac{[2\text{-oxo-4-ROOH}] + [4\text{-oxo-2-ROOH}]}{[2,4\text{-DiROOH}]}$ (28%), $[\text{HO}_2]$ (16%)		$(2.98 \pm 0.96) \times 10^9$
Intercept Fig. C.18b ($\frac{\alpha_{(2,4)\text{-oxo-ROOH, average}}}{\alpha_{2,4\text{-DiROOH, average}}}$)	intercept fit Fig. C.18 (8.8%), $\frac{[2\text{-oxo-4-ROOH}] + [4\text{-oxo-2-ROOH}]}{[2,4\text{-DiROOH}]}$ (28%)		0.16 ± 0.05
$\alpha_{2,4\text{-DiROOH, 2-OO-4-ROOH}}$ $\alpha_{2\text{-oxo-4-ROOH}}$ $\alpha_{2\text{-O-4-ROOH}}$ $\alpha_{2,4\text{-DiROOH, 4-OO-2-ROOH}}$ $\alpha_{4\text{-oxo-2-ROOH}}$ $\alpha_{4\text{-O-2-ROOH}}$	$\frac{\alpha_{(2,4)\text{-oxo-ROOH, average}}}{\alpha_{2,4\text{-DiROOH, average}}}$ (29%), $\frac{\alpha_{2\text{-O-4-ROOH}}}{\alpha_{2,4\text{-DiROOH, 2-OO-4-ROOH}}}$ (28%), $\frac{[4\text{-oxo-2-ROOH}]}{[2\text{-oxo-4-ROOH}]}$ (28%)		0.80 ± 0.07 0.10 ± 0.04 0.10 ± 0.03 0.64 ± 0.26 0.13 ± 0.05 0.23 ± 0.21
$k_{1,6\text{ H-shift, (2,4)-OOROOH average}}$	(slope Fig. C.18b) $\times \alpha_{2,4\text{-DiROOH, average}} k_{(2,4)\text{-OOROOH}+\text{HO}_2}$	slope Fig. C.18 (32%), $k_{\text{RO}_2+\text{HO}_2}$ (52%) ^a , $\alpha_{2,4\text{-DiROOH, average}}$ (14%)	0.045 ± 0.028
Slope Fig. C.19 ($\frac{k_{\text{RO}_2+\text{HO}_2}}{k_{1,6\text{ H-shift, 2-RO}_2 \text{ \& } 3\text{-RO}_2}}$)	slope fit Fig. C.19 (2.6%), Ratios from Equation C.19 (28%), $[\text{HO}_2]$ (16%)		$(1.10 \pm 0.35) \times 10^{-10}$
$k_{1,6\text{ H-shift, 2-RO}_2 \text{ \& } 3\text{-RO}_2}$	$k_{\text{RO}_2+\text{HO}_2} / (\text{slope Fig. C.19})$	slope Fig. C.19 (32%), $k_{\text{RO}_2+\text{HO}_2}$ (52%) ^a	0.18 ± 0.11

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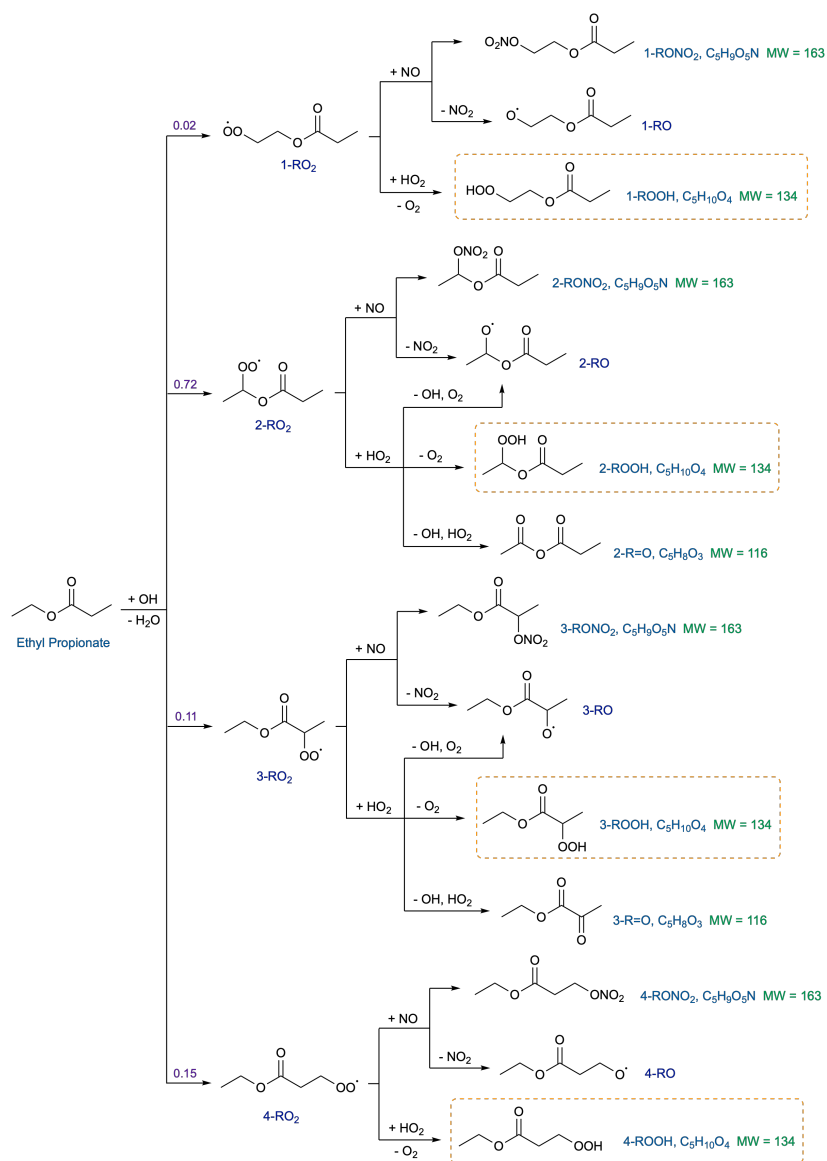
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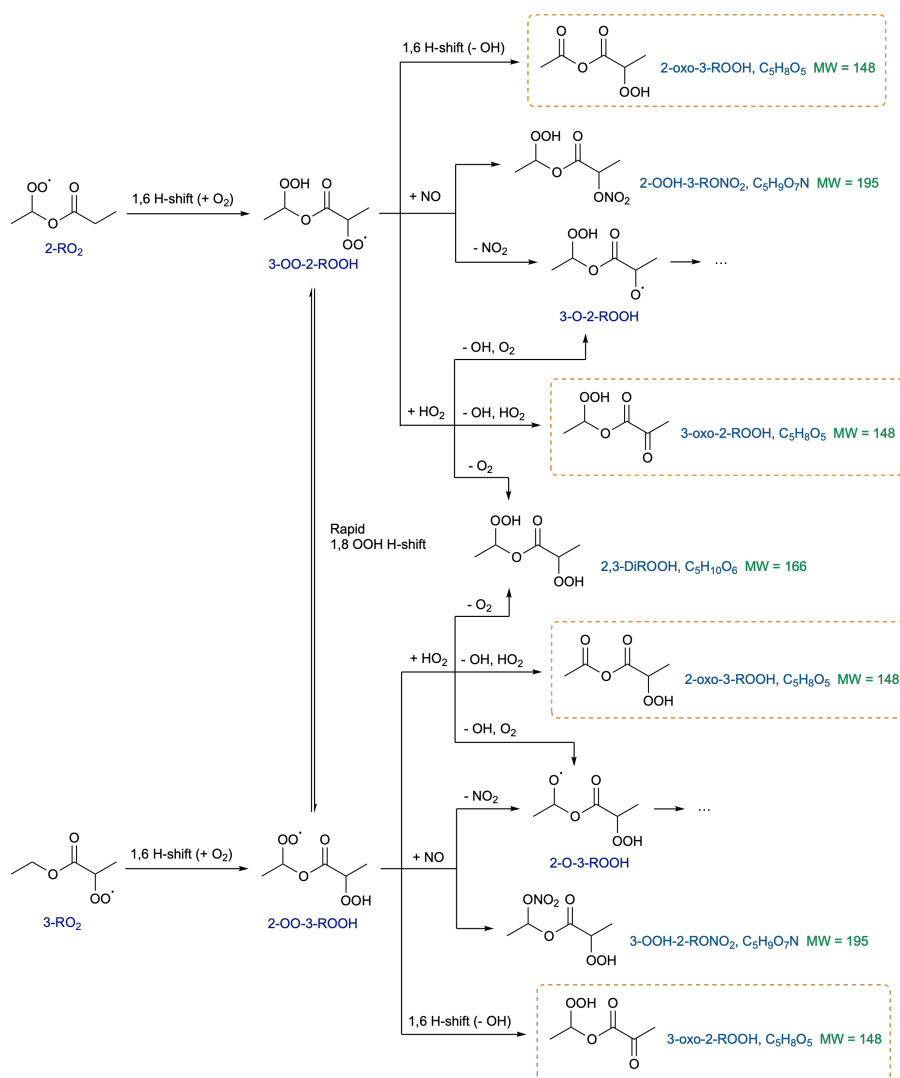
Appendix D

SUPPLEMENTARY INFORMATION FOR CHAPTER 5

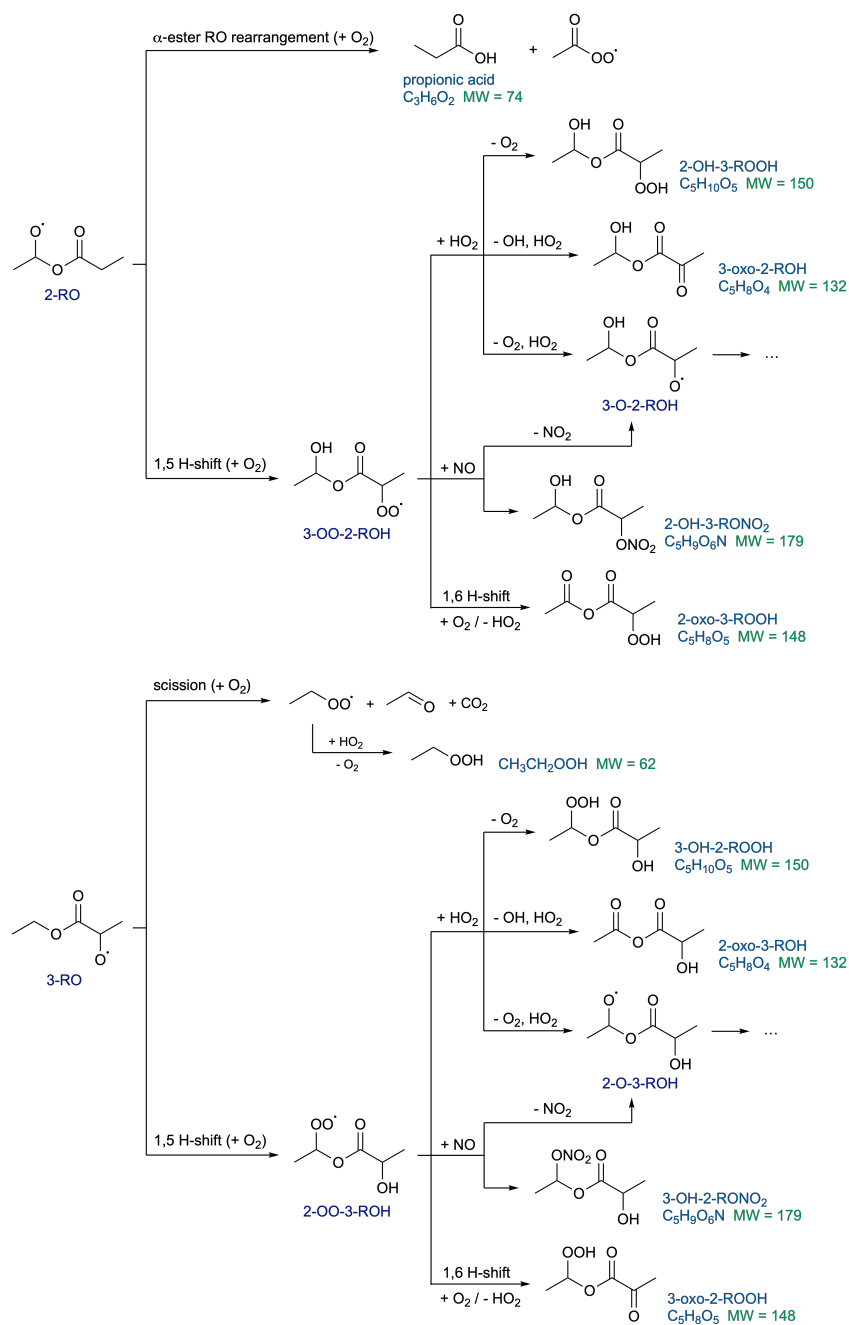
D.1 Additional Reaction Mechanisms



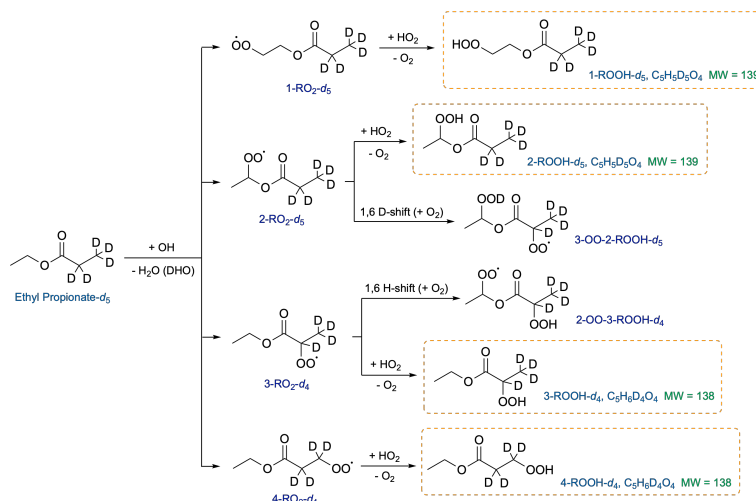
Scheme D.1: Initial step of OH-initiated photo-oxidation of ethyl propionate (EP). The branching fractions of the initial steps are denoted in purple (derived in Section D.6.1). The subsequent bimolecular reactions of generated RO₂ with NO/HO₂ and respective products are also shown. Further pathways from RO₂ H-shift reactions are shown in Scheme D.2. Subsequent reactions of the alkoxy radicals are shown in Scheme D.3. The molecular masses of major closed-shell products are denoted in green. Products detectable by our instrument are shown in orange boxes.



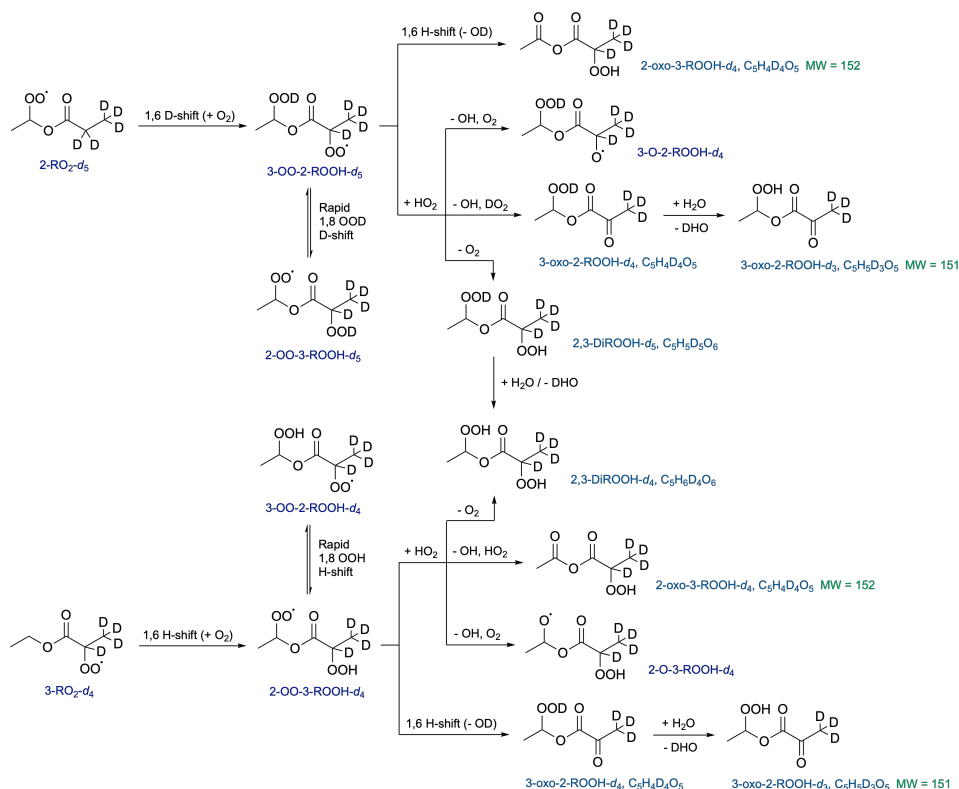
Scheme D.2: Mechanism of EP 2-RO₂ and 3-RO₂ 1,6 H-shift reactions. Subsequent reactions of generated hydroperoxy RO₂ (2-OO-3-ROOH and 3-OO-2-ROOH), including their bimolecular reaction with NO/HO₂, unimolecular H-shift reactions, and respective products are also shown. The molecular masses of major closed-shell products are denoted in green. Products detectable by our instrument are shown in orange boxes.



Scheme D.3: Unimolecular reactions of alkoxy radicals 2-RO and 3-RO. The subsequent bimolecular and unimolecular reactions of OO-ROH and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.



Scheme D.4: Initial step of OH-initiated photo-oxidation of ethyl propionate- d_5 (EP- d_5). The subsequent bimolecular reactions of generated RO_2 with HO_2 and respective products are also shown. Further pathways from deuterated RO_2 H-shift reactions are shown in Scheme D.5 The molecular masses of major closed-shell products are denoted in green. Products detectable by our instrument are shown in orange boxes.



Scheme D.5: Mechanism of EP $2-RO_2-d_5$ and $3-RO_2-d_4$ 1,6 H/D-shift reactions. Subsequent reactions of generated hydroperoxy RO_2 , including their bimolecular reaction with HO_2 , unimolecular H-shift reactions, and respective products are also shown. The molecular masses of major closed-shell products are denoted in green.

D.2 Gas Chromatographic Analysis

D.2.1 Ethyl Propionate- d_5 (EP- d_5) Oxidation with HO_2

Shown in Figure D.1 are the gas chromatograms of reaction products from an EP and an EP- d_5 experiment under similar conditions of $[\text{HO}_2] \sim 1$ ppb. The deuterated oxidation products elute at similar temperature as their non-deuterated counterparts, which enables us to identify ROOH and oxoROOH isomers based on the m/z of the deuterated products. As shown in Scheme D.4 and D.5, the EP- d_5 oxidation products formed via pathways where no deuterium (D) atom is abstracted, such as 2-ROOH- d_5 and 1-ROOH- d_5 ($m/z = 224$), will have molecular mass 5 Da higher than the non-deuterated products. The deuterated products from pathways that involve abstracting D atoms, either by OH or RO_2 radicals, will have a lower molecular mass, such as 3-ROOH- d_4 , 4-ROOH- d_4 ($m/z = 223$), and the deuterated oxoROOH. RO_2 D-shift reactions yield autoxidation products with molecular masses 1 Da lower than expected, since the shifted deuterium on the hydroperoxide group ($-\text{OOD}$) undergoes rapid D/H exchange reaction with the hydrogen in background H_2O in the sampling system. Notice that the m/z 223 peaks below the m/z 224 peaks likely correspond to ROOH formed from the "non-fully deuterated" EP- d_4 that account for the 95% isotopic purity of purchased EP- d_5 .

Regarding the elution order of the ROOHs, 2-ROOH and 1-ROOH are assigned based on their relative product yields given the branching fraction of 2- RO_2 and 1- RO_2 from the initiation step (Section D.6). 3-ROOH and 4-ROOH are assigned based on our expectation on their interaction with the GC column. Since 4-ROOH has the $-\text{OOH}$ group at the primary carbon position, it is expected to interact more strongly with the column and therefore elutes later than 3-ROOH.

D.2.2 Ethyl Propionate (EP) Oxidation with NO

Shown in Figure D.2 are the gas chromatograms of reaction products of an EP photo-oxidation experiments with ~ 500 ppb EP, ~ 2000 H_2O_2 , and ~ 100 ppb NO. We detect reaction products from reaction pathways of alkoxy radical 2-RO (Scheme D.3), including propionic acid (PA) and isomers of hydroxynitrates (OH-RONO_2).

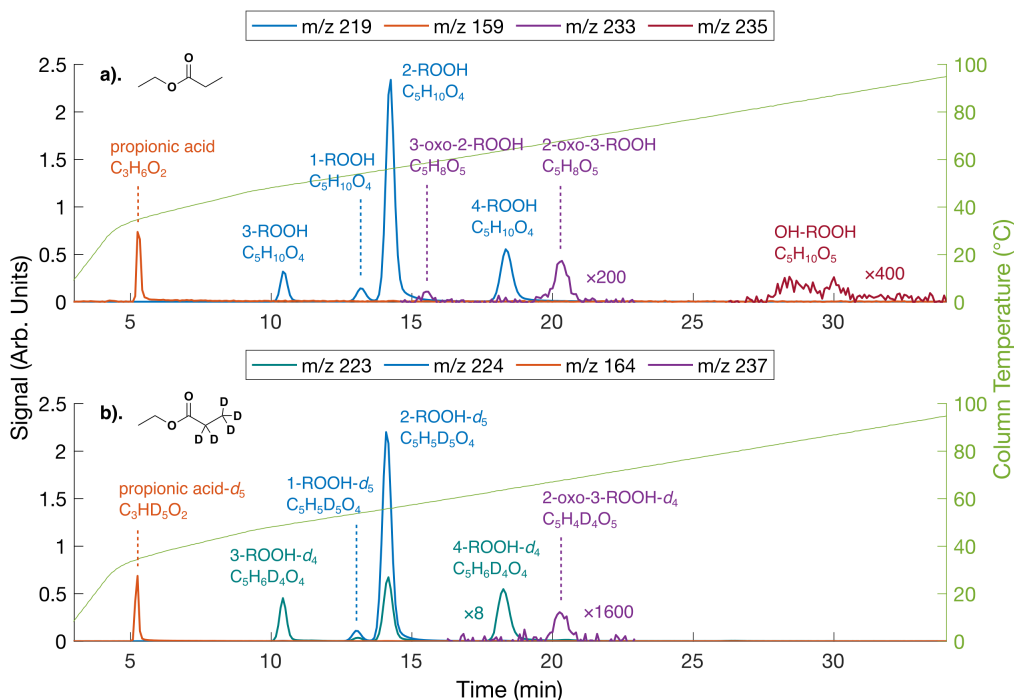


Figure D.1: Gas chromatograms of major reaction products from oxidation experiments of a) EP and b) EP- d_5 with HO_2 . Most reaction products are detected at m/z = mass neutral + 85, except the propionic acid (PA) that are detected at m/z = mass neutral + 85 (from ion-molecule clustering reactions) and + 19 (from fluoride transfer reactions), which are shown in Figure D.3. Certain signals in the figure are scaled up by a factor denoted in the figure.

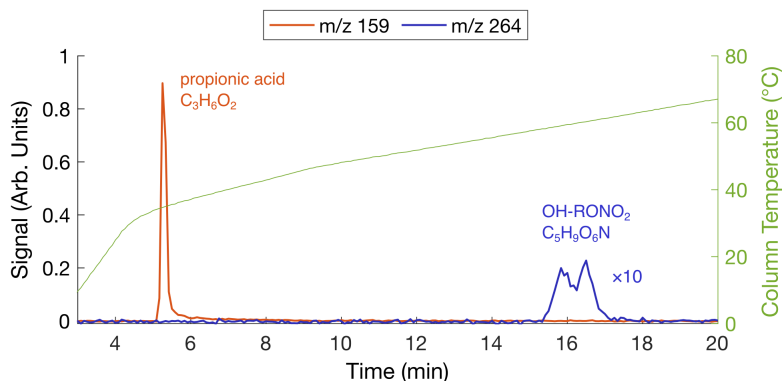


Figure D.2: Gas chromatograms of major reaction products from an EP oxidation experiment with ~ 100 ppb NO. Certain signals in the figure are scaled up by a factor denoted in the figure.

D.2.3 Propionic Acid

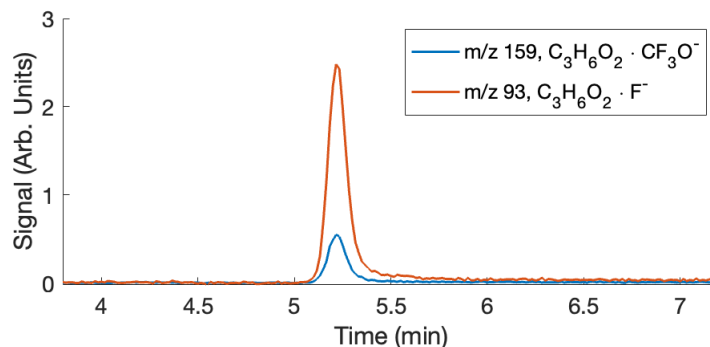


Figure D.3: Gas chromatograms of major product ions of propionic acid (PA). The signals of all detected product ions are summed to quantify the overall yields of PA

D.3 Experimental Conditions

Table D.1: Experimental conditions. All concentrations are in ppb. All experiments are conducted at ambient temperature of 294 ± 1 K.

Exp. No.	[EP] ₀	[CH ₃ OH] ₀	[H ₂ O ₂] ₀	Bulb Type	Bulb #	Oxidation time (min)
1	509	9948	2040	254 nm	1	8
2	667	10311	1988	350 nm	8	100
3	640	10045	2169	254 nm	8	1
4	538	10024	2090	350 nm	8	120
5	653	10624	2123	254 nm	3	3 6
6	633	10363	2147	254 nm	8	2
7	619	9799	2116	254 nm	1	8 14
8	594	10010	1998	254 nm	3	5

D.4 CIMS Calibration

D.4.1 Estimate CIMS Sensitivity

In our studies, the sensitivities of multifunctional oxidation products are calibrated based on their calculated ion-molecule collision rate with CF_3O^- and measured CIMS sensitivity of a compound that forms well-bound ion cluster with CF_3O^- (ethylene glycol in our studies). The ion-molecule collision rate ($k_{\text{cap}}(T)$) are calculated based on the method by Su and Chesnavich:¹

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}} \quad (\text{D.1})$$

$$x = \frac{\mu_D}{\sqrt{2\alpha k_B T}} \quad (\text{D.2})$$

$$K_{cap} = \begin{cases} 0.4767x + 0.6200 & x \geq 2 \\ \frac{(x + 0.5090)^2}{10.526} + 0.9754 & x \leq 2 \end{cases} \quad (\text{D.3})$$

$$k_{cap}(T) = K_{cap} \times k_L \quad (\text{D.4})$$

where q is the charge of the electron, α is the polarizability of the molecule, μ_D is the dipole moment, μ is the reduced mass of the molecule and the ion, k_B is the Boltzmann constant, and T is the temperature.

For molecules of similar sizes and thus similar molecular masses, the differences in their ion-molecule collision rates depend primarily on their dipole moments and polarizabilities. The polarizability of a molecule correlates with the total number of valence electrons in the molecule. Based on the compounds we investigated in previous studies, we find a linear relationship between their polarizability and number of valence electrons, as shown in Figure D.4.

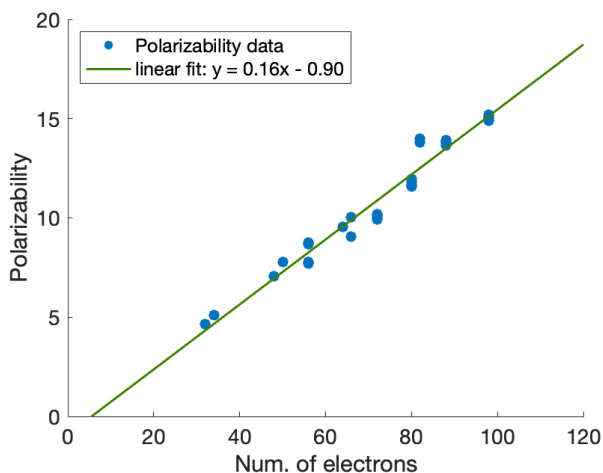


Figure D.4: Polarizability ($\text{\AA}^3$) vs. total number of valence electrons of multifunctional organic compounds investigated in previous studies (Table D.2, B.5, and C.2), and the linear regression fit.

Based on the linear fit in Figure D.4, we estimate the polarizabilities of EP oxidation products (Scheme D.1, D.2, D.3) to be ~ 10 to 13 . For their dipole moments, we anticipate, based on calculations of structurally similar compounds, them to fall in the range of $2.5 - 4$ D (Table D.2, B.5, C.2).

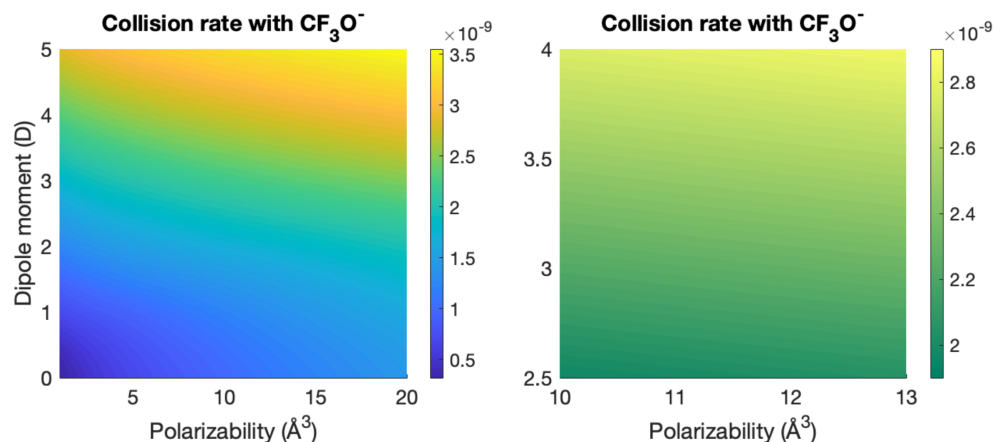


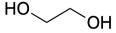
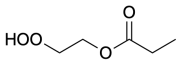
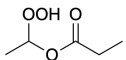
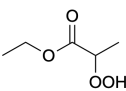
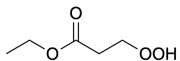
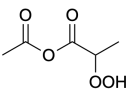
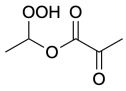
Figure D.5: Calculated CF_3O^- ion-molecule collision rate ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of an organic molecule with $\text{MW} = 140$ of various polarizabilities and dipole moments. The right panel is the zoom-in view of the left panel at our estimated polarizabilities and dipole moments of EP oxidation products.

Shown in Figure D.5 are the calculated ion-molecule collision rate of CF_3O^- and an organic compound with molecular mass of 140 (the average molecular mass of multifunctional EP oxidation products) of various polarizabilities and dipole moments. We therefore estimate the average CF_3O^- ion-molecule collision rate of EP oxidation products to be $\sim (2.4 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Thus, in our preliminary analysis, where we assume the CIMS sensitivities of all multifunctional oxidation products to be the same, the resulting uncertainty in the inferred concentrations of those oxidation products is approximately 20%.

D.4.2 Calculated CIMS sensitivity

The CIMS sensitivities of EP oxidation products can also be calculated based on the same method documented in Section A.3. The following table list the CIMS sensitivities of oxidation products calibrated based on their calculated ion-molecule collision rates and the measured sensitivity of ethylene glycol (Sigma-Aldrich, 99.8%).

Table D.2: Calculated dipole moments (μ_D), polarizabilities (α), CF_3O^- -molecule collision rate coefficients (k_c), and CIMS sensitivities for molecules of interests in the system. ^a Normalized relative to that of ethylene glycol. ^b measured sensitivity data and uncertainties.

Molecule	m/z	μ_D (D)	α ($\text{\AA}^3$)	k_c ($10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Relative k_c^a	Sensitivity (10^{-4} cts/ppbv)
Ethylene glycol 	147	2.08	5.11	1.90	1	3.12 (± 0.25) ^b
propionic acid 	159	1.63	6.30	1.59	0.84	2.61 (± 0.21)
$\text{CH}_3\text{CH}_2\text{OOH}$ 	147	1.69	5.48	1.67	0.88	2.74 (± 0.22)
1-ROOH 	219	3.56	11.24	2.60	1.37	4.26 (± 0.34)
2-ROOH 	219	3.63	11.36	2.64	1.39	4.33 (± 0.35)
3-ROOH 	219	3.83	11.37	2.75	1.45	4.51 (± 0.36)
4-ROOH 	219	3.59	11.30	2.61	1.38	4.29 (± 0.34)
2-oxo-3-ROOH 	233	3.12	11.31	2.32	1.22	3.80 (± 0.30)
3-oxo-2-ROOH 	233	1.76	11.48	1.61	0.84	2.64 (± 0.21)

D.5 Experimental Results

D.5.1 Table of Results

Table D.3: Experimental results for EP oxidation experiments. All concentrations are in ppb. HO_2 concentrations are determined by the box model.

Exp. No.	$[\text{HO}_2]$	[1-ROOH]	[2-ROOH]	[3-ROOH]	[4-ROOH]	[PA]	$[\text{CH}_3\text{CH}_2\text{OOH}]$
1	1.05	0.20	3.60	0.35	1.09	1.56	0.26
2	0.18	0.12	2.05	0.21	0.62	0.94	0.14
3	2.43	0.12	2.30	0.22	0.74	1.14	0.18
4	0.19	0.10	1.64	0.16	0.53	0.76	0.15

Exp. No.	[HO ₂]	[1-ROOH]	[2-ROOH]	[3-ROOH]	[4-ROOH]	[PA]	[CH ₃ CH ₂ OOH]
5	1.99	0.22	4.23	0.39	1.36	1.88	0.35
	1.98	0.48	8.66	0.82	2.83	3.79	0.71
6	2.60	0.27	5.10	0.47	1.51	2.46	0.40
7	1.04	0.20	3.21	0.33	1.02	1.86	0.30
	1.02	0.34	5.71	0.60	1.68	3.19	0.52
8	1.69	0.26	4.68	0.45	1.49	2.41	0.41

Exp. No.	[HO ₂]	[2-oxo-3-ROOH]	[3-oxo-2-ROOH]	[OH-ROOH]	[oxo-ROH]
1	1.05	0.010	0.003	0.005	0.003
2	0.18	0.008	0.005	0.002	–
3	2.43	0.004	0.001	0.003	0.002
4	0.19	0.008	0.006	0.002	–
5	1.99	0.009	0.003	0.006	0.003
	1.98	0.020	0.005	0.012	0.006
6	2.60	0.010	0.003	0.007	0.003
7	1.04	0.010	0.003	0.004	0.003
	1.02	0.018	0.006	0.008	0.005
8	1.69	0.011	0.003	0.007	0.005

D.5.2 Vapor Wall Loss

Table D.4: Observed vapor wall loss rate for certain oxidation products. Concentrations of those products in Table D.3 are corrected according to those rates

	Vapor Wall Loss Rate (s ⁻¹)
Hydroperoxides (ROOH)	2.87×10^{-5}
Ketohydroperoxides (oxoROOH)	5.75×10^{-5}
2-OH-3-ROOH	6.50×10^{-5}

D.6 Detailed Reaction Kinetics

The reaction kinetics regarding the formation of key oxidation products discussed in this work are listed in Table D.5. Derivation of certain parameters are discussed later.

Table D.5: Major bimolecular and unimolecular reactions and respective rate constants. All rate constants are evaluated at 294 K and 993 hPa. ^a Calculated based on estimations from Cometto et al.² and Calvert et al.³ ^b Calculated based on Jenkin et al.⁴ ^c Branching ratios of bimolecular reactions, rate coefficients of unimolecular reactions, and equilibrium constants of equilibrium reactions from derivations in this work.

Bimolecular Reaction	Rate Constant ($10^{-11} \frac{\text{cm}^3}{\text{molecule} \cdot \text{s}}$)	Branching Ratio ^c (α)
EP + OH $\rightarrow$ 1-RO ₂	0.22 ^a	0.02
$\rightarrow$ 2-RO ₂		0.77
$\rightarrow$ 3-RO ₂		0.09
$\rightarrow$ 4-RO ₂		0.12
1-RO ₂ + HO ₂ $\rightarrow$ 1-ROOH + O ₂	1.86 ^b	1
2-RO ₂ + HO ₂ $\rightarrow$ 2-ROOH + O ₂	1.86 ^b	0.52
$\rightarrow$ 2-R=O + OH + HO ₂		0.22
$\rightarrow$ 2-RO + OH + O ₂		0.26
3-RO ₂ + HO ₂ $\rightarrow$ 3-ROOH + O ₂	1.86 ^b	0.40
$\rightarrow$ 3-R=O + OH + HO ₂		0.26
$\rightarrow$ 3-RO + OH + O ₂		0.34
4-RO ₂ + HO ₂ $\rightarrow$ 4-ROOH + O ₂	1.86 ^b	1
2-OO-3-ROOH + HO ₂ $\rightarrow$ 2,3-ROOH + O ₂	2.04 ^b	0.50
$\rightarrow$ 2-oxo-3-ROOH + OH + HO ₂		0.30
$\rightarrow$ 2-O-3-ROOH + OH + O ₂		0.20
3-OO-2-ROOH + HO ₂ $\rightarrow$ 2,3-ROOH + O ₂	2.04 ^b	0.35
$\rightarrow$ 3-oxo-2-ROOH + OH + HO ₂		0.20
$\rightarrow$ 3-O-2-ROOH + OH + O ₂		0.45
Unimolecular Reaction of Peroxy Radicals	Rate Constant ^c (s ⁻¹)	
1-RO ₂ $\xrightarrow{\text{O}_2}$ 3-OO-1-ROOH	0	
2-RO ₂ $\xrightarrow{\text{O}_2}$ 3-OO-2-ROOH	0.009	
3-RO ₂ $\xrightarrow{\text{O}_2}$ 2-OO-3-ROOH	0.001	
4-RO ₂ $\xrightarrow{\text{O}_2}$ 2-OO-4-ROOH	0.002	
2-OO-3-ROOH $\rightarrow$ 3-oxo-2-ROOH + OH	0.01	
3-OO-2-ROOH $\rightarrow$ 2-oxo-3-ROOH + OH	0.01	
2-OO-3-ROOH $\xrightarrow{\text{cyclization?}}$...	1.5	
Chemical Equilibrium	Equilibrium constant ^c	
3-OO-2-ROOH $\rightleftharpoons$ 2-OO-3-ROOH	3.0	

D.6.1 Branching Fractions of EP + OH and RO₂ + HO₂ Reactions

We begin with inferring the branching fractions of EP RO₂+HO₂ reactions based on observed yields of relevant products (Scheme D.1 to D.3) as well as estimates from previous studies.^{4,5} For 1-RO₂+HO₂ and 4-RO₂+HO₂ reactions, we do not observe potential reaction products from pathways other than ROOH formation. We thus assume a branching fraction of 1 for the formation of 1-ROOH and 4-ROOH, which is consistent with values reported in for reactions between primary RO₂ and HO₂ in literatures.⁴

For other simple peroxy radicals, since not all products from their reactions with HO₂ are detected, we rely on literature values to infer the branching ratios of specific reaction pathways. We assume the branching fractions for formation of 2-ROOH and 3-ROOH from respective bimolecular reactions to be 0.52 and 0.4, based on reported values for structurally similar RO₂.^{4,6-8} Then based on the yields of products from major unimolecular reactions of the corresponding alkoxy radicals, i.e. propionic acid from 2-RO and CH₃CH₂OOH from 3-RO, we derive the branching fractions of alkoxy formation pathways and the remaining ketone formation pathway (Table D.3, $\alpha_{2\text{-RO}}/\alpha_{2\text{-ROOH}} = 0.5$, $\alpha_{3\text{-RO}}/\alpha_{3\text{-ROOH}} = 0.85$, derived branching fractions in Table D.5).

Based on the inferred reaction parameters of simple RO₂ bimolecular reactions, we estimate the branching fractions of the initial step of EP + OH reaction to formation of the various simple RO₂ from the yields of simple ROOHs. At high [HO₂] where RO₂ H-shift chemistry are insignificant compared to their bimolecular chemistry, we estimate α_{RO_2} from EP + OH reaction by:

$$\alpha_{\text{RO}_2} = \frac{[\text{ROOH}]/\alpha_{\text{ROOH}}}{[1\text{-ROOH}] + \frac{[2\text{-ROOH}]}{\alpha_{2\text{-ROOH}}} + \frac{[3\text{-ROOH}]}{\alpha_{3\text{-ROOH}}} + [4\text{-ROOH}]} \quad (\text{D.5})$$

where α_{ROOH} is the branching fraction to formation of ROOH from bimolecular reactions between respective RO₂ and HO₂. The derived branching fractions of the initial step are in Table D.5. The derived branching fractions agree well with predictions based on structure-activity relationships (SAR) and previous computational studies.⁹⁻¹²

For reactions of multifunctionalized RO₂ with HO₂, including 2-OO-3-ROOH, 3-OO-2-ROOH, and OO-ROH radicals, an important constraint for their branching fractions is provided by the ratio of the yields of OH-ROOH and oxo-ROH (Scheme D.3), which helps us infer the ratio between the branching fractions of the ketone-

and hydroperoxide-forming pathways in the bimolecular reactions of these peroxy radicals with HO_2 (Table D.3, $\alpha_{\text{R=O}}/\alpha_{\text{ROOH}} = 0.57$). We again infer the branching fractions of the hydroperoxide formation pathways from literature values for similarly functionalized RO_2 ,^{4,5} and further derive the branching fractions of the remaining ketone and alkoxy formation pathways, as shown in Table D.5.

D.6.2 RO_2 Unimolecular Reactions

In the main text, we estimate the average 1,6 H-shift rate coefficients of 2- RO_2 and 3- RO_2 . The simple RO_2 -specific H-shift rates can be derived by analyzing the variation in the ratios of the yields of various simple ROOH as a function of $[\text{HO}_2]$, as shown in Figure D.6. The method for estimating the RO_2 H-shift rate coefficients based on the yields of their corresponding ROOH were described in detailed in previous publications.^{13,14} Briefly, for RO_2 with faster H-shift processes, the yield of ROOH from which they are derived will decrease more substantially at lower $[\text{HO}_2]$. We use box model simulation to capture the variation in the ratios between the yields of ROOH at decreasing $[\text{HO}_2]$ to estimate the RO_2 -specific H-shift rates. Our estimates for the rate coefficients of H-shift reactions of simple RO_2 are listed in Table D.5.

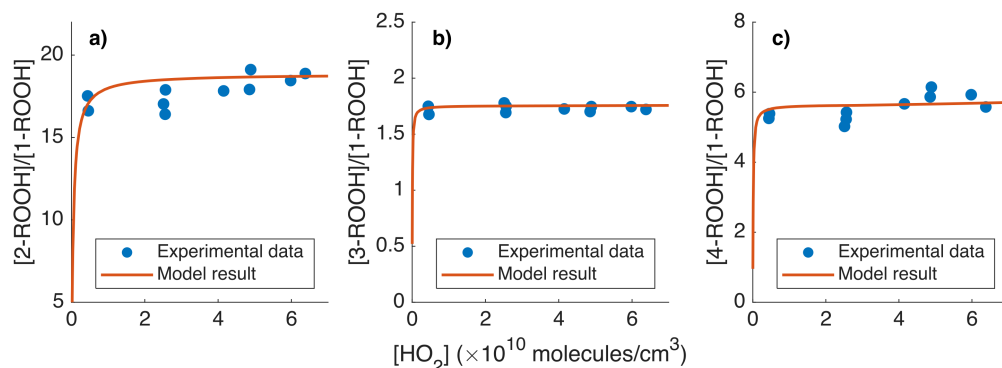


Figure D.6: Yields of various simple ROOH vs. $[\text{HO}_2]$. (a) $[2\text{-ROOH}]/[1\text{-ROOH}]$, (b) $[3\text{-ROOH}]/[1\text{-ROOH}]$, (c) $[4\text{-ROOH}]/[1\text{-ROOH}]$. Model results are based on derived parameters in Table D.5.

Since we lack enough information to derive rate coefficients of H-shift reactions of multifunctional RO_2 (2-OO-3-ROOH, 3-OO-2-ROOH, and OO-ROH), we estimate these values based on our previous studies on multifunctional RO_2 , assuming them to be slightly faster than, but still comparable to those of simple RO_2 , i.e. on the order of 0.01 s^{-1} . One reaction parameter we can derive for those RO_2 is the equilibrium constant of the chemical equilibrium between 2-OO-3-ROOH and 3-OO-2-ROOH

(Scheme D.2), which can be derived by comparing the yields of 2-oxo-3-ROOH and 3-oxo-2-ROOH. Shown in Figure D.7 is the experimental and model result of $[2\text{-oxo-3-ROOH}]/[3\text{-oxo-2-ROOH}]$ at varied $[\text{HO}_2]$. Using box model simulation, we estimate the equilibrium constant to be ~ 3.0 .

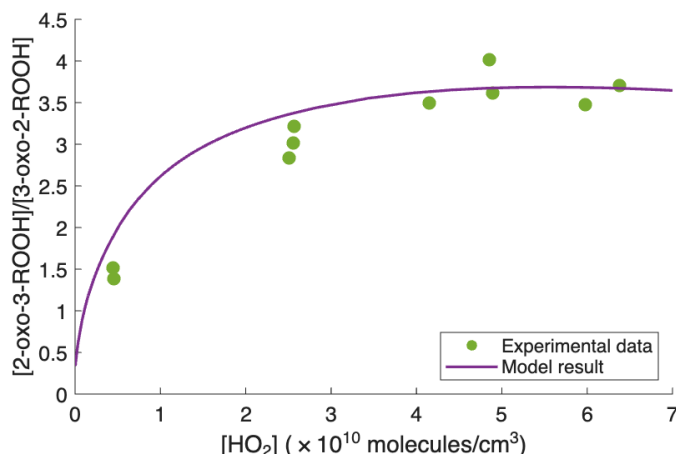


Figure D.7: $[2\text{-oxo-3-ROOH}]/[3\text{-oxo-2-ROOH}]$ vs. $[\text{HO}_2]$. Model results are based on derived parameters shown in Table D.5.

D.6.3 RO Unimolecular Reactions

The rate coefficients of RO unimolecular reactions can be derived based on the our derivation of $\alpha_{\text{ROOH}}/\alpha_{\text{OO-ROH}}$ in Section 5.3.2.2. Notice that, however, the derived reaction branching fractions and rate coefficients in Section 5.3.2.2 may contradict our derivation in Section 5.3.2.1 that are shown in Table D.5.

With the derived values of $\alpha_{\text{ROOH}}/\alpha_{\text{OO-ROH}}$ and $\alpha_{\text{RO}}/\alpha_{\text{ROOH}}$ as described in previous sections, we can determine the fraction of RO radicals that undergo the H-shift pathways among all unimolecular pathways of RO, i.e. $\alpha_{\text{OO-ROH}}/\alpha_{\text{RO}}$. The rate coefficients of H-shift reactions of RO radicals can thus be derived by:

$$k_{\text{H-shift, RO}} = k_{\text{major unimolecular, RO}} \times \frac{\alpha_{\text{OO-ROH}}}{\alpha_{\text{RO}}} \quad (\text{D.6})$$

For rate coefficients of the major unimolecular reactions of simple RO radicals, we rely on the calculated values of those processes based on methods in Zhao et al.¹⁵ For 2-RO, the most important pathway is the α -alkoxy rearrangement reactions, occurring at $5.0 \times 10^4 \text{ s}^{-1}$. For 3-RO, the fastest pathway is the β -scission reaction at $5.9 \times 10^4 \text{ s}^{-1}$. Based on those values and Equation D.6, the derived rate coefficients of RO H-shift reactions are shown in Table D.6

Table D.6: Rate coefficients of unimolecular reactions of RO radicals based on results in Section 5.3.2.2. All values are evaluated at 294 K and 993 hPa. ^a Values calculated based on methods detailed in Zhao et al.¹⁵ ^b Values derived in this work.

Unimolecular Reaction of Alkoxy Radicals	Rate Constant (s ⁻¹)	
	Theory ^a	Experiment ^b
2-RO $\xrightarrow{\text{rearrangement (+ O}_2\text{)}} \text{PA} + \text{CH}_3\text{C(O)OO}$	5.0×10^4	
2-RO $\xrightarrow{\text{1,5 H-shift (+ O}_2\text{)}} \text{3-OO-2-ROH}$	17	4.7×10^2
3-RO $\xrightarrow{\text{scission (+ O}_2\text{)}} \text{CH}_3\text{CH}_2\text{OO} + \text{CH}_3\text{CHO} + \text{CO}_2$	5.9×10^4	
3-RO $\xrightarrow{\text{1,5 H-shift (+ O}_2\text{)}} \text{2-OO-3-ROH}$	2.5×10^4	2.5×10^3

D.6.4 Secondary Chemistry

The secondary reactions of first-generation closed-shell products we implement in the box model include their reactions with OH radical and photolysis. The kinetics of the secondary OH reactions are directly adopted from Master Chemical Mechanism.⁶ For compounds that lack information regarding their reactions with OH, the reaction kinetics of structurally similar compounds are used. The photolysis rates of compounds with photo-sensitive functional groups, such as those with hydroperoxide and carbonyl groups, are either calculated using the actinic flux of our UV lamps and the measured absorption cross section structurally similar compounds,¹⁶ or taken from measured values of the similar compounds in our chamber. Details about the method we use to determine the photolysis rate coefficients of major reaction products are also described in our previous publications.^{13,14}

D.7 Sources of Uncertainties

The major source of uncertainties in our derived branching fractions and rate coefficients includes: the estimated experimental [HO₂] (~16%), measured concentrations of reaction products (~22%), and estimated rate coefficients of RO₂+HO₂ reactions (~52%). Details regarding derivation of those error are described in previous studies.^{13,14} A detailed uncertainty analysis of major reaction parameters derived in this study is in Table D.7.

Table D.7: Sources of uncertainties for reaction parameters determined in this study. ^a Uncertainty based on evaluation in Jenkin et al.^{4,7} ^b Uncertainty based on evaluation in Dillon and Crowley.⁸ and Praske et al.⁵ ^c Uncertainty based on evaluation in Praske et al.⁵ ^d Uncertainty in $k_{RO_2+HO_2}$ are derived from that of $k_{C_2H_5O_2+HO_2}$ based on method in JPL documentation.¹⁷

Quantity	Constraints	Sources of Uncertainty	Value
α_2 -ROOH α_2 -RO α_2 -R=O	$\frac{[\text{propionic acid}]}{[2\text{-ROOH}]} (28\%)$		0.52 ± 0.09^a 0.26 ± 0.12 0.24 ± 0.21
α_3 -ROOH α_3 -RO α_3 -R=O	$\frac{[CH_3CH_2OOH]}{[3\text{-ROOH}]} (28\%)$		0.40 ± 0.16^b 0.34 ± 0.14 $0.26 + 0.30/-0.26$
α_1 -RO ₂ α_2 -RO ₂ α_3 -RO ₂ α_4 -RO ₂	$\frac{[ROOH]/\alpha_{ROOH}}{[1\text{-ROOH}] + \frac{[2\text{-ROOH}]}{\alpha_2\text{-ROOH}} + \frac{[3\text{-ROOH}]}{\alpha_3\text{-ROOH}} + [4\text{-ROOH}]}$	[ROOH] (22%), α_2 -ROOH (17%) α_3 -ROOH (40%)	0.02 ± 0.01 0.77 ± 0.09 0.09 ± 0.03 0.12 ± 0.05
α_3 -OO-2-ROOH, 2,3-DiROOH α_3 -oxo-2-ROOH α_3 -O-2-ROOH α_2 -OO-3-ROOH, 2,3-DiROOH α_2 -oxo-3-ROOH α_2 -O-3-ROOH	$\frac{[\text{oxo-ROH}]}{[\text{OH-ROOH}]} (28\%)$		0.35 ± 0.10^c 0.20 ± 0.06 0.45 ± 0.16 0.50 ± 0.08^a 0.30 ± 0.08 0.20 ± 0.16
$K_{eq, 3\text{-OO-2-ROOH} \leftrightarrow 2\text{-OO-3-ROOH}}$	$\frac{[2\text{-oxo-3-ROOH}]}{[3\text{-oxo-2-ROOH}]} (28\%), \alpha_3\text{-oxo-2-ROOH} (27\%), \alpha_2\text{-oxo-3-ROOH} (30\%)$		4.2 ± 2.1
$\alpha_{\text{oxoROOH, average}}$	$\frac{\alpha_3\text{-oxo-2-ROOH} + K_{eq} \alpha_2\text{-oxo-3-ROOH}}{1 + K_{eq}}$	$K_{eq, 3\text{-OO-2-ROOH} \leftrightarrow 2\text{-OO-3-ROOH}} (50\%)$ $\alpha_3\text{-oxo-2-ROOH} (27\%), \alpha_2\text{-oxo-3-ROOH} (30\%)$	0.28 ± 0.08

Quantity	Constraints	Sources of Uncertainty	Value
Slope Fig. 5.2 $\left(\frac{k_{RO_2+HO_2}}{\alpha_{oxoROOH,average} k_{1,6 \text{ H-shift, 2-RO2 \& 3-RO2}}} \right)$	slope fit Fig. 5.2 (10%), $\frac{[ROOH]}{[oxoROOH]}$ (40%), $[HO_2]$ (16%)		$(7.98 \pm 3.53) \times 10^{-9}$
$k_{1,6 \text{ H-shift, 2-RO2 \& 3-RO2}}$	$\frac{k_{RO_2+HO_2}}{\alpha_{oxoROOH,average} (\text{slope fig. 2})}$	slope Fig. 5.2 (44%), $\alpha_{oxoROOH,average}$ (29%), $k_{RO_2+HO_2}$ (52%) ^d	0.008 ± 0.006
Intercept Fig. 5.4a $\left(\frac{\alpha_{2-ROOH}}{\alpha_{3-OO-2-ROH}} \right)$	intercept fit Fig. 5.4a (5.6%), $\frac{[2-ROOH]}{[2-oxo-3-ROOH]}$ (28%), $[HO_2]$ (16%)		209 ± 68
$\alpha_{3-OO-2-ROH}$	$\alpha_{2-ROOH} / (\text{intercept Fig. 5.4a})$	α_{2-ROOH} (17%), intercept Fig. 5.4a (33%)	0.0025 ± 0.0009
Slope Fig. 5.4a $\left(\frac{(\text{Intercept Fig. 5.4a}) \times k_{3-OO-2-ROH+HO_2}}{k_{1,6 \text{ H-shift, 3-OO-2-ROH}}} \right)$	slope fit Fig. 5.4a (5.7%), $\frac{[2-ROOH]}{[2-oxo-3-ROOH]}$ (28%), $[HO_2]$ (16%)		$(5.10 \pm 1.67) \times 10^{-9}$
$k_{1,6 \text{ H-shift, 3-OO-2-ROH}}$	$\frac{(\text{intercept Fig. 5.4a}) \times k_{3-OO-2-ROH+HO_2}}{(\text{slope Fig 5.4a})}$	slope Fig. 5.4a (33%), intercept Fig. 5.4a (37%), $k_{RO_2+HO_2}$ (52%) ^d	0.72 ± 0.52
Intercept Fig. 5.4b $\left(\frac{\alpha_{3-ROOH}}{\alpha_{2-OO-3-ROH}} \right)$	intercept fit Fig. 5.4b (24%), $\frac{[2-ROOH]}{[2-oxo-3-ROOH]}$ (28%), $[HO_2]$ (16%)		33 ± 13
$\alpha_{2-OO-3-ROH}$	$\alpha_{3-ROOH} / (\text{intercept Fig. 5.4b})$	α_{3-ROOH} (25%), intercept Fig. 5.4a (40%)	0.014 ± 0.007
Slope Fig. 5.4b $\left(\frac{(\text{Intercept Fig. 5.4b}) \times k_{2-OO-3-ROH+HO_2}}{k_{1,6 \text{ H-shift, 2-OO-3-ROH}}} \right)$	slope fit Fig. 5.4b (8.0%), $\frac{[3-ROOH]}{[3-oxo-2-ROOH]}$ (28%), $[HO_2]$ (16%)		$(2.49 \pm 0.83) \times 10^{-9}$
$k_{1,6 \text{ H-shift, 2-OO-3-ROH}}$	$\frac{(\text{intercept Fig. 5.4b}) \times k_{2-OO-3-ROH+HO_2}}{(\text{slope Fig 5.4b})}$	slope Fig. 5.4b (33%), intercept Fig. 5.4b (40%), $k_{RO_2+HO_2}$ (52%) ^d	0.19 ± 0.14

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