Chapter 5

Hydrogen Isotope Effects and Mechanism of Aqueous Ozone and Peroxone Decompositions

Abstract

Hydrogen peroxide enhances the reactivity of ozone in aqueous solution; however, the exact reasons are not clear. If H_2O_2 enhances free radical production, as it is generally believed, then a chain mechanism propagated by ($\cdot OH/\cdot O_2^-$) species should account for O_3 decomposition rates in neat H_2O, $^HR_{-O_3}$, and in peroxone ($O_3 + H_2O_2$) solutions, $^{HP}R_{-O_3}$. We found, however, that 1) the radical mechanism correctly predicts $^HR_{-O_3}$ but vastly overestimates $^{HP}R_{-O_3}$, 2) solvent deuteration experiments preclude radical products from the ($O_3 + HO_2^-$) reaction. The modest kinetic isotope effect (KIE) we measure in H_2O/D_2O: $^HR_{-O_3}/^DR_{-O_3} = 1.5 \pm 0.3$, is compatible with a chain process driven by electron- and/or O-atom transfer processes. But the large KIE found in peroxone: $^{HP}R_{-O_3}/^{DP}R_{-O_3} = 19.6 \pm 4.0$, is due to an elementary ($O_3 + HO_2^-$) reaction involving $H–O_2^-$ bond cleavage. Since the KIE of the hypothetical H-atom transfer: $O_3 + HO_2^- \xrightarrow{2b} HO_3\cdot + \cdot O_2^-$, would emerge as a $KIE^{\frac{1}{2}}$ factor in the rates of the ensuing radical chain, the magnitude of the observed KIE must be associated with the hydride transfer reaction that yields a diamagnetic species: $O_3 + HO_2^- \xrightarrow{2a} HO_3^- + O_2$. HO_3^-/H_2O_3 may be the bactericidal trioxide recently identified in the antibody-catalyzed addition of $O_2(^1\Delta_g)$ to H_2O.

Introduction

Ozone is a powerful but selective oxidant,[1] and an efficient but transient bactericide.[2,3] Raising concerns about the toxic and mutagenic by-products of water chlorination, and the implementation of more stringent regulations, have renewed interest in the use of O_3, alone or in conjunction with H_2O_2.[4-7] Hydrogen peroxide enhances and extends the apparent reactivity of ozone,[3,8,9] which is generally sluggish and essentially inert toward saturated organic species despite favorable energetics.[1] This paper addresses the mechanism of such enhancement.[10-14]

The chemistry of aqueous O_3 has been investigated for over 85 years.[15-17] It is well established that O_3 decay rates increase with pH in the absence and presence of H_2O_2,[18,19] supporting the notion that OH^- and HO_2^-, rather than H_2O and H_2O_2, respectively, are the species involved.[6,7,12,13,20,21] The detection of $\cdot OH$, $\cdot O_2^-$, and $\cdot O_3^-$ intermediates in these systems apparently validates the spirit,[22] although not the letter, of the free radical mechanism originally proposed by Weiss.[18,23-26] The present view is that a common free radical mechanism may account for the decomposition of aqueous O_3 under all conditions. Recent tests indicate, however, that the currently accepted free radical scheme (See Table 1) fails to reproduce experimental rates in neutral and acid solutions.[23,27,28] This apparent mechanistic deficiency has been explained in terms of the apparent inability of the various homogeneous radical termination reactions to limit the length of the free radical chains propagated by $\cdot OH/\cdot O_2^-$ radicals.[23,27,29-31] Although it is possible to bring the calculated and experimental O_3 decomposition rates in pure water into agreement by invoking the presence of subsaturation (under atmospheric CO_2) levels of carbonate as a OH-radical scavenger, this expedient proves to be insufficient in the

presence of H_2O_2.[14,32] It has been speculated that the significant discrepancies remaining in this case could be due to wall effects or to the presence of unspecified amounts of dissolved organic carbon, DOC.[23] Here, we explore further the fact that experimental O_3 decay rates in slightly acidic H_2O_2 solutions are much slower than predicted by radical mechanisms, and as a consequence we arrive at a different conclusion.

The issue revolves around the actual stoichiometries of the (O_3 + OH^-) and (O_3 + HO_2^-) initiation reactions, reactions 1a-c, 2a-c, respectively (Table 1). Reactions 1a and 1b are mechanistically indistinguishable radical-forming processes that generate the rapidly interconvertible ·OH and ·O_2^- chain carriers, respectively.[33] In contrast, reaction 1c, which produces HO_2^-, must be followed by reaction 2b to initiate a free radical chain. This is the currently preferred initiation pathway, which subsumes the decompositions of O_3 in pure water and in the presence of H_2O_2, the peroxone mixture, into a common free-radical mechanism.[18,27] We now report deuterium isotope effects on O_3 decomposition rates in ultrapure water and in peroxone solutions that provide compelling evidence against the formation of free radicals in the reaction between O_3 and HO_2^-. The magnitude of the observed kinetic isotope effect is consistent a hydride transfer process yielding a closed-shell trioxide HO_3^-, the conjugate anion of H_2O_3.[34-52] H_2O_3 may be related to the recently reported bactericidal trioxide formed in the antibody-catalyzed addition of $^1O_2$ to H_2O.[49,52]

Experimental Section

Decomposition rates of aqueous O_3 solutions were measured in a capped silica cuvette (4 cm^3, 1 cm optical depth) by kinetic spectrophotometry at $\lambda = 260$ nm

(ε_{O_3} = 3292 M^{-1} cm^{-1})[53] using a Hewlett Packard 8452A diode-array spectrophotometer. Solutions were stirred with a PTFE-coated spin bar, and kept at (15 ± 0.1) ^{o}C by means of a Hewlett Packard 89090A Peltier temperature controller. Solutions were prepared by sparging water with O_3 produced by an Osmonics V10-0 ozone generator fed with prepurified O_2 gas. We used Milli-Q Plus-UV water (resistivity ρ = 18.2 MΩ cm), or ultrapure water obtained from a Corning MegaPure system (Barnstead/Thermolyne) that involves further purification by double distillation in a fused silica still. The 1 ≤ [DOC]/ppbv ≤ 5 levels present in Milli-Q water (as reported by the manufacturer) are expected to be reduced to undetectable levels by double distillation. pH readings in D_2O as solvent were converted into pD by adding 0.41, i.e.: pD = $pH_{reading}$ + 0.41.[54,55] pH was adjusted using concentrated $HClO_4$ rather than with buffers, because most anions (other than ClO_4^-) are able to scavenge ·OH-radicals.[33] We repeatedly verified that the pH/pD of all solutions remains within 0.1 pH units of the initial value after ozone is consumed.

Hydrogen peroxide (30% w/w, EM Science), D_2O (Cambridge Isotopes), KI (Sigma), and $(NH_4)_6Mo_7O_{24}$ • $4H_2O$ (Alfa Products) were used without further purification. Borosilicate glass wool (Corning) was washed with hot 16 M HNO_3 (EM Science, Tracepur Plus), rinsed with purified water and dried. Since commercial H_2O_2 solutions contain stabilizers, we synthesized H_2O_2 by sonication of ultrapure water contained in a sealed all-glass reactor coupled to an external 358 kHz piezoelectric transducer operated at 100 W (Allied Signal-ELAC Nautik USW) under continuous argon sparging to prevent the fixation of atmospheric N_2 as NO_3^-.[56] H_2O_2 solutions were otherwise prepared by dilution of 30% H_2O_2 in purified H_2O or D_2O, adjusted to pH 5.0 or 5.3, respectively, prior to mixing with ozone solutions, and quantified by UV-

spectroscopy at $\lambda = 248$ nm ($\varepsilon_{H_2O_2} = 25$ M^{-1}cm^{-1}),[57] or by iodometry using ammonium molybdate (0.02% w/w, 1.1 mM) as a catalyst.[58] Notice that H/D $< 2 \times 10^{-5}$ for the < 1 mM H_2O_2 solutions in D_2O used in these experiments, and that H_2O_2 instantly exchanges H/D when dissolved in D_2O. [57]

Results and Discussion

Kinetic Measurements

Ozone dissolved in pure H_2O at pH 5.0, 15 ^oC, decays quasi-exponentially with a pseudo-first order rate constant: $^{1H}k_{-O_3} = 6.0 \times 10^{-5}$ s^{-1} (Fig. 1) [the numerical superscript designates the apparent reaction order; H(D) refer to $H_2O(D_2O)$, and HP(DP) to $H_2O_2(D_2O_2)$]. The addition of H_2O_2 markedly accelerates decomposition rates, $^{HP}R_{-O_3} = {}^{1HP}k_{-O_3} [O_3] = {}^{2HP}k_{-O_3} [O_3] [H_2O_2]$, with $^{2HP}k_{-O_3} = {}^{1HP}k_{-O_3}/ [H_2O_2] = 28$ M^{-1} s^{-1}, see Figs. 2 and 3. We verified that the stoichiometry of the peroxone reaction varies from $\Delta O_3/\Delta H_2O_2 \sim 2.7$ to 7.1 as $[O_3]/[H_2O_2]$ increases from 0.5 to 2.1.

Discrepancies between experimental rates and those predicted by radical chain mechanism have been variously ascribed to unspecified DOC (dissolved organic carbon) levels,[27] to spurious radical scavengers, either in the water or the reagents, or to wall reactions.[20,23,31,59-61] Unidentified impurities could alternatively accelerate or retard reaction rates. Walls were to provide for additional radical termination channels. We checked these claims by using water purified in two successive stages, and by substantially modifying the surface-to-volume ratio, S/V, in our experiments. Milli-Q water, which is produced by ion exchange and filtration followed by UV mineralization, reportedly contains ~ 5 μgC L^{-1}. The Milli-Q water-fed Corning double-distillation

system (see above) should yield ultrapure water. O_3 degradation rates (whether in the absence or presence of H_2O_2) were, however, independent (within experimental reproducibility) of water quality. We also tested whether the Sn(II) traces used as stabilizer, or the nM levels of NO_3^-, $PO_4H_2^-$, and Cl^- present in ~100 µM H_2O_2 solutions obtained by dilution of commercial H_2O_2, had a detectable effect on reaction rates, by synthesizing H_2O_2 via sonication of ultrapure water at 358 kHz under argon (see above). O_3 degradation rates were found to be independent of the H_2O_2 source.

Previous studies reported slightly faster ozone decomposition rates at low pH in vessels having smaller S/V's. The effect was ascribed to catalysis of radical terminations by reactor walls. Heterogeneous radical terminations seem unlikely to be competitive, however, under present conditions. For a stationary radical chain initiated by reaction 2b: $R_{2b} = 2.8 \times 10^6 \, M^{-1} \, s^{-1} \, [HO_2^-]$, terminated by reaction 18: $R_{18} \sim 1 \times 10^{10} \, M^{-1} \, s^{-1} \, [X]^2$ (see Table 1), where X is $\cdot OH/\cdot O_2^-$, at pH 5.0, $[O_3] = 10$ µM, $[H_2O_2] = 100$ µM, with pK_a (H_2O_2) = 11.8, the condition $R_{2b} = R_{18}$ leads to $[X]_{ss} \sim 2 \times 10^{-10}$ M. Thus, the half-life of X toward homogeneous radical recombination is of the order of a few seconds. Assuming a diffusion coefficient: $D \sim 2 \times 10^{-5} \, cm^2 \, s^{-1}$, the average diffusional displacement experienced by X in such timescale: $\delta = (2 \, D \, t)^{\frac{1}{2}} \sim 6 \times 10^{-3}$ cm, is considerably shorter than the typical dimensions of any of our reactors. Accordingly, we found identical O_3 decomposition rates in the unpacked 605 mL, S/V = 0.66 cm^{-1} reactor, in the same reactor packed with glass wool up to S/V = 2.06 cm^{-1}, or in the 3 mL, S/V = 4.5 cm^{-1} cuvette.

Model calculations

We simulated our experimental O_3 decay profiles by numerical integration of mechanisms based on the elementary reactions assembled in Table 1 using the FACSIMILE software package.[62] Reaction rate constants were obtained from updated literature reports.[27,33] The concentration of bicarbonate, a pervasive and effective OH-radical scavenger under normal laboratory conditions,[14,30,63] was used as an adjustable parameter to bring agreement between calculations and present measurements in neat H_2O at pH 5.0.

In the absence of added H_2O_2, O_3 decomposition is initiated by its reaction with OH^-. Three stoichiometries are possible: 1a and 1b that lead to $\cdot OH$, $\cdot O_3^-$, $HO_2\cdot$ or $\cdot O_2^-$ radicals, while 1c yields HO_2^-, the conjugate base of H_2O_2. Since $HO_2\cdot$ deprotonates into $\cdot O_2^-$, reaction 8, and $\cdot O_3^-$ is rapidly converted into $\cdot OH$ via reactions 12 and 13, reactions 1a and 1b are expected to be operationally indistinguishable radical initiations (See Table 1). Our calculations confirm that either initiation yields identical O_3 decomposition rates, $^HR_{-O_3}$. In contrast, any HO_2^- produced in reaction 1c must react with O_3 via reaction 2b to trigger a radical chain. Since reaction 2b competes with the difussion-controlled protonation of HO_2^- into relatively inert H_2O_2, reaction 4, in this case the onset of a chain decomposition is delayed until $[H_2O_2]$ reaches steady state.

Accordingly, we were able to simulate O_3 decay profiles in H_2O at pH 5.0 by alternatively using reactions 1a or 1b, with $[HCO_3^-] = 3$ μM, using literature rate parameters. Notice that the bicarbonate level required for the optimal fit is smaller than $[HCO_3^-]_{sat} = 5$ μM in water saturated with atmospheric CO_2 at pH 5.0 (Fig. 1).[64] We verified that calculated

$^H R_{-O_3}$'s are inversely proportional to $[HCO_3^-]$. However, we found that radical initiation via the sequence (1c + 2b) qualitatively and quantitatively fails to reproduce our $^H R_{-O_3}$ measurements (Fig. 1, dashed line). The reason can be traced to the fact that the HO_2^- formed in reaction 1c is mostly converted into H_2O_2 via reaction 4, rather than into free radicals via reaction 2b. Since $pK_a(H_2O_2) = 11.8$, and H_2O_2 is largely consumed by OH-radicals in reaction 6 (see Table 1), $[H_2O_2]$ slowly builds up at pH 5.0, while maintaining $[HO_2^-]$ at very low levels throughout: $[HO_2^-]_{ss} < 6 \times 10^{-15}$ M. Thus, current radical mechanisms are actually inconsistent with reaction 1c being either the exclusive or major reaction pathway in OH^- attack on O_3.

In the presence of modest H_2O_2 concentrations, O_3 largely reacts with HO_2^-, reactions 2a-c, rather than with OH^-.[7] Of the three possible stoichiometries, reaction 2a produces HO_3^-, the conjugate anion of HOOOH, via hydride transfer. Since reaction 2c yields inert products, it would lead to $\Delta O_3/\Delta H_2O_2 = 1$, at variance with observations. Our calculations show that in the presence of 56 μM H_2O_2, at the same total bicarbonate levels ($[HCO_3^-] = 3$ μM) required to fit O_3 losses in neat water at pH 5.0, a radical mechanism initiated by reaction 2b leads to calculated O_3 decay rates about 37 times faster than measured values (Fig. 2). The reason for the exaggerated kinetic response to H_2O_2 additions predicted by the mechanism is, of course, that HO_2^- is in equilibrium with H_2O_2, i.e.,: $[HO_2^-] = 1.6 \times 10^{-7} [H_2O_2]$ at pH 5.0. The addition of 56 μM H_2O_2 thus increases $[HO_2^-]_{ss}$ from 6×10^{-15} M to 9.0×10^{-12} M, and radical initiation rates by more than three orders of magnitude. It should be apparent that any radical scheme pivoting on reaction 2b as radical initiation will be just as sensitive to H_2O_2 additions regardless of other mechanistic features, and that the magnitude of the discrepancy lies beyond the

combined uncertainties of reported rate parameters. Furthermore, notice that any other acceptable (i.e., within reported error limits) set of propagation and/or termination reaction rate parameters chosen to minimize the divergence between calculated and experimental O_3 decomposition rates in peroxone solutions will worsen the agreement achieved in neat water. Since it is difficult to conceive alternative terminations for the $\cdot OH/\cdot O_2^-$ carriers faster than the diffusionally controlled reactions 17 and 18 (see Table 1), and disregarding unidentifed DOC as radicals scavengers, or radical annihilation on walls (which, incidentally, should have a detrimental effect on O_3 decay rates in neat H_2O as well) we do not envision any obvious mechanistic expedient that could attenuate the incidence of reaction 2b on calculated rates. Therefore, the significant failure of model calculations under specific conditions, i.e., at pH 5.0, exposes a basic flaw of radical mechanisms that seems circumscribed to reactions 1c and 2b. This negative result, by excluding the formation of paramagnetic species in the reaction between O_3 and HO_2^- within a limited set of stochiometries, suggests an alternative pathway involving a hydride transfer mechanism, reaction 2a. Below we show that solvent deuteration experiments confirm this possibility.

Isotope Effects

We found that solvent deuteration leads to a small deuterium kinetic isotope effect, KIE, in pure water: $^HR_{-O_3}/^DR_{-O_3} = 1.5 \pm 0.3$, but dramatically depresses rates in the peroxone mixture: $^{HP}R_{-O_3}/^{DP}R_{-O_3} = 19.6 \pm 4.0$ (Fig. 3). Since it is well established that O_3 decay rates are proportional to $[OH^-]$ and $[HO_2^-]$, respectively,[65] it is necessary to normalize relative rates in H_2O/D_2O by the actual $[OH^-]/[OD^-]$ and $[HO_2^-]/[DO_2^-]$ ratios

prevalent in each set of experiments to arrive at the KIE's. The difference $pK_W(D_2O)$ − $pK_W(H_2O) = 0.71$, is almost independent of temperature between 15 °C and 25 °C.[66] Therefore [OH⁻] in H_2O at pH 5.0 is essentially identical to [OD⁻] in D_2O at pD 5.71, or, considering that pD = pH + 0.41,[55] in D_2O at pH 5.3. Thus, the ratio of $^{1H}k_{-O_3}$ measured in H_2O at pH 5.0 over $^{1D}k_{-O_3}$ determined in D_2O at pH 5.3: $^{1H}k_{-O_3}/^{1D}k_{-O_3} = 1.5 \pm 0.3$, is the KIE. Similarly, since: $pK_a(D_2O_2) - pK_a(H_2O_2) = 0.69$,[67] the ratio: $[HO_2^-]/[DO_2^-] = 1.0$, also applies to peroxone solutions in H_2O and D_2O at pH 5.0, and 5.3, respectively. Therefore, the experimental ratio: $^{HP}R_{-O_3} / {}^{DP}R_{-O_3} = 19.6 \pm 4.0$, is the KIE for the ($O_3$ + HO_2^-) reaction.[68] The reported errors reflect the experimental dispersion, but do not incorporate the uncertainties of the ancillary pK_a data.

A rough estimate of the KIE: $^{H}k/^{D}k \sim \exp(1.44\ \Delta ZPE/T) = 13.5$ at 288 K, expected for transferring H/H⁻ from HO_2^- to a generic acceptor can be obtained by assuming negligible H-O_2^- bonding in the transition state, and by omitting the role of bending coordinates. $\Delta ZPE = 517$ cm⁻¹ is the difference of zero point energies associated with O-H(D) stretching vibrations in HO_2^-, $\bar{\nu}_{O-H} = 3810$ cm⁻¹, and DO_2^-, $\bar{\nu}_{O-D} = 2776$ cm⁻¹.[68,69] Against this frame of reference, the experimental KIE value represents strong evidence of a primary kinetic isotope effect associated with an elementary H/H⁻ transfer from HO_2^- into O_3 as the rate determining step.

Reactions 2a and 2b both involve H−O_2^- bond breaking and should display similar primary KIE's. However, the deuterium KIE of a putative reaction 2b will not be directly expressed in the overall rates of the radical chain decomposition of O_3 that would follow. The reason is that a chain initiated by a bimolecular reaction between O_3 and

HO_2^-, driven by bimolecular reactions between O_3 and radical carriers, and terminated by second-order radical associations, proceeds with rates $^{HP}R_{-O_3}$ proportional to $k_{2b}^{1/2}$. We verified this statement by evaluating the sensitivity of calculated O_3 decomposition rates to k_{2b} variations using a radical mechanism for peroxone chemistry exclusively initiated by reaction 2b: a twentyfold reduction of O_3 decomposition rates upon deuteration would require an untenably large KIE: $^{H}k_{2b}/$ $^{D}k_{2b}$ ~ 400. Therefore, the magnitude of the deuterium KIE for the decomposition of O_3 in peroxone, 'vis á vis' the small KIE for the decomposition of O_3 in pure water, clearly rules out a radical chain mechanism for the O_3 + H_2O_2 reaction.

Thermochemical considerations

It is possible to establish that the proposed reaction 2a is exothermic by reference to *ab initio* thermochemistry for the following reaction in the gas phase:

$$HO_3^- \rightarrow HO_2^- + O(^3P) \tag{26}$$

The calculated value: $\Delta E_{26} = + 264$ kJ mol^{-1},[43] together with: $\Delta_f H(O^3P)_g = 249$ kJ mol^{-1}, and $\Delta_f H(O_3)_g = 143$ kJ mol^{-1},[70] leads to: ΔH_{2a} ~ $\Delta_f H(O^3P)_g - \Delta_f H(O_3)_g - \Delta E_{26} = -158 \pm 20$ kJ mol^{-1}, by disregarding small solvation energy differences between HO_2^-/HO_3^- and $O_3/O(^3P)$ species. The fate of HO_3^-/H_2O_3 may involve reaction with O_3 and H_2O_2, or decomposition, reactions 27 and 28:[39]

$$HO_3^- \rightarrow OH^- + O_2 \tag{27}$$

$$HO_3^- \rightarrow \cdot OH + \cdot O_2^- \tag{28}$$

From $\Delta_fH(HO_2^-)_g = -94.6$ kJ mol^{-1},[71] $\Delta_fH(HO_2^-)_{aq} = -160.3$ kJ mol^{-1},[72] we derive:

$\Delta H_{solv}(HO_2^-) = -65.7$ kJ mol^{-1}. Therefore, from $\Delta_fH(\cdot O_2^-)_g = -43.5$ kJ mol^{-1},[73]

$\Delta_fH(HO_3^-)_g = -109.2$ kJ mol^{-1},[43] and assuming $\Delta H_{solv}(HO_2^-) \sim \Delta H_{solv}(HO_3^-) \sim$

$\Delta H_{solv}(\cdot O_2^-)$ to within ± 10 kJ mol^{-1}, we get $\Delta_fH(\cdot O_2^-)_{aq} \sim -109$ kJ mol^{-1}, and $\Delta_fH(HO_3^-)_{aq}$

~ -175 kJ mol^{-1}. Combining the preceding estimates with: $\Delta_fH(HO^-)_{aq} = -230.0$ kJ

mol^{-1},[72] $\Delta_fH(\cdot OH)_{aq} \sim 0$ kJ mol^{-1},[74] $\Delta_fH(O_2\ X^3\Sigma_g^-)_{aq} = -6.7$ kJ mol^{-1}, $\Delta_fH(O_2\ ^1\Delta_g)_{aq} = 87.4$

kJ mol^{-1} (from Ref. 73, and assuming $\Delta H_{solv}(O_2) = -\Delta H_{vap}(O_2) = -6.7$ kJ mol^{-1}) we

estimate: $\Delta H_{27} = -62$ kJ mol^{-1}, or $\Delta H_{27} = +32$ kJ mol^{-1}, whether $O_2(X^3\Sigma_g^-)$ or $O_2(^1\Delta_g)$

are formed as a products, respectively. Thus, the relative stability of ground state HO_3^-

(C_s, $^1A'$) is not thermochemical but derives from the fact that its exothermic

decomposition into $O_2(X^3\Sigma_g^-)$ is spin forbidden.[43] In contrast, reaction 28 is considerably

endothermic: $\Delta H_{28} = +66$ kJ mol^{-1}, and therefore disallowed. Thus, neither HO_3^- nor its

decomposition products are able to initiate the radical chain decomposition of O_3. H_2O_3

had been previously detected chemically and spectroscopically as the marginally stable

species (half-life ~ 2 s at pH 1.5, 298 K) formed by association of •OH and HO$_2$• radicals

during the radiolysis of oxygenated aqueous solutions.[45-47] Recently, H_2O_3 has been

positively identified as a product of the reaction of O_3 with alcohols, 1,3-dioxolanes, or

1,2 disubstituted hydrazines in non-aqueous solvents.[40,42,75] H_2O_3 has a half-life of 16 min

in dry acetone-d_6 at 293 K, and water catalyzes its decomposition.[75] Wentworth et al.

recently proposed the formation of a bactericidal trioxide in the antibody-catalyzed

oxidation of water,[50] that hydroxylates benzoic acid such as the OH-radical would, in

contrast with O_3. Thus, HO_3^-/H_2O_3 behaves as an oxidizer that simulates the chemistry of

the hydroxyl radical.[50,52] The general reactivity pattern of HO_3^-/H_2O_3 in aqueous solution is being elucidated.[76]

Finally, we can calculate $^{HP}R_{-O_3}$ rates in satisfactory agreement with experimental values (Fig. 2), by using $k_{2a} = 2.75 \times 10^6$ M^{-1} s^{-1}, $k_{2b} = 5.0 \times 10^4$ M^{-1} s^{-1}, i.e.: $k_{2a} + k_{2b} = 2.8 \times 10^6$ M^{-1} s^{-1}, $k_{2b}/k_{2a} = 0.018$, within the framework of the mechanism of Table 1. In other words, only a small contribution, if any, of the radical-forming channel, reaction 2b, to the overall stoichiometry of the $(O_3 + HO_2^-)$ reaction makes model calculations fall back in line with the actual effect of H_2O_2 additions on O_3 decomposition rates in water at pH 5.0.

Conclusions:

The magnitude of the deuterium kinetic isotope effect (KIE) for the reaction between O_3 and HO_2^- in aqueous solutions at 288 K precludes a radical chain mechanism for peroxone chemistry. The proposed stoichiometry: $O_3 + HO_2^- \xrightarrow{2a} HO_3^- + O_2$, is thermochemically feasible and, at variance with: $O_3 + HO_2^- \xrightarrow{2b} HO_3\cdot + \cdot O_2^-$, leads to predicted O_3 decomposition rates in agreement with experimental values at pH 5.0.

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Table 1
Selected reactions from the mechanism of aqueous ozone decomposition.

	Reaction	Rate constants ($M^{-1}s^{-1}$)	Ref.
1a	$O_3 + OH^- \rightarrow \cdot O_3^- + \cdot OH$	$k_1 = \Sigma\, k_{1i} = 70$	12, 65
1b	$O_3 + OH^- \rightarrow HO_2\cdot + \cdot O_2^-$		
1c	$O_3 + OH- \rightarrow HO_2- + O_2$		
2a	$O_3 + HO_2^- \rightarrow HO_3^- + O_2$	$k_2 = \Sigma\, k_{2i} = 2.8 \times 10^6$	12, 65
2b	$O_3 + HO_2^- \rightarrow HO_3\cdot + \cdot O_2^-$		
2c	$O_3 + HO_2^- \rightarrow OH^- + 2\,O_2$		
3,4	$H_2O_2 \leftrightarrow HO_2^- + H^+$	$k_3 = 7.9 \times 10^{-2};\ k_4 = 5.0 \times 10^{10}$	27
5	$O_3 + \cdot OH \rightarrow HO_2\cdot + O_2$	$k_5 = 1.1 \times 10^8$	33, 65
6	$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O$	$k_6 = 2.7 \times 10^7$	33
7	$HO_2^- + \cdot OH \rightarrow HO_2\cdot + OH^-$	$k_7 = 7.5 \times 10^9$	33
8,9	$HO_2\cdot \leftrightarrow \cdot O_2^- + H^+$	$k_8 = 7.9 \times 10^5;\ k_9 = 5 \times 10^{10}$	23
10	$O_3 + \cdot O_2^- \rightarrow \cdot O_3^- + O_2$	$k_{10} = 1.6 \times 10^9$	33
11,12	$HO_3\cdot \leftrightarrow \cdot O_3^- + H^+$	$k_{11} = 3.3 \times 10^2;\ k_{12} = 5.2 \times 10^{10}$	12
13	$HO_3\cdot \rightarrow \cdot OH + O_2$	$k_{13} = 1.1 \times 10^5$	12
14	$OH + HCO_3^- \rightarrow H_2O + CO_3\cdot^-$	$k_{14} = 1.2 \times 10^7$	33
15	$CO_3\cdot^- + HO_2^- \rightarrow CO_3^{2-} + HO_2\cdot$	$k_{15} = 3.0 \times 10^7$	33
16	$CO_3\cdot^- + H_2O_2 \rightarrow HCO_3^- + HO_2\cdot$	$k_{16} = 4.3 \times 10^5$	33
17	$\cdot OH + \cdot OH \rightarrow H_2O_2$	$k_{17} = 7.7 \times 10^9$	33
18	$\cdot OH + \cdot O_2^- \rightarrow O_2 + OH^-$	$k_{18} = 1.1 \times 10^{10}$	33
19	$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O$	$k_{19} = 9.8 \times 10^5$	33
20	$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2$	$k_{20} = 3.7 \times 10^{10}$	33
21	$HO_2\cdot + \cdot O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^-$	$k_{21} = 9.7 \times 10^7$	33
22	$CO_3\cdot^- + CO_3\cdot^- \rightarrow CO_2 + CO_4^{2-}$	$k_{22} = 2.0 \times 10^7$	33
23	$CO_3\cdot^- + \cdot O_3^- \rightarrow CO_3^{2-} + O_3$	$k_{23} = 6.0 \times 10^7$	33

24	$CO_3 \cdot^- + O_3 \rightarrow$	$k_{24} = 1.0 \times 10^5$	33
25	$CO_3 \cdot^- + HO_3 \cdot \rightarrow HCO_3^- + O_3$	$k_{25} = 1.0 \times 10^8$	33
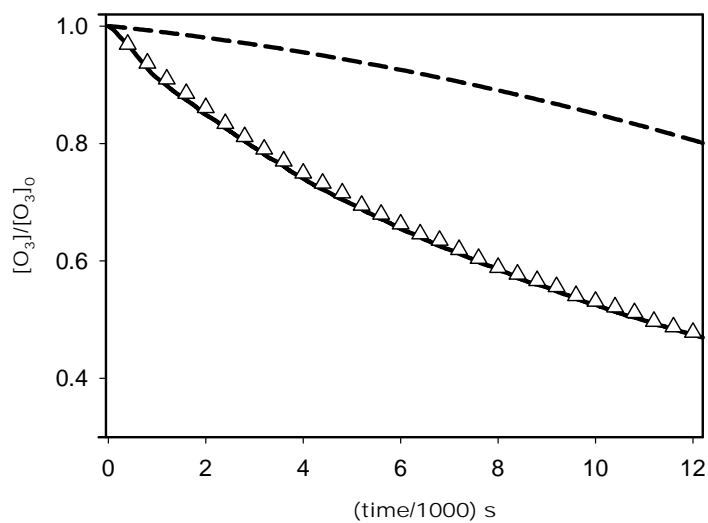
Figure 1: O_3 decay in ultrapure water at pH 5.0, $[O_3]_0 = 110$ µM. 1) ⎯ : experimental data; 2) Δ: calculated with the radical mechanism of Table 1 using reactions 1a, or 1b as initiations; 3) --- : calculated with the radical mechanism of Table 1 using reactions (1c + 2b) as initiations. Calculations performed assuming $[HCO_3^-] = 3$ µM .
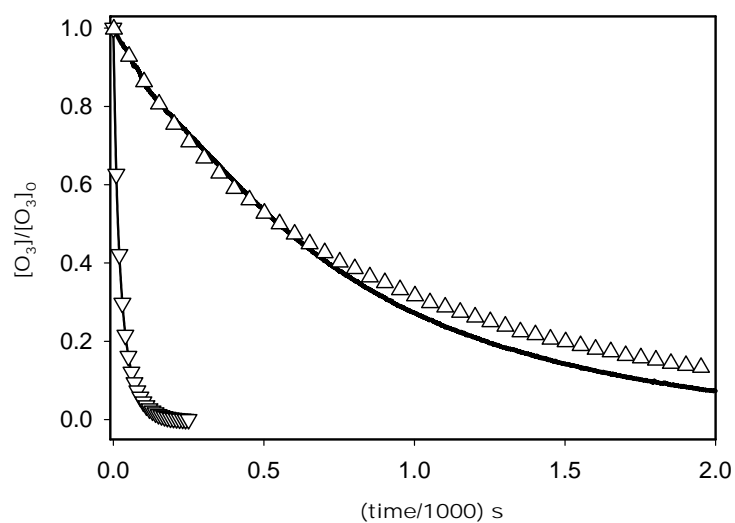
FIGURE 2

Figure 2: O_3 decay ($[O_3]_0 = 110$ μM) in the presence of $[H_2O_2] = 56$ μM at pH 5.0. 1) —— : experimental data; 2) ∇ : calculated with the mechanism of Table 1 using reactions 1a, or 1b, or (1c + 2b) as radical initiations; 3) Δ : calculated with the mechanism of Table 1 using reactions 1a, or 1b, plus reaction 2a. Calculations performed assuming $[HCO_3^-] = 3$ μM.
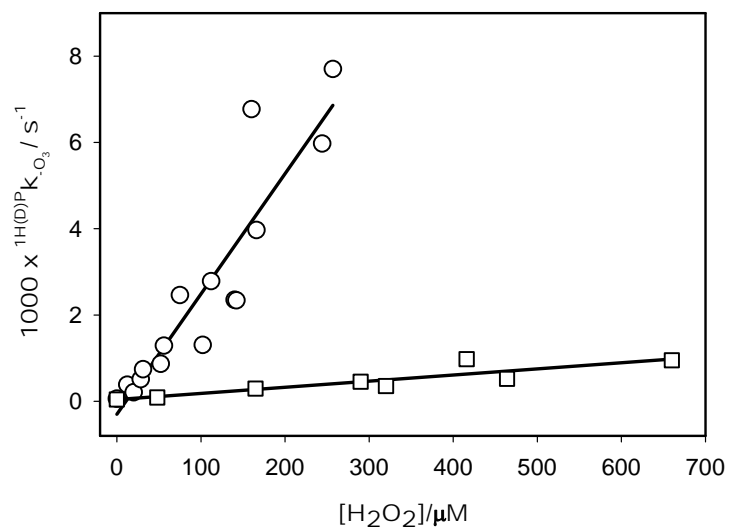
FIGURE 3

Figure 3: Experimental pseudo-first order rate constants for the decay of O_3, $^{1H(D)P}k_{-O_3}$, as function of $[H_2O_2]$. 1) O : in H_2O at pH 5.0; 2) □: in D_2O at pH 5.3. See text.