Appendix for Chapter 4

Appendix 4.1 Long residence time experiments

A-4.1.1 NO_3+2-butene

The long residence time CRDS experiments on the NO_3 oxidation of 2-butene utilized thermal decomposition of N_2O_5 as the NO_3 source. The optical cavity was identical to that used in the NO_3 study (Chapter 3). An oxygen carrier gas was flowed over a N_2O_5 trap (P_{vapor} = 1.5 Torr) and into a heated (T = 40˚C) Pyrex ringdown cell. 2-butene (10 Torr of a 15% 2-butene/N_2 mixture) was slowly injected into the system. Residence times ranged from 500 milliseconds to 1 second. On this timescale, products from secondary chemistry were collected in the cell.

In Fig. 4.1, we showed that the different reaction pathways of the NO_3-peroxy radical lead to alcohol and carbonyl compound production. Hydroxyl (OH) overtones and alkyl (CH) stretches have absorptions in the NIR region, which can be observed using the pulsed CRDS apparatus. The hydroxyl peroxy radical (HO_2) is also formed in the oxidation scheme (blue box in Fig. 4.1). HO_2 reacts not only with the NO_3-peroxy radical, but with NO_3 itself to form the hydroxyl radical (OH):[1]

$$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2 \qquad \text{(A-4.1 a)}$$

$$\rightarrow HNO_3 + O_2 \qquad \text{(A-4.1 b)}$$

$$k_{298K}\,(HO_2 + NO_3) < 3.5 \times 10^{-12}\ cm^3\ molec^{-1}\ s^{-1} \qquad \text{(A-4.1 c)}$$

OH is very reactive and attacks 2-butene to initiate its own complex oxidation scheme:

$OH + R{=}R' + O_2 \rightarrow R\text{-}R'(OH)OO$ (OH-peroxy radical) (A-4.2)

The CRD spectrum of the long residence experiments is shown in Fig. A-4.1. The observed products are red shifted from the observed peroxy radical absorptions. Spectral identification is difficult without more chemical information. We mentioned at the end of Chapter 4 that we plan to couple a chemical ionization mass spectrometer to the CRDS apparatus. It will be interesting to repeat the long residence experiments in the extended apparatus.

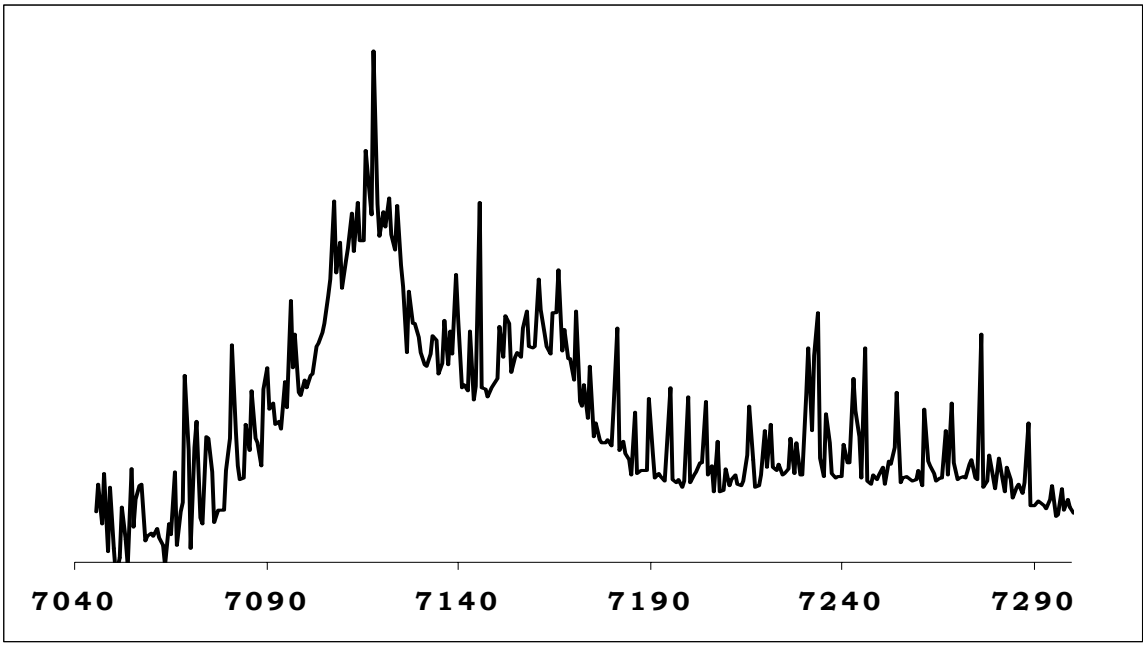

Figure A-4.1. CRD spectrum from long residence cell experiments with NO_3 + 2-butene.

A-4.1.2 O_3+2-butene

The oxidation of 2-butene by ozone (O_3) has been studied by many groups:[2-11]

$O_3 + CH_3HC=CHCH_3 \rightarrow CH_3C(O)H + CH_3CHOO$ (A-4.3)

The latter product CH_3CHOO is called the Criegee intermediate and is both a biradical and zwitterion (Fig. A-4.2). The fate of the Criegee intermediate is of strong interest to the atmospheric community, as it has been predicted to be a possible OH and epoxide source:

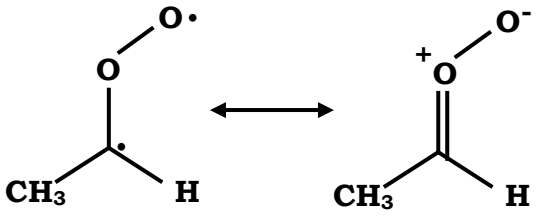

Figure A-4.2. The Criegee intermediate, drawn as a biradical (left) and zwitterion (right).

$CH_3CHOO \rightarrow CH_3HCOO$ (dioxirane) (A-4.4 a)

$\rightarrow [H_2C=CH(OOH)]^*$ (hydroperoxide) (A-4.4 b)

$[H_2C=CH(OOH)]^* \rightarrow HCOCH_2 + OH$ (A-4.4 c)

We examined the oxidation products using the same long residence time CRDS apparatus as above. Oxygen was flowed through an ozonizer before interacting with the 2-butene at room temperature in the flow cell. Similarities in the observed CRD spectra (Fig. A-4.1 and Fig. A-4.3) suggest parallel reaction pathways for NO_3 and O_3 oxidation of 2-butene.

CRD spectra were also collected to the blue, in the 7720-7850 cm^{-1} region, for both NO_3 and O_3-initiated oxidation of 2-butene. We observed identical spectra for the two experiments. (Fig. A-4.4). The structure of the spectra indicated a small compound. We first thought that the absorption belonged to HO_2; however the absorption did not match the published spectrum of the $\tilde{A} \leftarrow \tilde{X}$ transition of HO_2.[12] It could be that

the products in the spectra are from OH oxidation of alkenes. Further research is clearly needed.

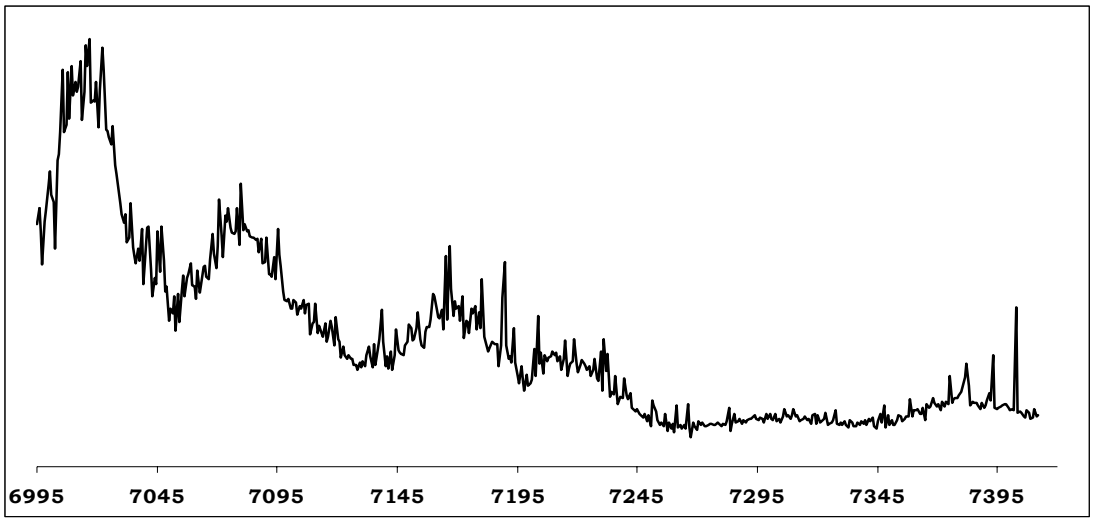

Figure A-4.3. CRD spectrum from a long residence cell experiment with O_3 + 2-butene.

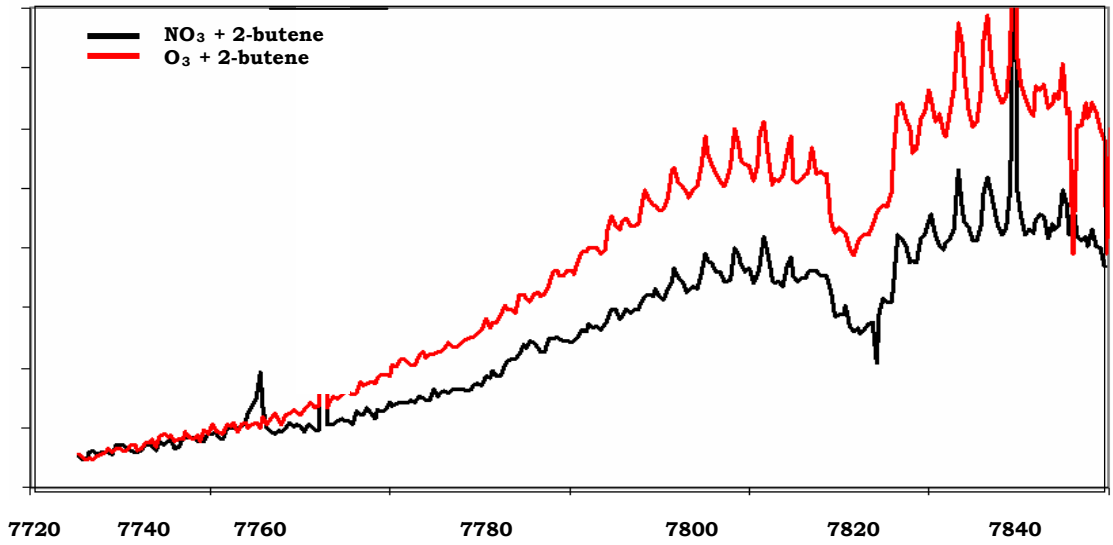

Figure A-4.4. CRD spectra from long residence cell experiments with NO_3 + 2-butene and O_3 + 2-butene.

Appendix 4.2 References

(1) Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M.; Moortgat, G. K.; Wine, P. H.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; Finlayson-Pitts, B. J.; Huie, R. E.; Orkin, V. L. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 15,* 2006.

(2) Hasson, A. S.; Orzechowska, G.; Paulson, S. E. *Journal of Geophysical Research-Atmospheres* **2001**, *106*, 34131.

(3) Orzechowska, G. E.; Paulson, S. E. *Journal of Physical Chemistry A* **2005**, *109*, 5358.

(4) Grosjean, D.; Grosjean, E.; Williams, E. L. *Environmental Science & Technology* **1994**, *28*, 186.

(5) Horie, O.; Moortgat, G. K. *Atmospheric Environment Part a - General Topics* **1991**, *25*, 1881.

(6) Rickard, A. R.; Johnson, D.; McGill, C. D.; Marston, G. *Journal of Physical Chemistry A* **1999**, *103*, 7656.

(7) Donahue, N. M.; Kroll, J. H.; Anderson, J. G.; Demerjian, K. L. *Geophysical Research Letters* **1998**, *25*, 59.

(8) Drozd, G. T.; Kroll, J.; Donahue, N. M. *Journal of Physical Chemistry A* **2011**, *115*, 161.

(9) Lambe, A. T.; Zhang, J. Y.; Sage, A. M.; Donahue, N. M. *Environmental Science & Technology* **2007**, *41*, 2357.

(10) Chew, A. A.; Atkinson, R. *Journal of Geophysical Research - Atmospheres* **1996**, *101*, 28649.

(11) Gutbrod, R.; Kraka, E.; Schindler, R. N.; Cremer, D. *Journal of the American Chemical Society* **1997**, *119*, 7330.

(12) Fink, E. H.; Ramsay, D. A. *J. Mol. Spectrosc.* **2002**, *216*, 322.