

Laboratory studies of the self and cross reactions of atmospheric peroxy radicals

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Abstract

My studies focused on the self and cross reactions of peroxy radicals (RO_2). These are important gas phase reactions in the atmosphere when concentrations of nitrogen oxides are low. Hydroperoxide products of these reactions can undergo further reaction to form aerosol precursors, making RO_2 reactions critical to aerosol formation as well. The occurrence of multiple simultaneous reactions is frequently unavoidable when working with radical reactions. Self reactions of RO_2 further complicate matters by producing another peroxy radical (HO_2) through one of their product channels. Time resolved spectroscopic probes in the ultraviolet and near-infrared, specifically targeting each reactant, were used to measure the rate coefficients for the self and cross reactions of HO_2 and ethyl peroxy radicals ($\text{C}_2\text{H}_5\text{O}_2$). In addition the product branching fraction leading to HO_2 was determined for the $\text{C}_2\text{H}_5\text{O}_2$ self reaction with results very different from the literature.

Further work on the self reaction branching fractions of methyl peroxy, ethyl peroxy, and propyl peroxy was done to try and resolve the discrepancy with the literature. A photoionization mass spectrometry technique was used to monitor all of the stable reaction products on the timescale of the reaction. The literature work had used end product studies after the reactions had completed to measure all of the stable products. Results from the photoionization studies appear to agree with the spectroscopic work for the $\text{C}_2\text{H}_5\text{O}_2$ self reaction, indicating that additional secondary chemistry may have skewed the results in the literature.

Aerosol nucleation observed in low temperature experiments on the HO_2 self reaction was another area of work. Radical chemistry is the main driver of gas phase

atmospheric cycles, but is not currently thought to be at the center of new particle formation. Radical-molecule complexes between HO₂ and a number of species including methanol, water, and acetone could act as particle seeds at low temperature due to the stability of their hydrogen bonds. Most of the nucleation work described is on the HO₂-methanol complex, but all three were investigated. Lastly, the experimental calibrations and general procedures that went on throughout all this work are described.

Table of Contents

1	Introduction.....	1-1
1.1	A brief history and motivation.....	1-1
1.2	Thesis work.....	1-5
1.3	Challenges ahead	1-6
1.4	References.....	1-8
2	Near-IR kinetic spectroscopy (IR-KS) of the HO₂ and C₂H₅O₂ self and cross reactions.....	2-1
2.1	Introduction.....	2-1
2.2	Experimental.....	2-4
2.3	Results and analysis	2-10
2.4	Discussion.....	2-24
2.5	Conclusion	2-36
2.6	References.....	2-40
3	Peroxy radical self reactions studied by photoionization mass spectrometry....	3-1
3.1	Introduction.....	3-1
3.2	Experimental.....	3-2
3.3	Results and analysis	3-9
3.4	Discussion.....	3-43
3.5	Conclusion	3-54
3.6	References.....	3-56
4	Photoinduced nucleation of low temperature hydroperoxy radical chemistry..	4-1
4.1	Introduction.....	4-1
4.2	Experimental.....	4-3
4.3	Results.....	4-5
4.4	Discussion.....	4-17
4.5	Conclusion	4-20
4.6	References.....	4-22
5	Experimental work	5-1
5.1	Experimental setup.....	5-1

5.2	Absorption measurements.....	5-3
5.3	Pressure dependence of the HO ₂ and RO ₂ self reactions.....	5-13
5.4	Summary of path length, pressure dependence, and CH ₃ OH effect	5-27
5.5	NIR probe.....	5-28
5.6	Sensitivity of UV and NIR probes	5-36
5.7	References.....	5-37

List of Figures

Chapter 2

- Figure 2-1. (A)–(B) Example fit of NIR and UV data, respectively, for $\text{HO}_2 + \text{C}_2\text{H}_5\text{O}_2$
 (C)–(D) Example fit of IR and UV data for the $\text{C}_2\text{H}_5\text{O}_2$ self reaction 2-13
- Figure 2-2. Plot of k_2 vs. $[\text{C}_2\text{H}_2\text{O}_2]_0 / [\text{HO}_2]_0$ for T 221-296 K. Error bars are examples of data precision..... 2-15
- Figure 2-3. (A)–(B) Fits to the NIR and UV data, respectively, for $\text{C}_2\text{H}_5\text{O}_2$ self reaction while holding α at three different values 2-16
- Figure 2-4. Comparison of k_2 with previous work..... 2-17
- Figure 2-5. Comparison of k_{3obs} 2-20
- Figure 2-6. Comparison of α with previous work. 2-22
- Figure 2-7. Comparison of the fitted values for k_2 using either the previous recommendation for α or the value measured in this study. 2-25

Chapter 3

- Figure 3-1. Schematic of experimental system..... 3-3
- Figure 3-2. Four stable products of the $\text{C}_2\text{H}_5\text{O}_2$ self reaction..... 3-13
- Figure 3-3. (A) 1-D mass spectrum from the PIE data set. (B) PIE of acetaldehyde and ethene. (C) Mass contamination appears to have caused a discrepancy in the ethanol PIE. (D) PIE of ethyl hydroperoxide..... 3-14
- Figure 3-4. 1-D mass spectrum of four different pressures 3-15
- Figure 3-5. Some of the unidentified products and their likely parents..... 3-18
- Figure 3-6. (A) Removing acetaldehyde mass contamination from m/z 45 PIE. (B) A comparison of the PIE curves for the larger masses and some of their possible dissociation products 3-19
- Figure 3-7. Ratio of CH_3CHO counts to $\text{C}_2\text{H}_5\text{OH}$ counts and α values 3-21

Figure 3-8. Ratios of $[\text{CH}_3\text{CHO}] / [\text{C}_2\text{H}_5\text{OOH}]$ and $[\text{C}_2\text{H}_5\text{OH}] / [\text{C}_2\text{H}_5\text{OOH}]$	3-22
Figure 3-9. Expected products and reactants of $\text{C}_2\text{H}_5\text{O}_2$ self reaction using the DEK precursor chemistry	3-24
Figure 3-10. 1-D mass spectra from the DEK chemistry.....	3-25
Figure 3-11. Stable products of the 6 Torr, 248 nm, high O_2 data set in Run 2.....	3-26
Figure 3-12. The 1-D mass spectra in the m/z 4X range from the four data sets taken during Run 2.....	3-27
Figure 3-13. m/z 90 was not observed in every data set in Run 2	3-28
Figure 3-14. R plotted for the four data sets of Run 2	3-30
Figure 3-15. The ratios $[\text{CH}_3\text{CHO}] / [\text{C}_2\text{H}_5\text{OOH}]$ and $[\text{C}_2\text{H}_5\text{OH}] / [\text{C}_2\text{H}_5\text{OOH}]$ for the four data sets in Run 2.....	3-32
Figure 3-16. Mass resolution in the 4X range for Run 3	3-34
Figure 3-17. The three major products -HCHO, CH_3OH , and CH_3OOH - along with the reactant CH_3O_2 from the methyl peroxy self reaction.....	3-35
Figure 3-18. PIE scan of major reactants and products for the CH_3O_2 self reaction.....	3-36
Figure 3-19. (A) Mass resolution of the major reactants and products was good. (B) R for the CH_3O_2 self reaction	3-37
Figure 3-20. Major products and reactants for $\text{C}_3\text{H}_7\text{O}_2$ self reaction using the OxCl precursor chemistry.	3-38
Figure 3-21. PIE of major products and reactants from $\text{C}_3\text{H}_7\text{O}_2$ self reaction using OxCl precursor chemistry.	3-40
Figure 3-22. Other masses of interest from the $\text{C}_3\text{H}_7\text{O}_2$ reaction using OxCl precursor chemistry.	3-41
Figure 3-23. Major products and reactants using DPK chemistry for $\text{C}_3\text{H}_7\text{O}_2$	3-42
Figure 3-24. PIE identification using DPK precursor chemistry for $\text{C}_3\text{H}_7\text{O}_2$	3-43
Figure 3-25. Comparison of α measurements	3-52

Chapter 4

Figure 4-1. UV absorbance from the HO ₂ self reaction and the unexpected large absorbance at longer time scales.	4-6
Figure 4-2. Temperature dependence of the extinction in both the NIR and UV.....	4-7
Figure 4-3. Dependence of the UV extinction on CH ₃ OH concentration.....	4-8
Figure 4-4. Dependence of the peak UV extinction on [CH ₃ OH] at three different initial radical concentrations.....	4-9
Figure 4-5. Extinction in both the NIR and UV increases as a function of initial radical concentration.	4-10
Figure 4-6. Peak UV extinction as a function of initial radical concentration for various RH_{CH_3OH}	4-11
Figure 4-7. Comparison of extinction between the UV and NIR at higher [HO ₂] ₀	4-12
Figure 4-8. Changing the chemistry of the nucleation to include C ₂ H ₅ O ₂ provided some insight into the seed molecule	4-14
Figure 4-9. Greater extinction was observed in the absence of O ₂ , suggesting polymerization of the CH ₂ OH radical.	4-16

Chapter 5

Figure 5-1. IRKS apparatus.	5-1
Figure 5-2. Setup for penray lamp experiments.....	5-5
Figure 5-3. Curvature in the absorbance plot for N ₂ O was seen when using the PMT with the bialkali photocathode, but not when using the Cs-I photocathode.....	5-7
Figure 5-4. [CH ₃ OH] measured by the Hg lamp agrees with the concentration determined by the flows when the bubbler pressure is above 300 Torr.....	5-9
Figure 5-5. Initial radical dependence of the HO ₂ self reaction in the UV. Low initial concentrations were influenced by other removal processes	5-14
Figure 5-6. Initial radical dependence of the HO ₂ self reaction in the NIR.....	5-15

Figure 5-7. Pressure dependence of k_{HO_2} in both the UV and NIR compared with the literature value.....	5-16
Figure 5-8. Pressure dependence of $k_{HO_2}(UV)$ under conditions where no purge gas was used and the path length was fixed by the window - window distance.	5-17
Figure 5-9. RO_2 self reaction dependence on initial radical concentration.	5-19
Figure 5-10. Pressure dependence of $C_2H_5O_2$ self reaction did not change with or without the purge gas.....	5-21
Figure 5-11. A comparison of the different k_{HO_2} values from the work in Chapter 2 depending on whether the UV, IR, or UV and IR together were fit.	5-24
Figure 5 12. Diagram of the wavelength modulation setup for the NIR diode laser	5-29
Figure 5 13. HO_2 spectrum after background ratio.....	5-31
Figure 5 14. Baseline dip in $HO_2 + HO_2$ chemistry.....	5-33
Figure 5 15. DC signal from the detector after the excimer fires.	5-34
Figure 5 16. A signal is evident at the HO_2 frequency with only Cl_2 and O_2 present. A good baseline is also shown, determined by looking at its behavior while not on the HO_2 absorption line.	5-35

List of Tables

Chapter 2

Table 2-1. Chemical model used for fitting HO ₂ and C ₂ H ₅ O ₂ system of reactions.....	2-12
Table 2-2. Measured rate constant values for HO ₂ + C ₂ H ₅ O ₂	2-18
Table 2-3. Summary of results for the HO ₂ + C ₂ H ₅ O ₂ reaction rate constant	2-18
Table 2-4. Results of C ₂ H ₅ O ₂ self reaction at all temperatures and pressures	2-21
Table 2-5. Summary of experimental conditions for the determination of the HO ₂ + C ₂ H ₅ O ₂ reaction rate constant.....	2-38
Table 2-6. Summary of previous experiments on C ₂ H ₅ O ₂ + C ₂ H ₅ O ₂	2-39

Chapter 3

Table 3-1. All the reproducible masses identified in Runs 1A and 2 as well as their species assignment and a description of how their time trace appeared.	3-20
Table 3-2. Conditions and α values measured for each of the data sets in Run 2.	3-31

Chapter 5

Table 5-1. Summary of all the molecules and λ where absorption measurements were made.	5-5
Table 5-2. Path length measurements at different residence times, pressures, and amount of purge flow as a percentage of the total reactant flow.	5-10
Table 5-3. Simulation of purge effect on $k_{HO_2}(UV)$	5-26