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

Thesis by

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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 ($C_2H_5O_2$). In addition the product branching fraction leading to HO_2 was determined for the $C_2H_5O_2$ 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 $C_2H_5O_2$ 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 HO_2 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 HO_2 - methanol complex, but all three were investigated. Lastly, the experimental calibrations and general procedures that went on throughout all this work are described.

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