Synergy of hydrogen-bonding in the reactions of Criegee intermediates

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Unsaturated hydrocarbons are emitted into our atmosphere in large quantities from both human and natural sources. Ozonolysis of unsaturated hydrocarbons forms highly reactive Criegee intermediates (carbonyl oxides), which play important roles in atmospheric chemistry. We have studied the ultraviolet spectra of a few Criegee intermediates, including formaldehyde oxide (CH_2OO), acetaldehyde oxide (CH_3CHOO), acetone oxide ($(CH_3)_2COO$), methyl vinyl ketone oxide ($CH_3(C_2H_3)COO$) and methacrolein oxide ($CH_2C(CH_3)CHOO$). The UV spectra have laid the foundation for the optical probe of these important species.

We have quantified the most important decay pathways—unimolecular decay and reactions with water vapor—for these Criegee intermediates in the atmosphere. The kinetic data are crucial for determining their atmospheric fates. For fundamental chemistry, we have found a few interesting aspects. (i) The reactivity of a Criegee intermediate depends strongly on its structure. Various isomers may have reaction rate coefficients which are different by several orders of magnitude. (ii) Resonance stabilization due to the extended conjugation of a vinyl substitution group has a strong effect in the reactivity. (iii) Water molecule may catalyze reactions of Criegee intermediates through the mechanism of double H-atom transfer.

In particular, we found a strong synergy effect of water and ammonia molecules in their reaction with Criegee intermediates.

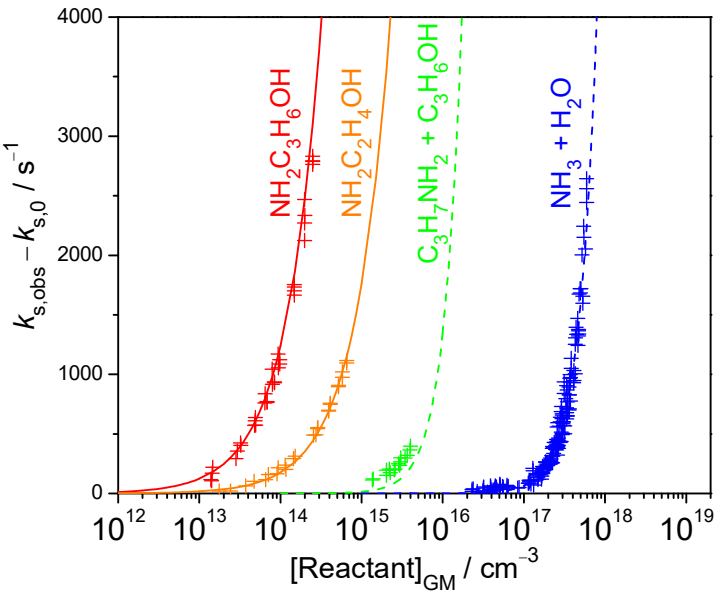

Fig. 1 Effective first-order rate coefficients of *syn*-CH_3CHOO reactions with various H-bonding molecules. $[Reactant]_{GM} = [A]^{0.5}[B]^{0.5}$ is chosen to represent the effective reactant concentration if two H-bonding molecules, A and B, are involved. The symbols are the actual experimental data points; the solid lines are estimated with the experimental bimolecular reaction rate coefficients whereas the dashed lines are estimated with the experimental termolecular reaction rate coefficients.