Structure Dependent Reactivity of Criegee Intermediates and the Implications in Atmospheric Chemistry

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Ozonolysis of alkenes produces highly reactive Criegee intermediates, which are thought to play an important role in atmospheric chemistry, in particular, the oxidation of SO_2. The SO_3 product would further react with water to form H_2SO_4, an important constituent of aerosols and acid rain. However, the impact of such oxidation reactions is affected by the reactions of Criegee intermediates with water vapor, because of high water concentrations in the troposphere. We have studied a few simple Criegee intermediates at near atmospheric conditions by using transient UV absorption. We found the CH_2OO and *anti*-CH_3CHOO react with water dimer very quickly, such that their steady-state concentrations would be low in the troposphere [1]. On the other hand, we demonstrated that water vapor does not react with dimethyl substituted Criegee intermediate $(CH_3)_2COO$, at least not fast enough to significantly consume $(CH_3)_2COO$ in the troposphere. And $(CH_3)_2COO$ reacts with SO_2 three times faster than CH_2OO does, indicating Criegee intermediates of a structure similar to $(CH_3)_2COO$ are potential candidates for an efficient oxidant in the atmospheric SO_2 oxidation. In addition, a significant pressure dependence was observed for the reaction of $(CH_3)_2COO$ with SO_2, suggesting the use of low pressure rate may underestimate the impact of this reaction [2]. Our works show that the reactivity of a Criegee intermediate towards water vapor strongly depends on its structure, which will influence the main decay pathways and steady-state concentrations for various Criegee intermediates in the atmosphere.

References

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[2] Hao-Li Huang, Wen Chao, and Jim Jr-Min Lin, Proc. Natl. Acad. Sci. USA, 112(35), 10857–10862 (2015).