2.142 Relative reactivity of stabilized Criegee intermediates from hydrocarbon ozonolysis toward carboxylic acids and water vapor.

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Abstract:

Criegee intermediates generated from hydrocarbon ozonolysis have potential importance in atmospheric oxidation and secondary organic aerosol formation. While Criegee intermediates with relatively simple structures have been extensively investigated by direct kinetic studies in recent years, there is limited information on chemical reactivities of more complicated and atmospheric relevant Criegee intermediates. Here, we report relative reactivity measurement studies of Criegee intermediates toward carboxylic acids and water vapor. Experiments were performed at atmospheric pressure using a glass flow tube, in which Criegee intermediates were generated from hydrocarbon ozonolysis and allowed to react with carboxylic acids and water vapor. Reaction products from the Criegee intermediate and carboxylic acid were monitored using a chemical ionization mass spectrometer as a function of the carboxylic acid or water vapor concentration. In studies on Criegee intermediates generated from isoprene ozonolysis, we found that the C_1 Criegee intermediate, CH_2OO, has high reactivity toward water dimer, $(H_2O)_2$, while most of the C_4 Criegee intermediates have low reactivity toward water vapor. The results are consistent with recent experimental and theoretical studies which suggest that the chemical structure of a Criegee intermediate strongly affects its reactivity toward water vapor.