Direct Measurement of the reaction of Criegee Intermediates with SO\(_2\)

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Carbonyl oxides, known as “Criegee intermediates” after Rudolf Criegee, who proposed their participation in ozonolysis, are important species in tropospheric chemistry. Most carbonyl oxides in the troposphere are produced by ozonolysis, but other tropospheric reactions can also produce Criegee intermediates. However, until recently no Criegee intermediate had been observed in the gas phase, and information about the reactivity of Criegee intermediates in gas-phase ozonolysis or in the troposphere have relied on indirect determinations.

In this work, the reactions of the two simplest Criegee intermediates, CH\(_2\)OO and CH\(_3\)CH\(_2\)OO with SO\(_2\) have been measured by laser photolysis / tunable synchrotron photoionization mass spectrometry. Diiodomethane and Diiodoethane photolysis produces RI radicals, which react with O\(_2\) to yield ROO + I, where R = CH\(_2\) or CH\(_3\)CH\(_2\). The Criegee intermediates are reacted with a large excess of SO\(_2\) and both the disappearance of Criegee intermediates and the formation of reaction products are observed by time-resolved photoionization mass spectrometry. Figure 1 shows a second order plot for the reaction of CH\(_3\)CH\(_2\)OO with SO\(_2\). The final analysis yields rate coefficients at 298 K (and 4 Torr) of (3.9 ± 0.7) \times 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for CH\(_2\)OO + SO\(_2\) and of (2.4 ± 0.3) \times 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for CH\(_3\)CH\(_2\)OO + SO\(_2\).

The direct determinations of the rate constants for CH\(_2\)OO and CH\(_3\)CH\(_2\)OO with SO\(_2\), are considerably higher than previous estimates. Placing the present results into a tropospheric chemistry model implies a substantial role of Criegee intermediates in sulfate chemistry. Oxidation of SO\(_2\) by CBs will lead to SO\(_3\) that will from H\(_2\)SO\(_4\) rapidly on reaction with water. The production of H\(_2\)SO\(_4\) via Criegee radical reaction will be at least as important as the OH radical production route. It is well known that sulfuric acid is a key component in the secondary particle formation in the atmosphere and thus this new route to form sulfuric acid could have a significant impact on aerosol formation in the atmosphere.

References
(2) Welz, O. et al., Science 2012, 335, 204.