Direct Measurement of the reaction of Criegee Intermediates with SO_2

Carl J. Percival,[1] Oliver Welz,[2] Arkke J. Eskola,[2] John D. Savee,[2] David L. Osborn,[2] Dudley E. Shallcross,[3] and Craig A. Taatjes.[2]

[1]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK

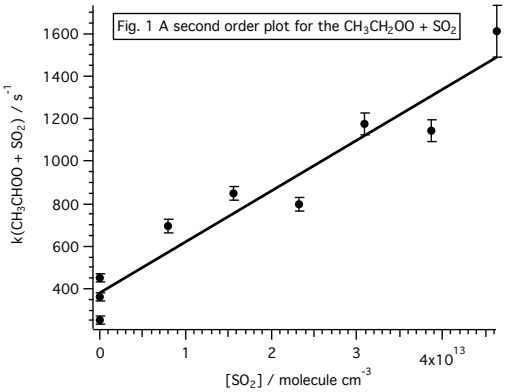
[2]Combustion Research Facility, Sandia National Laboratories, 7011 East Ave., MS 9055, Livermore, California 94551 USA.

[3]School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.

* Corresponding author: carl.percival@manchester.ac.uk

Carbonyl oxides, known as "Criegee intermediates" after Rudolf Criegee, who proposed their participation in ozonolysis,[1] 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.[2, 3] However, until recently[2, 4] 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.[5, 6]

In this work, the reactions of the two simplest Criegee intermediates, CH_2OO and CH_3CH_2OO 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, wher R = CH_2 or CH_3CH_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_3CH_2OO with SO_2 The final analysis yields rate coefficients at 298 K (and 4 Torr) of (3.9 ± 0.7) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $CH_2OO + SO_2$ and of (2.4 ± 0.3) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $CH_3CH_2OO + SO_2$.



The direct determinations of the rate constants for CH_2OO and CH_3CH_2OO with SO_2, are considerably higher than previous estimates. Placing the present results into a tropospheric chemistry model[7] 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_2SO_4 rapidly on reaction with water. The production of H_2SO_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

(1) Criegee, R.; Wenner, G. *Liebigs. Ann. Chem.* **1949**, 564, 9.
(2) Welz, O. et al., *Science* **2012**, 335, 204.
(3) Asatryan, R.; Bozzelli, J.W. *Phys. Chem. Chem. Phys.* **2008**, 10, 1769.
(4) Taatjes, C. A. et al., *J. Am. Chem. Soc.*, **2008**, 130, 11883.
(5) Johnson, D.;. Marston, G. *Chem. Soc. Rev.* **2008**, 37, 699.
(6) Donahue, N. M. et al., *Phys. Chem. Chem. Phys.* **2011**, 13, 10848.
(7) Archibald, A.T. *et al.*, *Atmos. Chem. Phys.* **2010**, 10, 8097.