

# Kinetic studies of Criegee intermediate reactions with SO<sub>2</sub> and RCOOH

Rabi Chhantyal-Pun,<sup>1\*</sup> Brandon Rotavera,<sup>2</sup> Arkke J. Eskola,<sup>2</sup> Lucy Blacker,<sup>1</sup> Matilda Ashcroft,<sup>1</sup> M. Anwar H. Khan,<sup>1</sup> David L. Osborn,<sup>2</sup> Craig A. Taatjes,<sup>2</sup> Carl J. Percival,<sup>3</sup> Dudley E. Shallcross,<sup>1</sup> and Andrew J. Orr-Ewing<sup>1</sup>

<sup>1</sup> School of Chemistry, University of Bristol, Bristol, UK

<sup>2</sup> Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA

<sup>3</sup> The School of Earth, Atmospheric and Environmental Science, University of Manchester, Manchester, UK

\* Corresponding author: rc13564@bristol.ac.uk

Criegee intermediates are important species formed during the ozonolysis of alkenes. Direct measurement studies have shown that reactions of stabilized Criegee intermediates with various species like SO<sub>2</sub>, NO<sub>2</sub> and carboxylic acids may have a significant effect in tropospheric chemistry.<sup>1,2</sup> Reaction rates of Criegee intermediates with simple carboxylic acids like HCOOH and CH<sub>3</sub>COOH have been shown to be near the collision limit and may be a significant sink for these otherwise stable species in the atmosphere.<sup>3,4</sup> Results obtained from our time-resolved Cavity Ring-Down Spectroscopy apparatus<sup>5</sup> for reactions of the Criegee intermediates, CH<sub>2</sub>OO and (CH<sub>3</sub>)<sub>2</sub>COO with SO<sub>2</sub> and carboxylic acids with various degree of halogenation (HCOOH, CH<sub>3</sub>COOH, CF<sub>3</sub>COOH, CF<sub>3</sub>CF<sub>2</sub>COOH, CClF<sub>2</sub>COOH and CHCl<sub>2</sub>COOH) will be presented, together with a Structure Activity Relationship based on these observations. Structure characterization of the products from these reactions using the Multiplexed PhotoIonization Mass Spectrometry apparatus as well as implications for Secondary Organic Aerosol formation, assessed using the global atmospheric model STOCHEM, will also be discussed.

## References

- (1) Welz, O.; Savee, J. D.; Osborn, D. L.; Vasu, S. S.; Percival, C. J.; Shallcross, D. E.; Taatjes, C. A. *Science*, **2012**, 335, 204-207.
- (2) Percival, C. J.; Welz, O.; Eskola, A. J.; Savee, J. D.; Osborn, D. L.; Topping, D. O.; Lowe, D.; Utembe, S. R.; Bacak, A.; McFiggans, G.; Cooke, M. C.; Xiao, P.; Archibald, A. T.; Jenkin, M. E.; Derwent, R. G.; Riipinen, I.; Mok, D. W. K.; Lee, E. P. F.; Dyke, J. M.; Taatjes, C. A.; Shallcross, D. E.; *Faraday Discuss.*, **2013**, 165, 45-73
- (3) Welz, O.; Eskola, A. J.; Sheps, L.; Rotavera, B.; Savee, J. D.; Scheer, A. M.; Osborn, D. L.; Lowe, D.; Booth, A. M.; Xiao, P.; Khan, M. A. H.; Percival, C. J.; Shallcross, D. E.; Taatjes, C. A.; *Angew. Chem. Int. Ed.*, **2014**, 53, 4547-4550.
- (4) Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A.; *J. Phys. Chem. A*, **2004**, 108, 615-620.
- (5) Chhantyal-Pun, R.; Davey, A.; Shallcross, D. E.; Percival, C. J.; Orr-Ewing, A. J.; *Phys. Chem. Chem. Phys.*, **2015**, 17, 3617-3626.