

H₂SO₄ formation from olefin ozonolysis in the presence of SO₂:

Influence of water vapour content and temperature

T. Berndt¹, T. Jokinen^{1,2}, M. Sipilä², R. L. Mauldin III^{2,3}, H. Herrmann¹, F. Stratmann¹, H. Junninen², M. Kulmala²

¹Leibniz Institute for Tropospheric Research, Leipzig, 04318, Germany

²Department of Physics, University of Helsinki, Helsinki, 00014, Finland

³University of Colorado, Boulder, Colorado, 80302, United States

Keywords: H₂SO₄, stabilized Criegee Intermediate, mass spectrometry

Presenting author email: berndt@tropos.de

For more than a decade the formation of new aerosol particles in the atmosphere has been the subject of intense studies in both, field and laboratory. H₂SO₄ was ascertained to play a central role in this process. A dominant pathway of H₂SO₄ generation represents the OH radical initiated oxidation of SO₂. Recently it was discovered that also other oxidants than OH radicals, very likely stabilized Criegee Intermediates (sCI), can significantly contribute to H₂SO₄ formation under atmospheric conditions (Mauldin *et. al.*, 2012). Criegee Intermediates originate from the reaction of ozone with unsaturated substances (olefins) and occur with different structures associated with a different chemical behaviour. Unfortunately, the formation yields of sCI as well as their chemical reactivity toward atmospheric trace gases (SO₂, acids, etc.) and water vapour are not well characterized and are, at least partly, subject of speculation. Welz *et. al.* (2012) reported on unexpectedly high rate coefficients of the reaction of CH₂OO with SO₂ and other trace gases. As a result from our laboratory, clearly lower rate coefficients for the reaction of a series of sCI with SO₂ have been measured (Berndt *et. al.*, 2012). Generally, there is a debate at the moment regarding the relevance of the sCI + SO₂ reaction in competition with the probably, much more important sCI + H₂O pathway.

This experimental study focuses on H₂SO₄ formation from the ozonolysis of tetramethylethylene (TME) and trans-2-butene in the presence and absence of an OH radical scavenger at atmospheric pressure conducted in the temperature range of 278 - 343 K and a relative humidity of 8 - 60%. The experiments have been performed in a flow tube (IfT-LFT) for close to atmospheric reactant concentrations, [olefin] = (1 - 4)·10¹⁰ molecule cm⁻³, [O₃] = 2·10¹¹ molecule cm⁻³. H₂SO₄ was detected by means of a high resolution mass spectrometer with a chemical ionization inlet, CI-API-TOF, utilizing NO₃⁻ ions for chemical ionization (Jokinen *et. al.*, 2012). In the case of the ozonolysis of TME, additional H₂SO₄

formation in the presence of the OH radical scavenger showed no clear RH dependence. In the trans-2-butene system, however, distinct RH-dependent H₂SO₄ production was detected, see for instance figure 1. The observed effects point to the occurrence of two oxidants for SO₂ (beside OH radicals) with different chemical behaviour, probably the syn- and anti-conformers of acetaldehyde oxide.

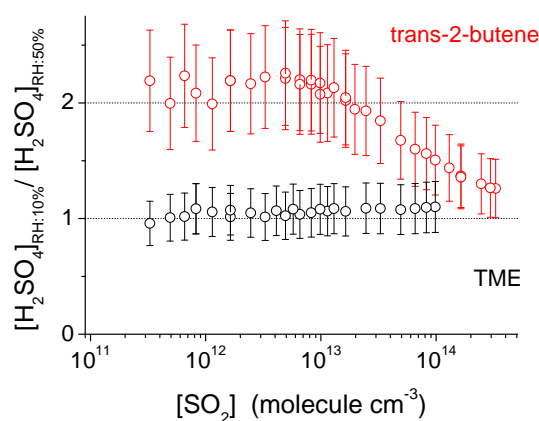


Figure 1: Ratio of measured H₂SO₄ at RH = 10 and 50 % as a function of SO₂ concentration, presence of an OH radical scavenger, 293 K.

Berndt, T., Jokinen, T., Mauldin III, R. L., Petäjä, T., Herrmann, H., Junninen, H., Paasonen, P., Worsnop, D. R., Sipilä, M., (2012), *J. Phys. Chem. Lett.*, 3, 2892-2896.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R. L., Kulmala, M., and Worsnop, D. R., (2012), *Atmos. Chem. Phys.*, 12, 4117-4125, doi: 10.5194/acp-12-4117-2012.

Mauldin III, R. L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kürten, T., Stratmann, F., Kerminen, V.-M., Kulmala, M., (2012), *Nature*, 488, 193–196, doi: 10.1038/nature11278.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., Taatjes, C. A., (2012), *Science*, 335, 204-207.