

# H<sub>2</sub>SO<sub>4</sub> formation from olefin ozonolysis in the presence of SO<sub>2</sub>:

## Influence of water vapour content and temperature

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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. H<sub>2</sub>SO<sub>4</sub> was ascertained to play a central role in this process. A dominant pathway of H<sub>2</sub>SO<sub>4</sub> generation represents the OH radical initiated oxidation of SO<sub>2</sub>. Recently it was discovered that also other oxidants than OH radicals, very likely stabilized Criegee Intermediates (sCI), can significantly contribute to H<sub>2</sub>SO<sub>4</sub> 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 (SO<sub>2</sub>, 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 CH<sub>2</sub>OO with SO<sub>2</sub> and other trace gases. As a result from our laboratory, clearly lower rate coefficients for the reaction of a series of sCI with SO<sub>2</sub> have been measured (Berndt *et al.*, 2012). Generally, there is a debate at the moment regarding the relevance of the sCI + SO<sub>2</sub> reaction in competition with the probably, much more important sCI + H<sub>2</sub>O pathway.

This experimental study focuses on H<sub>2</sub>SO<sub>4</sub> 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) · 10<sup>10</sup> molecule cm<sup>-3</sup>, [O<sub>3</sub>] = 2 · 10<sup>11</sup> molecule cm<sup>-3</sup>. H<sub>2</sub>SO<sub>4</sub> was detected by means of a high resolution mass spectrometer with a chemical ionization inlet, CI-API-TOF, utilizing NO<sub>3</sub><sup>-</sup> ions for chemical ionization (Jokinen *et al.*, 2012). In the case of the ozonolysis of TME, additional H<sub>2</sub>SO<sub>4</sub>

formation in the presence of the OH radical scavenger showed no clear RH dependence. In the trans-2-butene system, however, distinct RH-dependent H<sub>2</sub>SO<sub>4</sub> production was detected, see for instance figure 1. The observed effects point to the occurrence of two oxidants for SO<sub>2</sub> (beside OH radicals) with different chemical behaviour, probably the syn- and anti-conformers of acetaldehyde oxide.

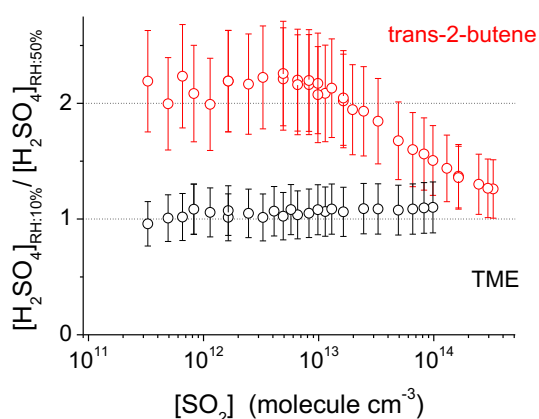


Figure 1: Ratio of measured H<sub>2</sub>SO<sub>4</sub> at RH = 10 and 50 % as a function of SO<sub>2</sub> concentration, presence of an OH radical scavenger, 293 K.

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