

## H<sub>2</sub>SO<sub>4</sub> formation from the gas-phase reaction of stabilized Criegee Intermediates with SO<sub>2</sub>: Influence of water vapour content and temperature

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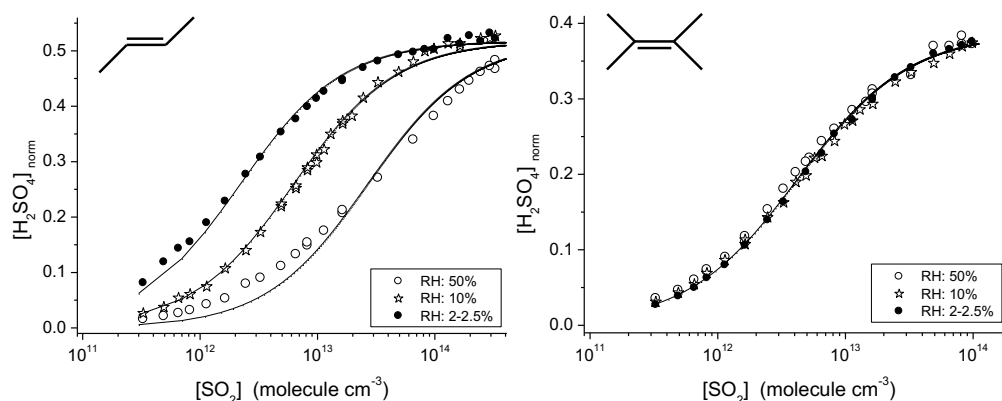
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H<sub>2</sub>SO<sub>4</sub> represents a key substance in the process of atmospheric nucleation. The importance of gas-phase products from olefin ozonolysis other than OH radicals, most likely stabilized Criegee Intermediates (sCI), for the process of atmospheric SO<sub>2</sub> oxidation to H<sub>2</sub>SO<sub>4</sub> has recently been discovered.

Subject of this work are investigations on H<sub>2</sub>SO<sub>4</sub> formation as a function of water vapour content (RH = 2 - 65 %) and temperature (278 - 343 K) starting from the ozonolysis of trans-2-butene and 2,3-dimethyl-2-butene (TME) forming acetaldehyde oxide and acetone oxide, respectively. Measurements have been conducted in an atmospheric pressure flow tube using NO<sub>3</sub><sup>-</sup>-CI-API-TOF mass spectrometry for H<sub>2</sub>SO<sub>4</sub> detection. Initial reactant concentrations were close to atmospheric levels: trans-2-butene: 4.0 · 10<sup>10</sup>, 2,3-dimethyl-2-butene (TME): 1.0 · 10<sup>10</sup>, O<sub>3</sub>: (2.0 - 2.2) · 10<sup>11</sup> molecule cm<sup>-3</sup>.

The sCI yields derived from H<sub>2</sub>SO<sub>4</sub> measurements at 293 K were 0.49 ± 0.22 for acetaldehyde oxide from trans-2-butene ozonolysis and 0.45 ± 0.20 for acetone oxide from TME ozonolysis. Our findings indicate a H<sub>2</sub>SO<sub>4</sub> yield from sCI + SO<sub>2</sub> of unity or close to unity.



The figures show normalized H<sub>2</sub>SO<sub>4</sub> concentrations as a function of SO<sub>2</sub> for three different relative humidities (RH). The deduced rate coefficient ratio for the reaction of sCI with H<sub>2</sub>O and SO<sub>2</sub>,  $k(\text{sCI}+\text{H}_2\text{O}) / k(\text{sCI}+\text{SO}_2)$ , was found to be strongly dependent on the structure of the Criegee Intermediate, for acetaldehyde oxide at 293 K:  $(8.8 \pm 0.4) \cdot 10^{-5}$  (syn- and anti-conformer in total) and for acetone oxide:  $< 4 \cdot 10^{-6}$ .

H<sub>2</sub>SO<sub>4</sub> formation from sCI was pushed back with rising temperature most probably due to an enhancement of sCI decomposition. The ratio  $k(\text{sCI}+\text{SO}_2) / k(\text{dec.})$  decreased by a factor of 34 (acetone oxide) increasing the temperature from 278 to 343 K. In the case of acetaldehyde oxide the temperature effect is less pronounced. The relevance of atmospheric H<sub>2</sub>SO<sub>4</sub> formation via sCI + SO<sub>2</sub> is discussed in dependence on the structure of the Criegee Intermediate.