

H₂SO₄ formation from the gas-phase reaction of stabilized Criegee Intermediates with SO₂: Influence of water vapour content and temperature

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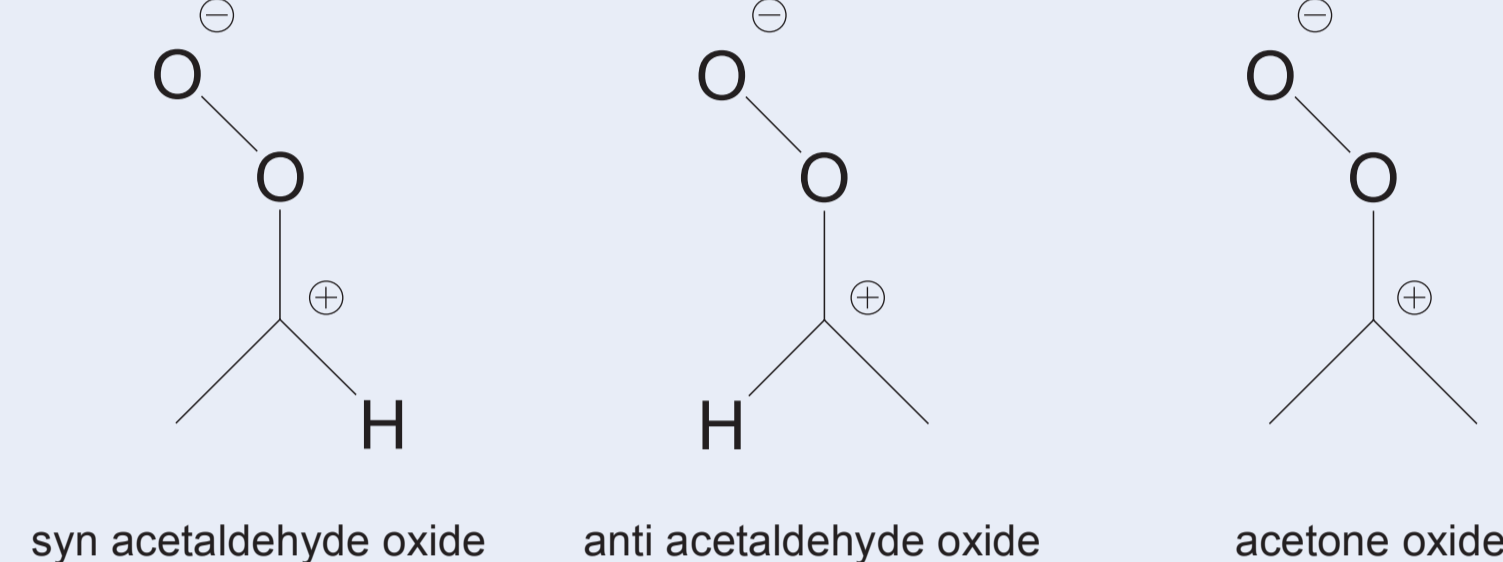
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Motivation

Very recently, it was discovered that the reaction of sCI with SO₂ is surprisingly fast and contributes significantly to atmospheric H₂SO₄ formation beside the well-known process via OH + SO₂ (Welz et al., 2012, Mauldin et al., 2012). Modelling results, however, call a substantial H₂SO₄ formation from sCI into question and point to the predominate fate of sCI in the reaction with H₂O vapour (Sarwar et al., 2013). For a reliable assessment of these processes the reactivity of a series of important sCI toward atmospherically relevant trace gases has to be known. But, up to now the knowledge is very sparse regarding the needed rate coefficients. Rate coefficients for the reaction of sCI with H₂O vapour, SO₂ or other trace gases are available for the simplest sCI, formaldehyde oxide (CH₂OO), and in only few cases for acetaldehyde oxide (CH₃CHOO) (Calvert et al., 1978, Welz et al., 2012, Taatjes et al., 2013). Indirect approaches based on end-product analysis or sCI titration were mostly used due to experimental difficulties of direct sCI probing (Calvert et al., 2000, Fenske et al., 2000, Berndt et al., 2012). Up to now, only a low-pressure experiment at 4 torr allows the direct monitoring of Criegee Intermediates (Welz et al., 2012, Taatjes et al., 2013). It is to be noted that there exist large discrepancies in the absolute values of the sCI rate coefficients, also for the important reactions with H₂O vapour and SO₂.

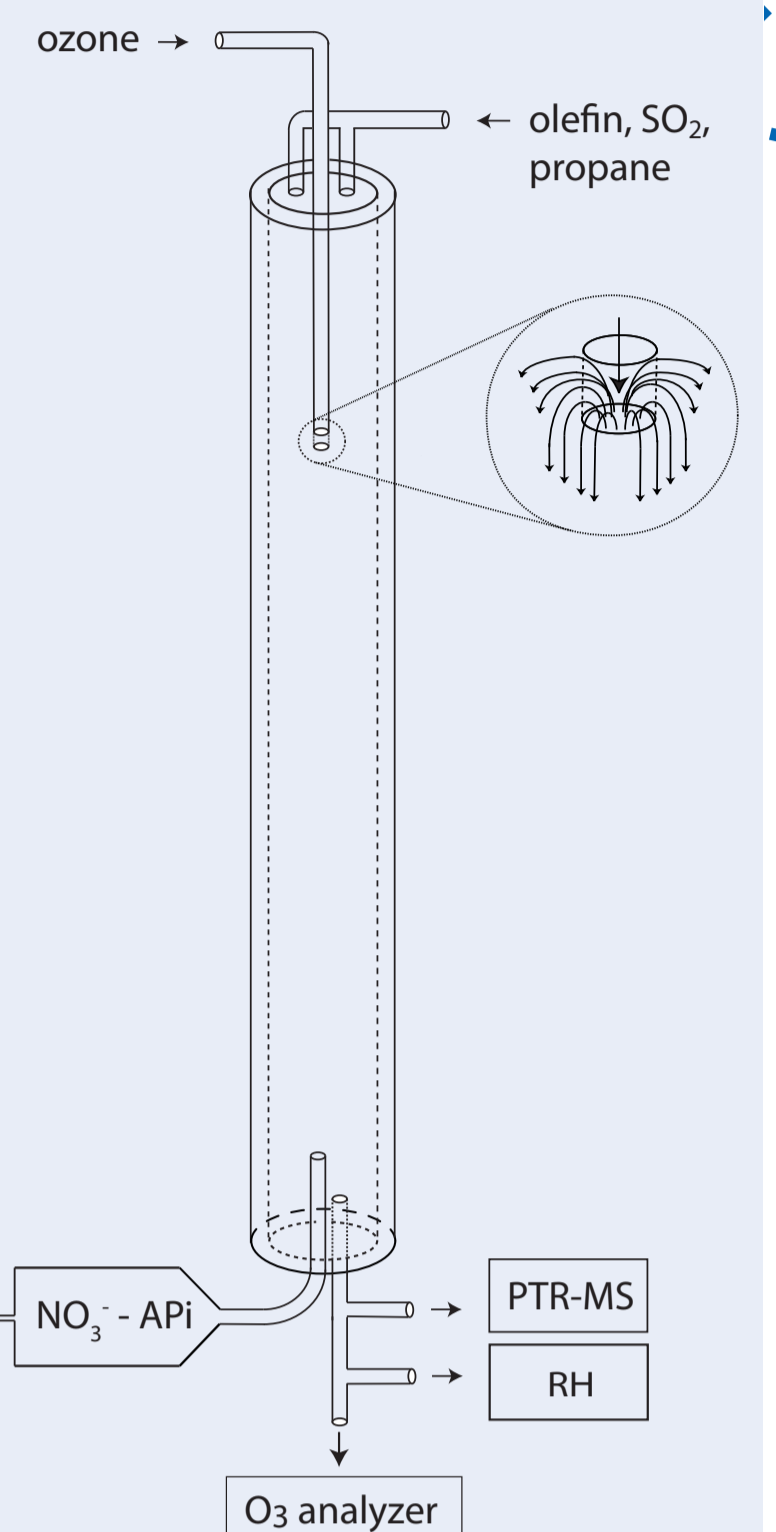
Subject of this work are investigations on H₂SO₄ formation from the reaction of acetaldehyde oxide (syn- and anti-conformer, CH₃CHOO) and acetone oxide ((CH₃)₂COO) with SO₂ for atmospheric conditions in a relatively wide range of the water vapour content in the temperature range 278 - 343 K. Criegee Intermediates are formed via gas-phase ozonolysis of trans-2-butene and 2,3-dimethyl-2-butene (TME).



Experiment

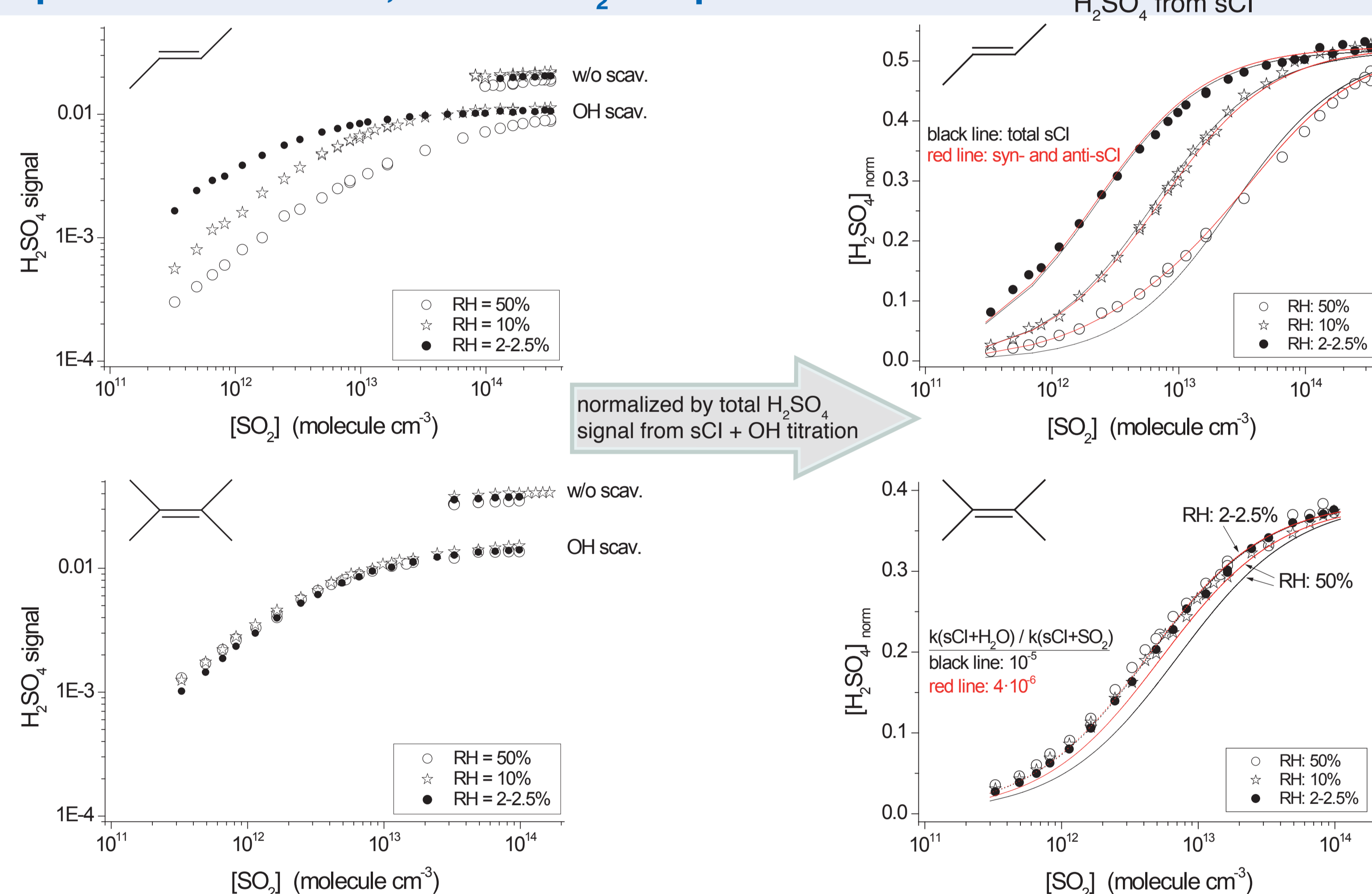
Institute for Tropospheric Research - Laminar Flow Tube, TROPOS-LFT:
 - length: 505 cm, 8 cm i.d.
 - carrier gas: purified air (99.999999 vol%)
 - atmospheric pressure
 - temperature: 278 - 343 K
 - flow: 30 l min⁻¹ (STP), residence time: 39.5 sec.
 - H₂O vapour: 0.047 - 1.17 vol%
 - reactant concentrations:
 [trans-2-butene] = 4.0 · 10¹⁰ cm⁻³
 [2,3-dimethyl-2-butene] = 1.0 · 10¹⁰ cm⁻³
 [O₃] = (2.0 - 2.2) · 10¹¹ cm⁻³
 [SO₂] = (2.9 - 3300) · 10¹¹ cm⁻³
 [C₃H₈] = (4.1 - 16.4) · 10¹⁵ cm⁻³ (OH scavenger)
 - olefin conversion: < 2%

H₂SO₄ detection: NO₃-CI-API-TOF
 - H₂SO₄ signal: S = ([HSO₄]_{tot} + [(HNO₃)₂(HSO₄)]) / ([NO₃]_{tot} + [(HNO₃)₂(NO₃)])
 - calibration factor: (1.85 ± 0.83) · 10⁹ cm⁻³
 - detection limit: 4 · 10⁴ cm⁻³ (5 min. integration)

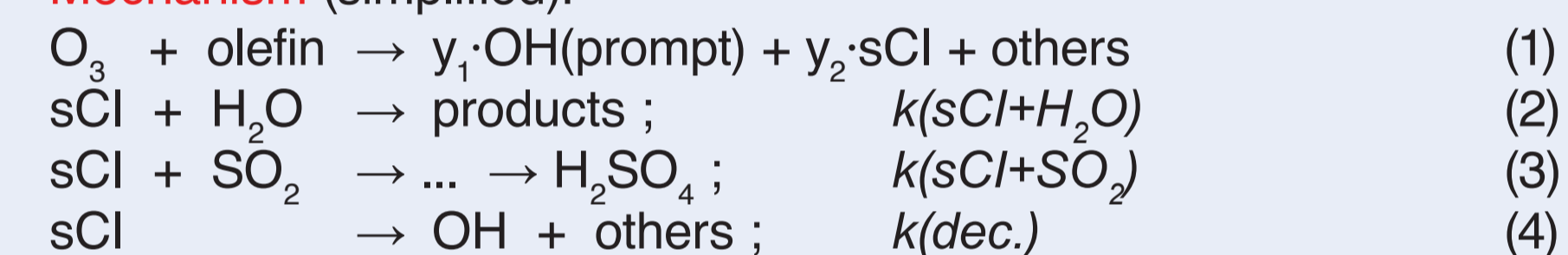


Results and Discussion

Experiments at 293 K, variable H₂O vapour content



Mechanism (simplified):



y_2 : 0.49 ± 0.22 (trans-2-butene) and 0.45 ± 0.20 (TME)
 $y_1 + y_2$: 0.92 ± 0.42 (trans-2-butene) and 1.20 ± 0.54 (TME)

$$[\text{H}_2\text{SO}_4]_{\text{norm}} = 1 / (1 + k(\text{dec.}) / (k(\text{sCI} + \text{SO}_2)[\text{SO}_2] + k(\text{sCI} + \text{H}_2\text{O})[\text{H}_2\text{O}] / (k(\text{sCI} + \text{SO}_2)[\text{SO}_2])) \cdot f \quad (\text{Eq. 1})$$

Acetaldehyde oxide (trans-2-butene ozonolysis):

one component (sCI) model (black line):

$k(\text{dec.}) / k(\text{sCI} + \text{SO}_2) = (1.2 \pm 0.1) \cdot 10^{-12} \text{ molecule cm}^{-3}$
 $k(\text{sCI} + \text{H}_2\text{O}) / k(\text{sCI} + \text{SO}_2) = (8.8 \pm 0.4) \cdot 10^{-5} \Rightarrow 6.1 \cdot 10^{-5}$ from literature: Calvert et al., 1978.

two component (syn- and anti-sCI) model (red line):

anti: $k(\text{dec.}) / k(\text{sCI} + \text{SO}_2) = (2.7 \pm 1.7) \cdot 10^{-11} \text{ molecule cm}^{-3}$

anti: $k(\text{sCI} + \text{H}_2\text{O}) / k(\text{sCI} + \text{SO}_2) = (1.4 \pm 0.1) \cdot 10^{-4}$

syn: $k(\text{dec.}) / k(\text{sCI} + \text{SO}_2) = (3.3 \pm 0.5) \cdot 10^{-12} \text{ molecule cm}^{-3}$
 \Rightarrow reaction with H₂O vapour neglected

\Rightarrow Analysis points to a preferred formation of the anti-conformer !

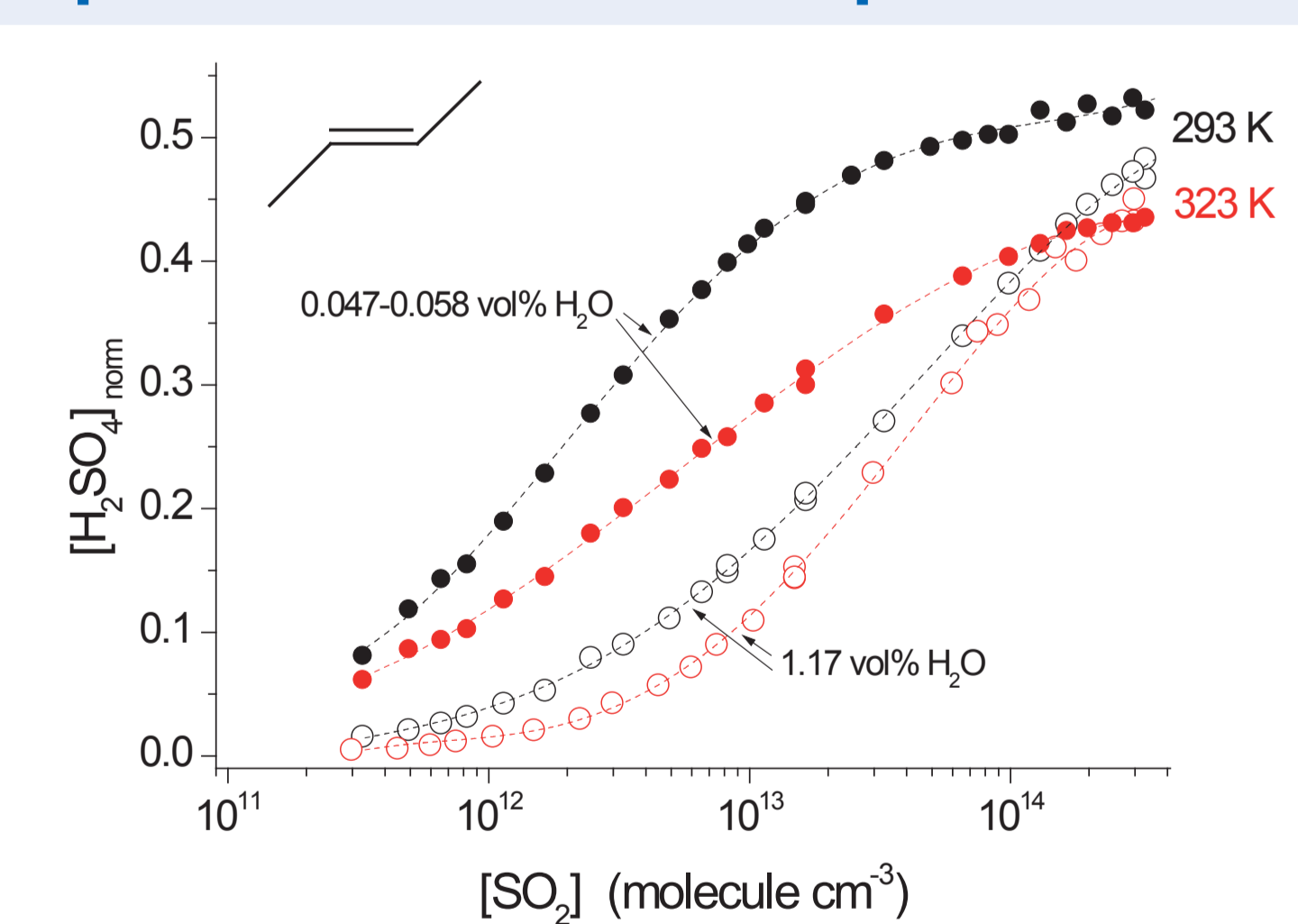
Acetone oxide (TME ozonolysis):

$k(\text{dec.}) / k(\text{sCI} + \text{SO}_2) = (4.2 \pm 0.3) \cdot 10^{-12} \text{ molecule cm}^{-3}$

$k(\text{sCI} + \text{H}_2\text{O}) / k(\text{sCI} + \text{SO}_2) < 4 \cdot 10^{-6} \Rightarrow$ only upper limit estimation possible

\Rightarrow Reaction of sCI with H₂O vapour is strongly dependent on the sCI structure !

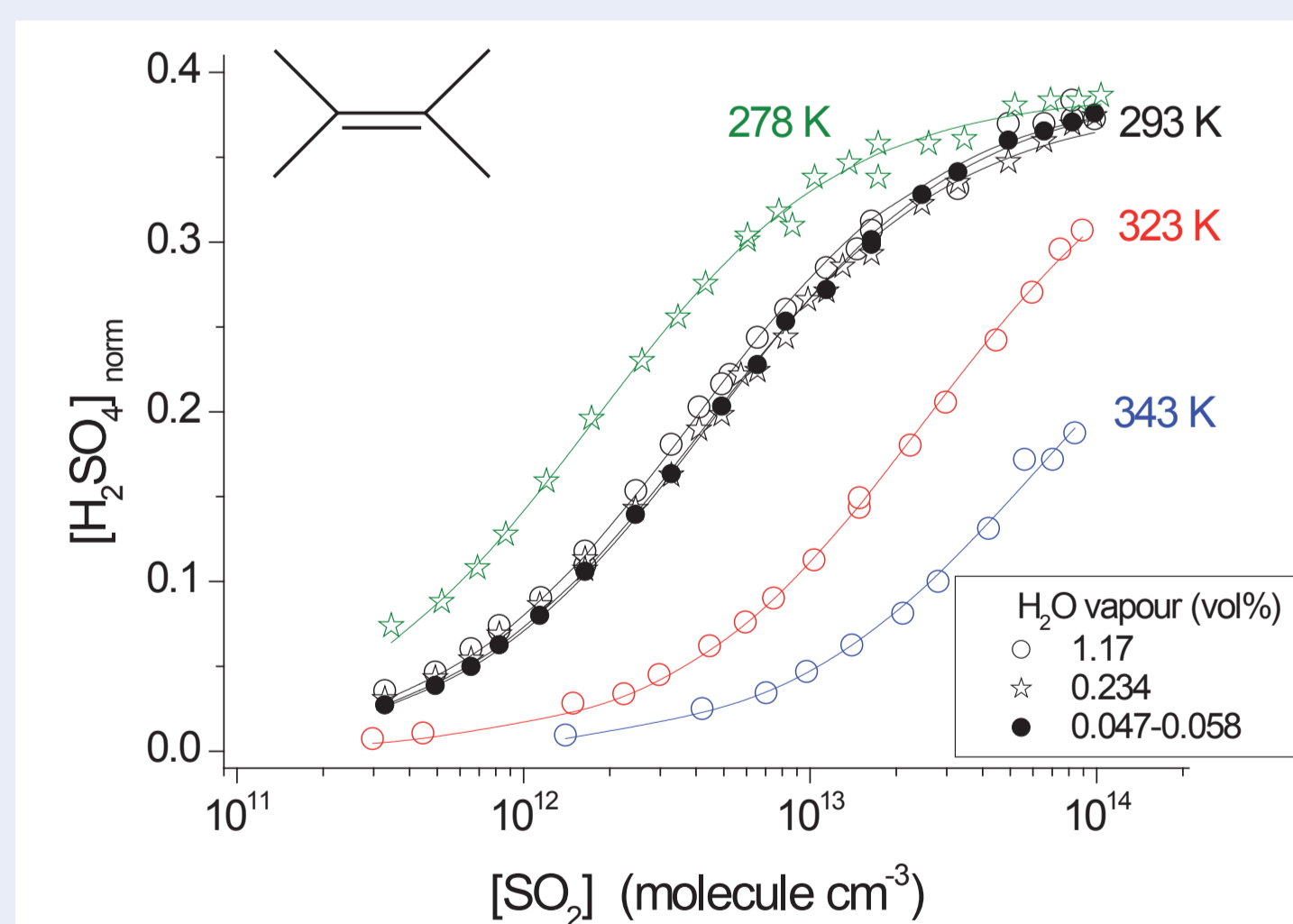
Experiments in the temperature range 278 - 343 K



Acetaldehyde oxide

\Rightarrow dashed lines connect the measurement points only !
 - increasing temperature lowers H₂SO₄ formation; $k(\text{dec.})$ is expected to be mainly responsible for the temperature dependence
 - temperature effect is less pronounced for high H₂O vapour content

\Rightarrow no strong temperature-dependent H₂SO₄ formation for atmospheric conditions



Acetone oxide

\Rightarrow full lines show modelling results according to Eq. 1 (w/o H₂O reaction)

- competition between the reaction of sCI with SO₂ vs. decomposition describes very well the measurements independent of H₂O vapour

- $k(\text{dec.}) / k(\text{sCI} + \text{SO}_2)$:

278 K: $(1.8 \pm 0.5) \cdot 10^{-12} \text{ molecule cm}^{-3}$

293 K: $(4.2 \pm 0.3) \cdot 10^{-12} \text{ molecule cm}^{-3}$

323 K: $(2.5 \pm 0.9) \cdot 10^{-13} \text{ molecule cm}^{-3}$

343 K: $(6.0 \pm 0.8) \cdot 10^{-13} \text{ molecule cm}^{-3}$

- Arrhenius parameter $\ln(k(\text{dec.}) / k(\text{sCI} + \text{SO}_2))$ vs. $1/T$

$E_{a,4} - E_{a,3} = 44.0 \pm 1.2 \text{ kJ mol}^{-1}$ and $\ln(A_4/A_3) = 47.5 \pm 0.5$

\Rightarrow strong temperature-dependent H₂SO₄ formation for atmospheric conditions

References

- Welz et al., Science, 335, 204-207, 2012.
- Mauldin et al., Nature, 488, 193-197, 2012.
- Sawar et al., Atmos. Environ., 68, 186-197, 2013.
- Calvert et al., Atmos. Environ., 12, 197-226, 1978.
- Taatjes et al., Science, 340, 177-180, 2013.
- Fenske et al., J. Phys. Chem., 104, 9921-9932, 2000.
- Berndt et al., J. Phys. Chem. Lett., 3, 2892-2896, 2012.

Summary

- \Rightarrow acetaldehyde oxide and acetone oxide show different reactivity toward H₂O vapour
- \Rightarrow atmospheric fate of acetaldehyde oxide is governed by the reaction with H₂O vapour, for acetone oxide thermal decomposition is most important
- \Rightarrow increasing temperature results in a decrease of H₂SO₄ formation (T-dependence of $k(\text{dec.})$), for acetaldehyde oxide only small effects due to the dominant reaction with H₂O vapour for acetone oxide a decrease of $k(\text{dec.}) / k(\text{sCI} + \text{SO}_2)$ by a factor of 34 increasing the temperature from 278 to 343 K
- \Rightarrow sCI reactivity and atmospheric fate is sCI-structure dependent

