

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263052726>

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

ARTICLE *in* ATMOSPHERIC ENVIRONMENT · MAY 2014

Impact Factor: 3.28 · DOI: 10.1016/j.atmosenv.2014.02.062

CITATIONS

19

READS

227

8 AUTHORS, INCLUDING:



[Torsten Berndt](#)

Leibniz Institute for Tropospheric Research

234 PUBLICATIONS 3,203 CITATIONS

[SEE PROFILE](#)



[Mikko Sipilä](#)

University of Helsinki

113 PUBLICATIONS 2,345 CITATIONS

[SEE PROFILE](#)



[R. L. Mauldin](#)

University of Colorado Boulder

196 PUBLICATIONS 4,747 CITATIONS

[SEE PROFILE](#)

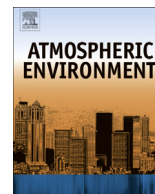


[Markku Kulmala](#)

University of Helsinki

1,365 PUBLICATIONS 35,655 CITATIONS

[SEE PROFILE](#)



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

Torsten Berndt^{a,*}, Tuija Jokinen^{a,b}, Mikko Sipilä^b, Roy L. Mauldin III^{b,c},
Hartmut Herrmann^a, Frank Stratmann^a, Heikki Junninen^b, Markku Kulmala^b

^a Leibniz-Institute for Tropospheric Research (TROPOS), 4318 Leipzig, Germany

^b Department of Physics, University of Helsinki, Finland

^c University of Colorado at Boulder, Boulder, CO, USA

HIGHLIGHTS

- The sCI reactivity towards water vapour is dependent on the sCI structure.
- Acetone oxide shows no measurable reaction with water vapour.
- Increasing temperature pushes back H₂SO₄ formation from sCI + SO₂.

ARTICLE INFO

Article history:

Received 26 August 2013

Received in revised form

24 February 2014

Accepted 27 February 2014

Keywords:

Gas-phase ozonolysis

Criegee Intermediate

Stabilization

Atmospheric H₂SO₄ formation

CI-API-TOF mass spectrometry

ABSTRACT

The importance of gas-phase products from alkene ozonolysis other than OH radicals, most likely stabilized Criegee Intermediates (sCI), for the process of atmospheric SO₂ oxidation to H₂SO₄ has been recently discovered. Subjects of this work are investigations on H₂SO₄ 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). H₂SO₄ production other than via the OH radical reaction was attributed to the reaction of SO₂ with sCI, i.e. acetaldehyde oxide arising from trans-2-butene ozonolysis and acetone oxide from TME. Measurements have been conducted in an atmospheric pressure flow tube using NO₃–CI-API-TOF mass spectrometry for H₂SO₄ detection. The sCI yields derived from H₂SO₄ measurements at 293 K were 0.49 ± 0.22 for acetaldehyde oxide and 0.45 ± 0.20 for acetone oxide. Our findings indicate a H₂SO₄ yield from sCI + SO₂ of unity or close to unity. The deduced rate coefficient ratio for the reaction of sCI with H₂O and SO₂, $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$, 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: $<4 \cdot 10^{-6}$. H₂SO₄ formation from sCI was pushed back with rising temperature in both reaction systems most probably due to an enhancement of sCI decomposition. The ratio $k(\text{dec})/k(\text{sCI} + \text{SO}_2)$ increased 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 H₂SO₄ formation via sCI + SO₂ is discussed in view of its dependence on the structure of the Criegee Intermediate.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

It was already found in the seventies that reactive intermediates from alkene ozonolysis (other than OH radicals) are able to oxidize

SO₂ under atmospheric conditions forming H₂SO₄ (Cox and Penkett, 1972). These reactive intermediates are most likely stabilized Criegee Intermediates (sCI) (Criegee, 1975). Very recently, it was discovered that the reaction of sCI with SO₂ is surprisingly fast and significantly contributes to atmospheric H₂SO₄ formation besides 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 a possibly

* Corresponding author.

E-mail address: berndt@tropos.de (T. Berndt).

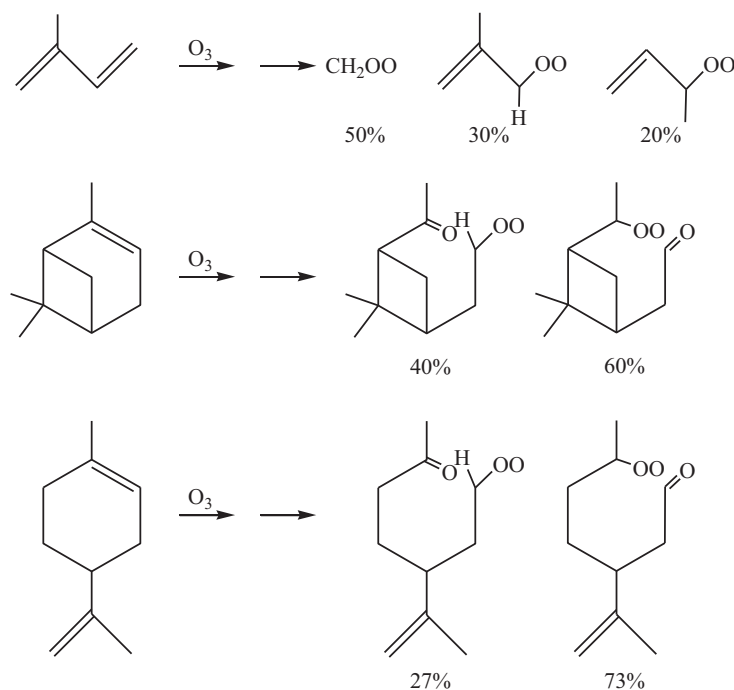
dominating fate of sCI in their reaction with water vapour (Sarwar et al., 2013; Li et al., 2013). For a reliable assessment of these processes the reactivity of a series of important sCI towards atmospherically relevant trace gases has to be known. However, up to now the knowledge regarding the needed rate coefficients is very sparse. Rate coefficients for the reaction of sCI with water vapour, SO₂ or other trace gases are only available for the simplest sCI, formaldehyde oxide (CH₂OO), and in only few cases for acetaldehyde oxide (CH₃CHOO) (Calvert et al., 2000; 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 large discrepancies in the absolute values of the sCI rate coefficients exist for the important reactions with water vapour and SO₂. The rate coefficient ratio $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$, however, shows much better agreement; for CH₂OO: $5.7 \cdot 10^{-5}$ (Atkinson and Lloyd, 1984; Kerr and Calvert, 1984), $2.3 \cdot 10^{-4}$ (Suto et al., 1985) and $<10^{-4}$ (Welz et al., 2012); for CH₃CHOO: $6.1 \cdot 10^{-5}$ (syn- and anti-conformer in total) from Calvert et al. (1978) re-evaluating data by Cox and Penkett (1972), $<1.7 \cdot 10^{-4}$ (syn-conformer) and $1.5 \cdot 10^{-4}$ (anti-conformer) (Taatjes et al., 2013).

It is not clear at the moment if the sCI reactivity observed for CH₂OO and CH₃CHOO and the corresponding rate coefficient ratio $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ are also applicable for other Criegee Intermediates. The gas-phase ozonolysis in the atmosphere produces a series of structurally different Criegee Intermediates. Schematic I shows the possible Criegee Intermediates derived from the primary attack of ozone toward isoprene, α -pinene and limonene. The

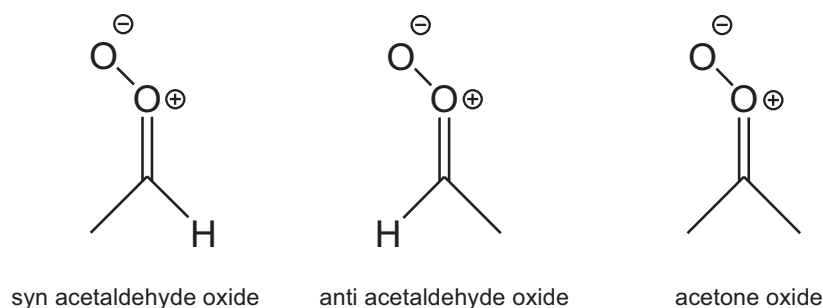
distribution of the Criegee Intermediates was taken from the MCMv3.2-mechanism (MCM, 2013).

There are no experimental kinetic data available especially for Criegee Intermediates with two organic groups bound to the C-atom of the COO-group, i.e. RR'COO or, in its most simple form (CH₃)₂COO. Quantum chemical calculations predict very low rate coefficients for the reaction of (CH₃)₂COO and (CH₃)(C₂H₅)COO with water vapour (Ryzhkov and Ariya, 2004; Kuwata et al., 2010). Consequently, it can be speculated that lower rate coefficient ratios $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ than $\sim 10^{-4}$ (as observed for CH₂OO and CH₃CHOO) are possible for the RR'COO Criegee Intermediates enhancing the importance of the reaction with SO₂. Note that a comparison of rate coefficients shows that (CH₃)₂COO reacts faster with SO₂ than CH₃CHOO supporting this hypothesis (Berndt et al., 2012).

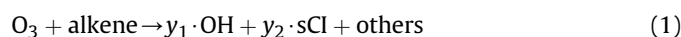
The reaction of sCI with water vapour produces hydroxy hydroperoxides, $\text{R}^1\text{R}^2\text{COO} + \text{H}_2\text{O} \rightarrow \text{R}^1\text{R}^2\text{C}(\text{OH})\text{OOH}$, where R¹ and R² are H or an organic group (Gäb et al., 1985; Hatakeyama and Akimoto, 1994). Quantum chemistry predicts that in the first step of the reaction of sCI with SO₂ a cyclic adduct is formed that either decomposes to the corresponding carbonyl R¹R²CO and SO₃ (oxidation channel) or to an organic acid R¹COOH and SO₂ (isomerization channel) (Jiang et al., 2010; Kurten et al., 2011). The latter channel works only if R² is an H-atom. The oxidation channel is also favoured in the case that migrating H-atoms are available (R²: H-atom). That points to the importance of SO₃ and subsequent H₂SO₄ formation from sCI + SO₂ (Jiang et al., 2010; Kurten et al., 2011). In contrast to this, another theoretical study describes SO₃ as a minor reaction product of the sCI + SO₂ reaction for relatively large sCI like (CH₃)₂COO at 1 bar forming collisionally stabilized SO₂-bearing secondary ozonides primarily (Vereecken et al., 2012).



Schematic I. Possible Criegee Intermediates from the ozonolysis of isoprene, α -pinene and limonene.



Subjects of the present work are investigations on H_2SO_4 formation from the reaction of acetaldehyde oxide (syn- and anti-conformer, CH_3CHOO) and acetone oxide ($(\text{CH}_3)_2\text{COO}$) with SO_2 for atmospheric conditions in a relatively wide range of the water vapour content. Criegee Intermediates are formed via gas-phase ozonolysis of trans-2-butene and 2,3-dimethyl-2-butene beside OH radicals and other products.



The runs are conducted in such a way that a continuous reaction of sCI with SO_2 and water vapour took place throughout the tube in contrast to our previous work using sCI titration by means of SO_2 at the flow-tube outlet (Berndt et al., 2012). Measured H_2SO_4 in the presence of OH radical scavenger is taken to characterize the reaction of sCI with SO_2 . The temperature dependence of the H_2SO_4 production in this system has been determined for the first time. It is to be noted, that the formed H_2SO_4 in the presence of OH radical scavenger was attributed to the sCI + SO_2 reaction in line with the current understanding of the ozonolysis mechanism. However, we are not able to totally rule out any contribution of other ozonolysis intermediates than sCI for the formation of H_2SO_4 . Drozd et al. (2011) discovered recently from TME ozonolysis that a second stabilized product is formed from CI, probably vinyl hydroperoxide. The importance of stabilized vinyl hydroperoxide formation is not clear at the moment and needs further investigations.

2. Experimental

Ozonolysis reactions have been carried out in the Institute for Tropospheric Research – Laminar Flow Tube, IfT-LFT, (i.d. 8 cm; length 505 cm) at atmospheric pressure using purified synthetic air as the carrier gas, cf. Fig. 1 (Berndt et al., 2004). A thermo-jacket maintained the tube at the adjusted temperature (278–343 K) using water as the working fluid. The humidified main carrier-gas stream was introduced at the top of the flow tube containing the alkene, SO_2 and propane as the OH radical scavenger. 55 cm downstream, O_3 diluted in the carrier gas was added through an inlet. The design of the inlet nozzle ensured rapid gas mixing. O_3 was supplied from an ozone generator UVP OG-2. The alkene concentration was detected by means of proton transfer reaction mass spectrometry (Ionicon, high sensitivity PTR-MS) (Lindinger et al., 1998), the relative humidity by means of a humidity sensor (Vaisala), and O_3 using a gas monitor (Thermo Environmental Instruments 49C). H_2SO_4 was measured using a NO_3^- -CI-API-TOF (chemical ionization – atmospheric pressure interface – time-of-flight) mass spectrometer (Eisele and Tanner, 1993; Junninen et al., 2010; Jokinen et al., 2012) sampling the centre flow at the tube outlet with a rate of 10 L min^{-1} (STP). The reaction time in the flow tube was 39.5 s and the H_2SO_4 wall loss 28%, see Supplementary Material. Initial concentrations were: trans-2-butene: $4.0 \cdot 10^{10}$, 2,3-dimethyl-2-butene (TME): $1.0 \cdot 10^{10}$, O_3 :

$(2.0\text{--}2.2) \cdot 10^{11}$, SO_2 : $(2.9\text{--}3300) \cdot 10^{11}$ and propane: $(4.1\text{--}16.4) \cdot 10^{15} \text{ molecule cm}^{-3}$.

The total carrier gas flow rate in the experiments was 30 L min^{-1} (STP). All gas flows were set by means of calibrated gas flow controllers (MKS 1259/1179). Trans-butene (99%, Messer), 2,3-dimethyl-2-butene (99%, Fluka) and propane (99.95%, Linde) were used without further purification. SO_2 was utilized from a calibration gas mixture of 1961 ppmv SO_2 in N_2 (Air Liquide). Synthetic air (99.998%, Air Products) was further purified by a cleaning device (GateKeeper CE-500KF-O-4R, AERONEX). The GateKeeper output impurities are stated to be lower than 500 pptv for NMHCs, H_2O and CO_2 in total.

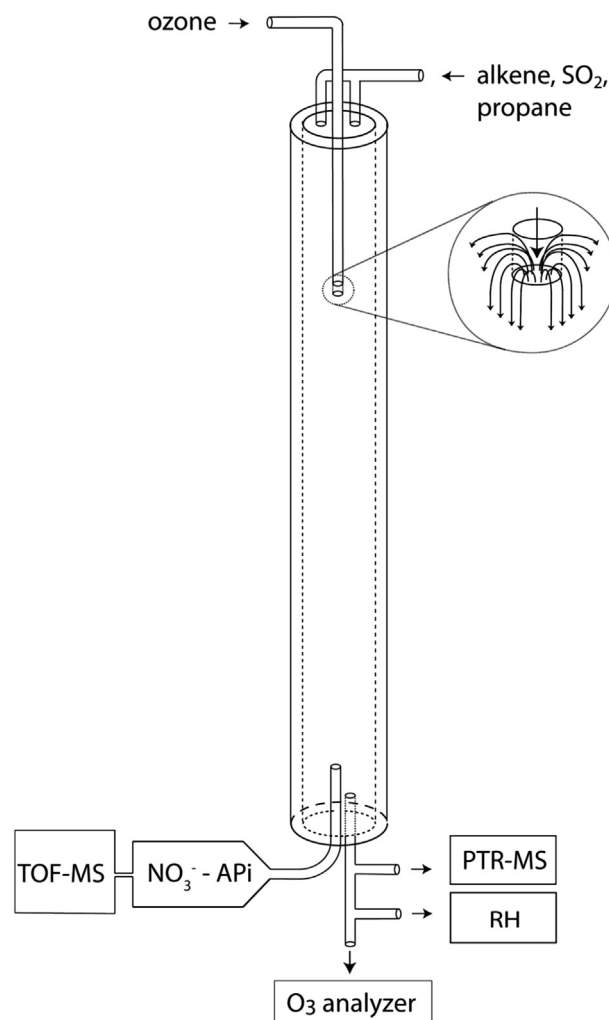
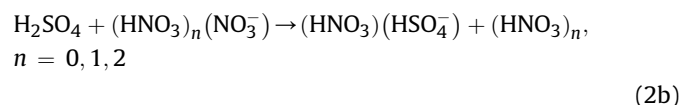


Fig. 1. Schematic of the experimental set-up.

2.1. NO_3^- -CI-API-TOF mass spectrometer and instrument sensitivity

The CI-API-TOF instrument consists of the chemical ionization region (Airmodus A07), the atmospheric pressure interface, and the time-of-flight mass spectrometer (resolving power: >3000 Th/Th, ToFwerk) (Junninen et al., 2010; Jokinen et al., 2012). H_2SO_4 in the sample flow (10 L min^{-1} (STP)) is chemically ionized by the reagent ions $(\text{HNO}_3)_n(\text{NO}_3^-)$, $n = 0, 1, 2$ (Viggiano et al., 1982). The reagent ions are produced by exposing nitric acid to a ^{241}Am alpha source.



The ionized sample is transferred through the atmospheric pressure interface to the time-of-flight mass spectrometer for mass-to-charge determination. The signal for H_2SO_4 is determined according to Equation (1):

$$S = \frac{[\text{HSO}_4^-] + [(\text{HNO}_3)(\text{HSO}_4^-)]}{[\text{NO}_3^-] + [(\text{HNO}_3)(\text{NO}_3^-)] + [(\text{HNO}_3)_2(\text{NO}_3^-)]} \quad (1)$$

The H_2SO_4 signal of the CI-API-TOF instrument (including the bended sampling tube) was calibrated for gas conditions of $T \sim 295 \text{ K}$ and $\text{RH} = 25\%$ using H_2O UV-photolysis at 184.9 nm by means of a Pen Ray lamp (Eisele and Tanner, 1993; Berresheim et al., 2000). In the presence of SO_2 ($1.5 \cdot 10^{13} \text{ molecule cm}^{-3}$), photolytically produced OH radicals were transformed to H_2SO_4 yielding H_2SO_4 concentration of $(1.8\text{--}9.1) \cdot 10^7 \text{ molecule cm}^{-3}$. The photon flux of the Pen Ray lamp was determined by O_2 actinometry, O_2 column: $8.4 \cdot 10^{18} \text{ molecule cm}^{-2}$ (Lanzendorf et al., 1997; Hofzumahaus et al., 1997; Dusanter et al., 2008), measuring produced O_3 by long-path UV absorption spectroscopy (Perkin–Elmer, Lambda 800). The H_2SO_4 detection limit was found to be $4 \cdot 10^4 \text{ molecule cm}^{-3}$ for a 5 min integration time. The error of the measured H_2SO_4 concentration is estimated to be $\pm 45\%$ (Mauldin et al., 1998).

Furthermore, it was tested whether changing the carrier-gas conditions ($T = 278\text{--}343 \text{ K}$, $\text{RH} = 2\text{--}65\%$) can influence the H_2SO_4 detection. Reagent ions were measured sampling pure carrier gas from the flow tube i) as a function of the carrier-gas RH at $T = 293 \text{ K}$, see Fig. S2, and ii) as a function of the carrier-gas temperature for $\text{RH} = 10\%$ (determined at 293 K), see Fig. S3. In both cases it was found that the total reagent ion concentration as well as the ion distribution depends on the carrier-gas conditions. A change of the reagent ion distribution implicates a possible change in the H_2SO_4 detection efficiency if not all rate coefficients of the ionization via pathways (2a) and (2b) are (almost) equal and independent of the parameters varied (RH, temperature). Absolute calibration of the H_2SO_4 signal as a function of RH and temperature was impossible due to technical limitations of the above mentioned approach and the lack of another well-defined H_2SO_4 source working in this range of conditions.

3. Results and discussion

3.1. Measurements at 293 K, SO_2 titration of OH radicals and sCI

In Fig. 2a and b the obtained H_2SO_4 signals from the ozonolysis of trans-2-butene and TME, respectively, are depicted as a function of RH according to Equation (1) along with the resulting ratios $[\text{H}_2\text{SO}_4](\text{presence of OH scavenger})$ divided by the total

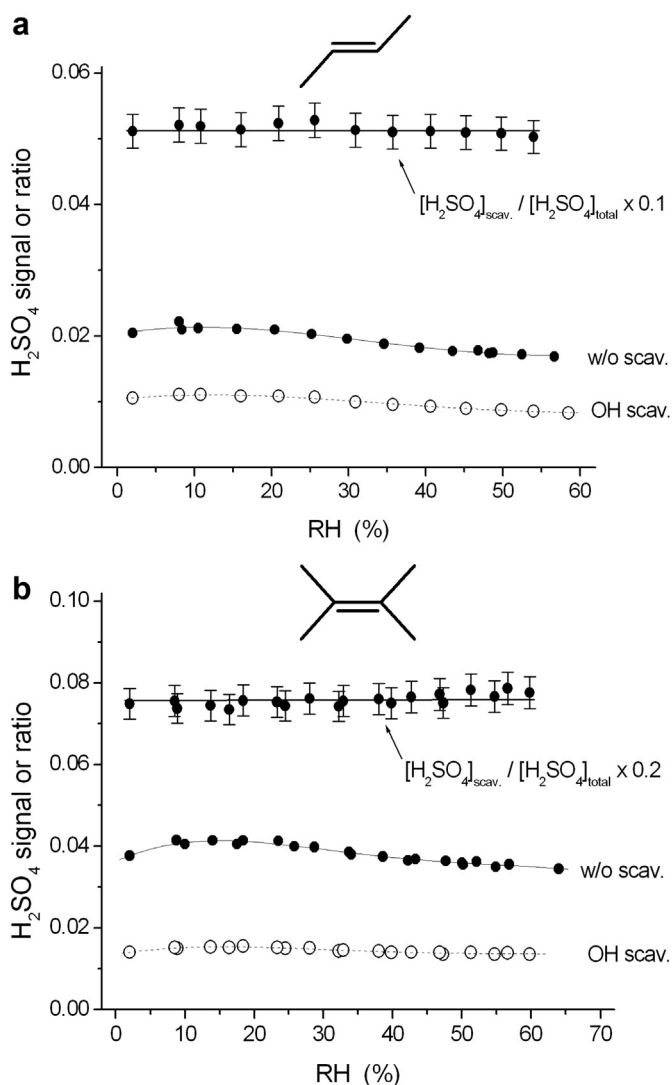


Fig. 2. H_2SO_4 signals in the absence and presence of an OH radical scavenger (C_3H_8) from the ozonolysis of trans-2-butene and TME as well as the resulting ratios $[\text{H}_2\text{SO}_4]$ (presence of OH scavenger) divided by the total $[\text{H}_2\text{SO}_4]$ (absence of OH scavenger) as a function of RH, $T = 293 \text{ K}$. Error bars show $\pm 5\%$ deviation. a) trans-2-butene: $[\text{SO}_2] = (1.64\text{--}3.28) \cdot 10^{14} \text{ molecule cm}^{-3}$, $[\text{C}_3\text{H}_8] = 1.64 \cdot 10^{16} \text{ molecule cm}^{-3}$. b) TME: $[\text{SO}_2] = 9.8 \cdot 10^{13} \text{ molecule cm}^{-3}$, $[\text{C}_3\text{H}_8] = 4.1 \cdot 10^{15} \text{ molecule cm}^{-3}$.

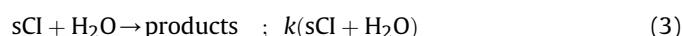
$[\text{H}_2\text{SO}_4](\text{absence of OH scavenger})$. A large excess of SO_2 ensured total conversion of sCI to H_2SO_4 (in the absence of the OH radical scavenger also total conversion of OH radicals to H_2SO_4). If needed, the OH radical scavenger concentration (C_3H_8) was chosen in such a way that more than 97% of OH radicals reacted with C_3H_8 . Thus, the H_2SO_4 signals stand either for OH radicals and sCI in total or for sCI alone. The shape of the H_2SO_4 signal curves for both alkenes showed a maximum in the RH range of 10–20% qualitatively similar to the change of the reactant ion distribution for $(\text{HNO}_3)_n(\text{NO}_3^-)$, $n = 0, 1, 2$, cf. Fig. S2. The ratio of the H_2SO_4 signals with and without C_3H_8 , however, was found to be independent of RH within the experimental uncertainties for both reaction systems, 0.512 ± 0.010 for trans-2-butene and 0.378 ± 0.007 for TME. (Errors represent one standard deviation.) That indicates that the shape of the H_2SO_4 signal curves reflects the RH dependence of the reactant ions concentration rather than an RH-effect on the H_2SO_4 formation for these conditions. Even for the highest RH of about 60% ($[\text{H}_2\text{O}] \sim 3.1 \cdot 10^{17} \text{ molecule cm}^{-3}$), the reaction of sCI with water vapour is not fast enough to be competitive with the sCI + SO_2

reaction ($[\text{SO}_2] = (9.8\text{--}32.8) \cdot 10^{13} \text{ molecule cm}^{-3}$) being in line with the rate coefficient ratios $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ available from literature (Calvert et al., 1978; Atkinson and Lloyd, 1984; Kerr and Calvert, 1984; Taatjes et al., 2013).

The absolute calibration of the H_2SO_4 signal at $\sim 295 \text{ K}$ and $\text{RH} = 25\%$ (Section 2.1.) allows to determine the sCI yield from the ozonolysis for these reaction conditions assuming a H_2SO_4 yield of unity from $\text{sCI} + \text{SO}_2$. The calculated amount of reacted alkenes were $5.64 \cdot 10^7 \text{ molecule cm}^{-3}$ (trans-2-butene) and $8.69 \cdot 10^7 \text{ molecule cm}^{-3}$ (TME); $t = 39.5 \text{ s}$, $k_1(\text{trans-2-butene}) = (1.74 \pm 0.33) \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Treacy et al., 1992), $k_1(\text{TME}) = (1.0 \pm 0.2) \cdot 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Witter et al., 2002). The sCI concentrations derived from the H_2SO_4 measurements in the presence of the OH radical scavenger result in a sCI yield of 0.49 ± 0.22 (trans-2-butene) and 0.45 ± 0.20 (TME). Error limits take into account the 45% uncertainty of the H_2SO_4 measurement. The obtained sCI yields of this study are 7.5% (trans-2-butene) and 27% (TME) lower compared to our previous data but within the range of uncertainties, 0.53 ± 0.24 (trans-2-butene) and 0.62 ± 0.28 (TME) (Berndt et al., 2012). The reason for the lower sCI yields compared to our former study cannot be given. For comparison, Dzozd and Donahue (2011) reported a sCI yield of 0.65 from TME ozonolysis using the hexafluoroacetone scavenger technique. Furthermore, the yield of OH radicals and sCI in total were 0.88 ± 0.40 (trans-2-butene) and 1.20 ± 0.54 (TME) inferred from the H_2SO_4 measurements without the OH radical scavenger. The fraction of additional H_2SO_4 from titration experiments without the scavenger is attributed to the “prompt” OH from the decomposition of excited CI (Kroll et al., 2001). The OH radical and sCI yield in total cannot exceed unity taking into account that per reacted alkene only one CI can be formed and from the CI only one OH radical can arise. A hypothetical H_2SO_4 yield from $\text{sCI} + \text{SO}_2$ clearly smaller than unity would lead to an increase of the sCI yield from the ozonolysis and, subsequently, to an increase of the total OH radical and sCI yield to values definitely higher than unity, see sample calculations in Table S3. Therefore, from our experiments we have to conclude that the H_2SO_4 yield from $\text{sCI} + \text{SO}_2$ must be unity or at least close to unity. A more precise determination is impossible caused by the relatively large uncertainty associated with the H_2SO_4 measurements. Finally, it is to be noted, that recent findings from quantum chemical calculations regarding the reaction of stabilized $(\text{CH}_3)_2\text{COO}$ with SO_2 at atmospheric pressure stating the formation of a collisionally stabilized SO_2 -bearing secondary ozonide (SOZ) with a yield of $\geq 97\%$ and only $\leq 3\%$ SO_3 (Vereecken et al., 2012). Our findings are only consistent with the quantum chemical prediction if a rapid hydrolysis of the SO_2 -bearing SOZ at a time scale of seconds (or less) takes place forming nearly exclusively H_2SO_4 .

3.2. SO_2 -dependent measurements for different RH at 293 K

The SO_2 concentration was varied in a wide range for a given relative humidity ($\text{RH} = 50\%$, 10% or $2\text{--}2.5\%$) in order to investigate the kinetics of the competitive reactions of sCI with water vapour and SO_2 .



The measured H_2SO_4 signals according to Equation (I) are given in Fig. 3a and b for both ozonolysis reactions.

Runs in the absence of the OH radical scavenger have been performed for SO_2 concentration of around $10^{14} \text{ molecule cm}^{-3}$, i.e. for conditions of OH radical and sCI titration as described before.

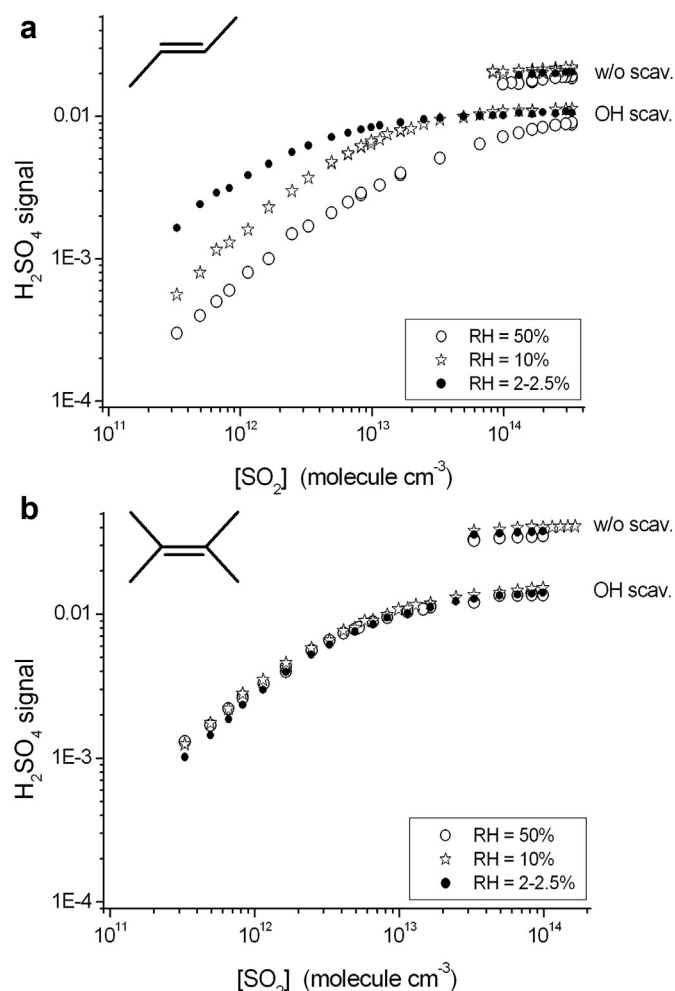


Fig. 3. H_2SO_4 signals in the absence and presence of an OH radical scavenger (C_3H_8) as a function of the SO_2 concentration for three different RH, $T = 293 \text{ K}$. a) trans-2-butene: $[\text{C}_3\text{H}_8] = 1.64 \cdot 10^{16} \text{ molecule cm}^{-3}$. b) TME: $[\text{C}_3\text{H}_8] = 4.1 \cdot 10^{15} \text{ molecule cm}^{-3}$.

The small differences of the H_2SO_4 signal heights depending on RH are again most probably due to the RH-dependent reagent ion concentrations, cf. Fig. S2. For the following data evaluation, the average H_2SO_4 signal levels from the titration experiments (w/o OH radical scavenger) for the respective RH were taken for normalizing the measurement series (presence of OH scavenger) and to remove the “reagent ion concentration” effect. The normalization also eliminates the H_2SO_4 wall loss from the data processing because the considered run as well the reference measurement have the same relative wall loss, see Supplementary Material.

The observed H_2SO_4 signals from acetaldehyde oxide (trans-2-butene ozonolysis) and acetone oxide (TME ozonolysis) showed a qualitatively different behaviour in the experiments in the presence of the OH scavenger changing the SO_2 concentration over three orders of magnitude, cf. Fig. 3a and b. For a given SO_2 concentration, $[\text{SO}_2] < \text{a few } 10^{13} \text{ molecule cm}^{-3}$, the H_2SO_4 production is significantly pushed back with rising RH in the case of acetaldehyde oxide due to the competition of pathways (3) and (4), while for acetone oxide the observed differences are within the experimental uncertainty. In the latter case, the reaction of sCI with water vapour is obviously not effective enough for the relatively high SO_2 concentrations in our experiment, $[\text{SO}_2] \geq 3 \cdot 10^{11} \text{ molecule cm}^{-3}$. A clear drop down of the H_2SO_4 signal with decreasing SO_2 is visible for each individual measurement series (constant RH) in Fig. 3a and b. This fact can be explained by the competition of the thermal

decomposition of sCl and the reaction of sCl with SO₂ via pathway (4) for a constant contribution of the reaction of sCl with H₂O via pathway (3).



The fraction of sCl producing H₂SO₄, $\text{sCl}_{\text{H}_2\text{SO}_4}/\text{sCl}_{\text{total}}$, is equal to the reaction rate of pathway (4) divided by the sum of the reaction rates of all sCl consuming steps:

$$\frac{\text{sCl}_{\text{H}_2\text{SO}_4}}{\text{sCl}_{\text{tot}}} = \frac{r_4}{r_3 + r_4 + r_5} = \frac{1}{1 + \frac{k(\text{dec})}{k(\text{sCl} + \text{SO}_2) \cdot [\text{SO}_2]} + \frac{k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]}{k(\text{sCl} + \text{SO}_2) \cdot [\text{SO}_2]}} \quad (II)$$

Equation (II) describes the water vapour- and SO₂-dependent H₂SO₄ formation from sCl and tends to unity for large SO₂ concentrations. The experimental H₂SO₄ data from sCl (presence of OH scavenger), as used in the following, have been normalized by the total H₂SO₄ signal from titration experiments of OH radicals and sCl in total (absence of OH scavenger). Therefore, setting $[\text{H}_2\text{SO}_4]_{\text{norm}}$ equal to $\text{sCl}_{\text{H}_2\text{SO}_4}/\text{sCl}_{\text{total}}$ a factor f is needed considering the normalization, $f = [\text{H}_2\text{SO}_4]_{\text{sCl-titration}}/([\text{H}_2\text{SO}_4]_{\text{sCl-titration}} + [\text{H}_2\text{SO}_4]_{\text{OH-titration}})$.

$$[\text{H}_2\text{SO}_4]_{\text{norm}} = \text{sCl}_{\text{H}_2\text{SO}_4}/\text{sCl}_{\text{total}} \cdot f = \frac{1}{1 + \frac{k(\text{dec})}{k(\text{sCl} + \text{SO}_2) \cdot [\text{SO}_2]} + \frac{k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]}{k(\text{sCl} + \text{SO}_2) \cdot [\text{SO}_2]}} \cdot f \quad (III)$$

Equation (III) can be simplified if the water-vapour term $k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$ is much smaller than $k(\text{dec})$.

$$[\text{H}_2\text{SO}_4]_{\text{norm}} = \frac{1}{1 + \frac{k(\text{dec})}{k(\text{sCl} + \text{SO}_2) \cdot [\text{SO}_2]}} \cdot f \quad (IV)$$

$$[\text{H}_2\text{SO}_4]_{\text{norm}} = [\text{H}_2\text{SO}_4]_{\text{norm/anti-sCl}} \cdot f_{\text{anti}} + [\text{H}_2\text{SO}_4]_{\text{norm/syn-sCl}} \cdot f_{\text{syn}} = \frac{1}{1 + \frac{k(\text{dec})_{\text{anti}}}{k(\text{sCl} + \text{SO}_2)_{\text{anti}} \cdot [\text{SO}_2]} + \frac{k(\text{sCl} + \text{H}_2\text{O})_{\text{anti}} \cdot [\text{H}_2\text{O}]}{k(\text{sCl} + \text{SO}_2)_{\text{anti}} \cdot [\text{SO}_2]}} \cdot f_{\text{anti}} + \frac{1}{1 + \frac{k(\text{dec})_{\text{syn}}}{k(\text{sCl} + \text{SO}_2)_{\text{syn}} \cdot [\text{SO}_2]}} \cdot f_{\text{syn}} \quad (V)$$

3.2.1. Acetaldehyde oxide (trans-2-butene ozonolysis)

In Fig. 4 the normalized data for the produced H₂SO₄ from sCl as given in Fig. 3a (presence of OH scavenger) are depicted together with the results according to Equation (III) (black line).

The corresponding parameters (“one sCl” model, syn- and anti-conformer in total) obtained as a result of non-linear regression analysis are: $k(\text{dec})/k(\text{sCl} + \text{SO}_2) = (1.2 \pm 0.1) \cdot 10^{12} \text{ molecule cm}^{-3}$, $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2) = (8.8 \pm 0.4) \cdot 10^{-5}$ and $f = 0.52 \pm 0.01$. Given error limits represent one standard deviation. The needed water vapour concentrations in Equation (III) were calculated from RH using a saturation vapour pressure of 23.4 mbar at 293 K (Goff, 1957). The comparison of our rate coefficient ratio $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2)$ with the value by Calvert et al. (1978), $6.1 \cdot 10^{-5}$ for both the syn- and anti-conformer in total, shows a good agreement. Furthermore, the rate coefficient ratio $(k(\text{dec}) + k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}])/k(\text{sCl} + \text{SO}_2) = (2.7 \pm 0.4) \cdot 10^{13} \text{ molecule cm}^{-3}$ can be calculated from the parameters of Equation (III) for RH: 50%. This value is in good agreement with $k(\text{loss})/k(\text{sCl} + \text{SO}_2) = (2.1 \pm 0.7) \cdot 10^{13} \text{ molecule cm}^{-3}$ for acetaldehyde oxide at RH: 50%, $k(\text{loss}) = k(\text{dec}) + k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$, from our previous experiments (Berndt et al., 2012) using a different experimental approach.

Especially for the measurements at RH = 50%, the best-fit curve according to Equation (III) (black line) is not able to describe the experimental data very well indicating that the reaction mechanism is more complex than considered according to pathways (3)–(5) assuming a single sCl. Acetaldehyde oxide exists as a syn- and anti-conformer. Conformer-specific kinetic measurements by Taatjes et al. (2013) showed different reactivity of syn- and anti-acetaldehyde oxide towards SO₂ and water vapour. Our indirect sCl detection method via H₂SO₄ is not able to distinguish between both conformers and only average effects can be measured. Nevertheless, the observed “average reactivity” is a useful parameter for the basic understanding of the sCl reactivity and particularly for atmospheric modelling.

In the following we try to estimate the individual reactivity of syn- and anti-acetaldehyde oxide from an extended data analysis comprising the syn- and anti-conformer as separate species (“two sCl” model). From results of quantum chemistry it is known that the syn-conformer reacts few orders of magnitude slower with water vapour than the anti-conformer (Ryzhkov and Ariya, 2004; Kuwata et al., 2010). Therefore, for simplicity, the reaction with water vapour was neglected in the case of the syn-conformer, see equation (V).

Non-linear regression analysis yielded for the data given in Fig. 4: $(k(\text{dec})/k(\text{sCl} + \text{SO}_2))_{\text{anti}} = (2.7 \pm 1.7) \cdot 10^{11} \text{ molecule cm}^{-3}$, $(k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2))_{\text{anti}} = (1.4 \pm 0.1) \cdot 10^{-4}$, $f_{\text{anti}} = 0.41 \pm 0.01$, $(k(\text{dec})/k(\text{sCl} + \text{SO}_2))_{\text{syn}} = (3.3 \pm 0.5) \cdot 10^{12} \text{ molecule cm}^{-3}$ and $f_{\text{syn}} = 0.12 \pm 0.01$, see the red curves in Fig. 4. This “two sCl”

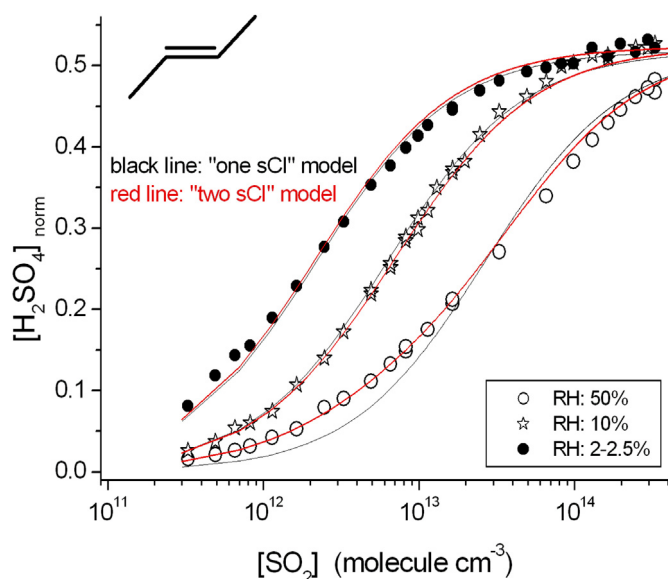


Fig. 4. Normalized concentrations of H_2SO_4 from sCl as a function of SO_2 for three different RH along with the results from non-linear regression analysis according to Equation (III) ("one sCl" model; black line) and for the "two sCl" analysis for syn- and anti-sCl according to Equation (V) (red line). Normalization has been done by the total H_2SO_4 signal from titration of OH radicals and sCl. Ozonolysis of trans-2-butene in the presence of C_3H_8 ($1.64 \cdot 10^{16}$ molecule cm^{-3}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approach is able to describe the experiments very well in the whole range of experimental conditions chosen. The obtained factor f_{anti} is about 3.5-fold f_{syn} pointing to a preferred formation of one sCl (probably the anti-conformer) compared to the other one. But, it has to be noted that this analysis comprises five free parameters and the physical relevance of these parameters should be not over-

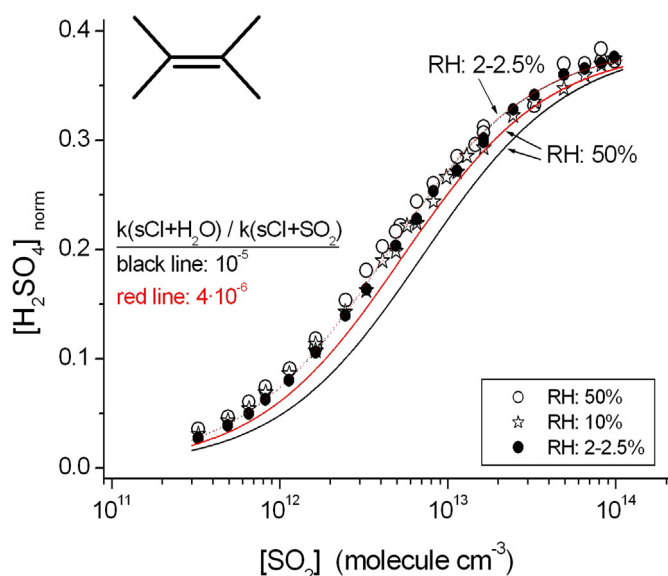


Fig. 5. Normalized concentrations of H_2SO_4 from sCl as a function of SO_2 for three different RH. The full lines (RH: 50%) and dashed lines (RH: 2–2.5%) show the results according to Equation (III) assuming either $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2) = 10^{-5}$ (in black) or $4 \cdot 10^{-6}$ (in red). Ozonolysis of TME in the presence of C_3H_8 ($4.1 \cdot 10^{15}$ molecule cm^{-3}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Parameters for stabilized acetone oxide (TME ozonolysis) according to Equation (IV), $f = [\text{H}_2\text{SO}_4]_{\text{sCl-titration}} / ([\text{H}_2\text{SO}_4]_{\text{sCl-titration}} + [\text{H}_2\text{SO}_4]_{\text{OH-titration}})$. Error limits represent two standard deviations.

Temperature (K)	Water vapour (vol%)	RH at 293 K (%)	$k(\text{dec})/k(\text{sCl} + \text{SO}_2)$ (molecule cm^{-3})	f
293	0.047–0.058	2–2.5	$(4.55 \pm 0.73) \cdot 10^{12}$	0.389 ± 0.002
293	0.234	10	$(4.25 \pm 1.09) \cdot 10^{12}$	0.380 ± 0.003
293	1.17	50	$(3.88 \pm 1.08) \cdot 10^{12}$	0.388 ± 0.003
278	0.234	—	$(1.75 \pm 0.51) \cdot 10^{12}$	0.388 ± 0.003
323	1.17	—	$(2.49 \pm 0.88) \cdot 10^{13}$	0.388 ± 0.006
343	1.17	—	$(5.98 \pm 0.76) \cdot 10^{13}$	0.326 ± 0.022

interpreted. Thus, further conclusions using these data are probably not justified.

3.2.2. Acetone oxide (TME ozonolysis)

Fig. 5 shows the normalized data for H_2SO_4 from sCl given in Fig. 3b (presence of OH scavenger) for the three RH investigated. Parameter estimation in the same way as performed for acetaldehyde oxide according to Equation (III) was impossible because there was no RH dependence of the H_2SO_4 signals measured (no experimental information for $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2)$). The parameters $k(\text{dec})/k(\text{sCl} + \text{SO}_2)$ and f from Equation (IV) were determined separately for each RH series neglecting the reaction $\text{sCl} + \text{H}_2\text{O}$. Results are given in Table 1. Equation (IV) was able to describe the experimental data very well in each case. The values $k(\text{dec})/k(\text{sCl} + \text{SO}_2)$ showed no significant difference for the different water vapour concentrations justifying the disregarding of the $\text{sCl} + \text{H}_2\text{O}$ reaction, i.e. $k(\text{dec})$ is considerably larger than $k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$ even for the highest RH. The average value for $k(\text{dec})/k(\text{sCl} + \text{SO}_2)$ is $(4.2 \pm 0.3) \cdot 10^{12}$ molecule cm^{-3} (RH: 2–50%).

An upper limit of the rate coefficient ratio $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2)$ was tried to be estimated by setting $k(\text{dec})/k(\text{sCl} + \text{SO}_2) = 4.2 \cdot 10^{12}$ molecule cm^{-3} and $f = 0.385$ as fix parameters in Equation (III), cf. Table 1. In Fig. 5, the full lines (RH: 50%) and dashed lines (RH: 2–2.5%) show the results of calculations according to Equation (III) assuming either $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2) = 10^{-5}$ (in black) or $4 \cdot 10^{-6}$ (in red). The latter value is regarded as the upper limit for $k(\text{sCl} + \text{H}_2\text{O})/k(\text{sCl} + \text{SO}_2)$ by

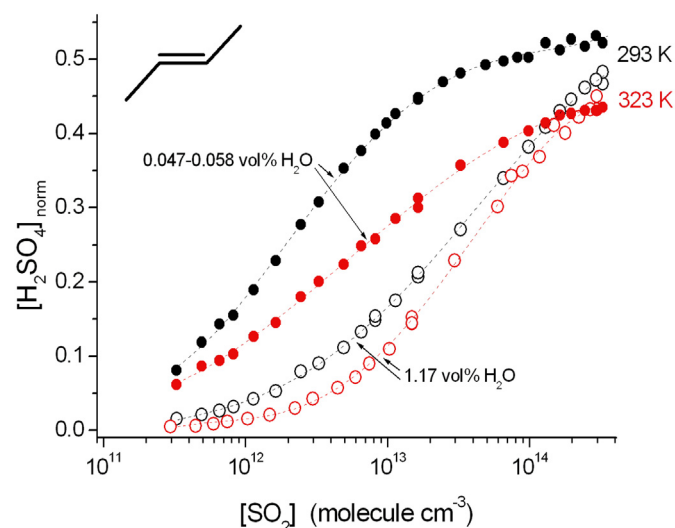


Fig. 6. Normalized H_2SO_4 concentrations produced by the reaction $\text{sCl} + \text{SO}_2$ (trans-butene ozonolysis) from measurement series at 293 and 323 K for a water-vapour content of 0.047–0.058 vol% (RH: 2–2.5% at 293 K) and 1.17 vol% (RH: 50% at 293 K), $[\text{C}_3\text{H}_8] = 1.64 \cdot 10^{16}$ molecule cm^{-3} . The dashed lines connect the measurement points only.

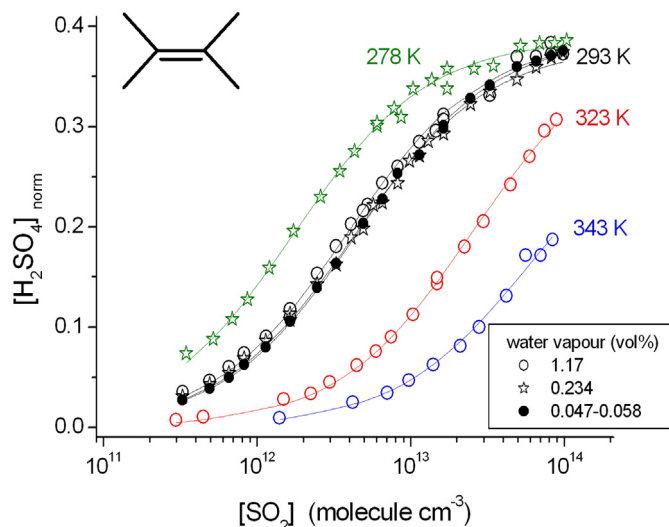


Fig. 7. H_2SO_4 formation from the reaction of sCI with SO_2 (TME ozonolysis) from measurement series at 278, 293, 323 and 343 K and different RH, $[\text{C}_3\text{H}_6] = 4.1 \cdot 10^{15} \text{ molecule cm}^{-3}$. The full lines represent the best fit results according to Equation (IV).

comparing the measurement points with the calculated curve for RH: 50%.

A comparison of the upper limit for $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ with other values is impossible due to the lack of such kinetic data in the literature. The average rate coefficient ratio $k(\text{dec})/k(\text{sCI} + \text{SO}_2) = (4.2 \pm 0.3) \cdot 10^{12} \text{ molecule cm}^{-3}$ is in good agreement with $k(\text{loss})/k(\text{sCI} + \text{SO}_2) = (3.9 \pm 0.7) \cdot 10^{12} \text{ molecule cm}^{-3}$ from our previous study measured at RH: 50% (Berndt et al., 2012). Here, $k(\text{loss})$ is set equal to $k(\text{dec})$ because the $\text{sCI} + \text{H}_2\text{O}$ reaction can be neglected in $k(\text{loss}) = k(\text{dec}) + k(\text{sCI} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$.

3.3. Temperature-dependent measurements

3.3.1. Acetaldehyde oxide

In Fig. 6 the normalized H_2SO_4 concentrations from sCI are given from measurement series at 293 and 323 K for a water vapour content of 0.047–0.058 vol% (RH: 2–2.5% at 293 K) and 1.17 vol% (RH: 50% at 293 K) each. The temperature increase from 293 to 323 K lead to a lower H_2SO_4 production from sCI for a given SO_2 concentration. This effect is smaller for the higher H_2O -vapour content. It is expected that the rate coefficient of the unimolecular decomposition of sCI (pathway (5)) shows the strongest temperature dependence compared to the bimolecular steps, i.e. pathways (3) and (4). That means that rising temperature results mainly in strengthening of the sCI decomposition pushing back the importance of H_2SO_4 formation from the reaction of sCI with SO_2 . For the lower water-vapour content, $k(\text{dec}) \sim k(\text{sCI} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$, the increase of $k(\text{dec})$ with rising temperature and lowering of the H_2SO_4 production becomes clearly visible. For the higher water-vapour content, $k(\text{dec}) \sim 0.05 \cdot k(\text{sCI} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$, however, the sCI loss

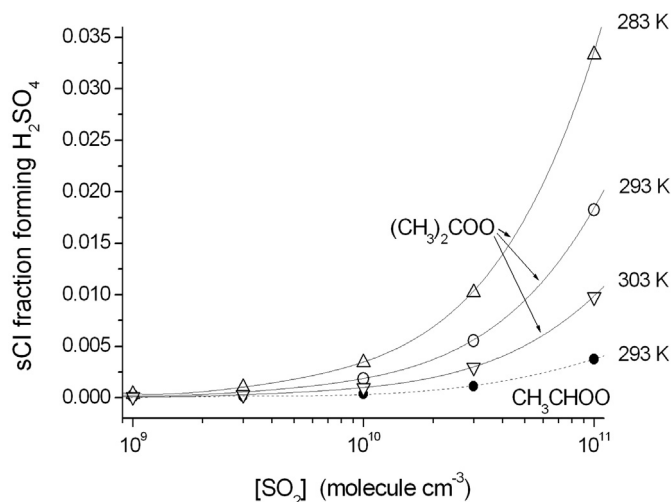


Fig. 8. Fraction of sCI forming H_2SO_4 at RH: 50% calculated from Equation (III). Used coefficients are summarized in Table 2.

is governed by the $\text{sCI} + \text{H}_2\text{O}$ reaction and only a small decrease of the H_2SO_4 concentration with increasing temperature emerges.

A more quantitative analysis is difficult due to the complexity of the reaction system. Different rate coefficients $k(\text{dec})$ with a different temperature dependence are possible for the syn- and anti-conformer of acetaldehyde oxide in the same way as observed for their reactions with SO_2 and water vapour (Taatzjes et al., 2013).

3.3.2. Acetone oxide

A distinct temperature dependence of the H_2SO_4 formation from the sCI + SO_2 reaction was observed in the case of acetone oxide from TME ozonolysis, cf. Fig. 7. Here, the competition of the thermal decomposition of sCI (pathway (5)) with the SO_2 reaction (pathway (4)) at different temperatures (and different RH) is clearly visible in each case (negligible $\text{sCI} + \text{H}_2\text{O}$ reaction). In each case the experimental data were very well described by Equation (IV). Corresponding values for $k(\text{dec})/k(\text{sCI} + \text{SO}_2)$ and the factor f are given in Table 1 as the result of non-linear regression analysis. The rate coefficient ratio increased by a factor of 34 increasing the temperature from 278 to 343 K. The formal Arrhenius plot, $\ln(k(\text{dec})/k(\text{sCI} + \text{SO}_2))$ vs. $1/T$, showed a straight line yielding $E_{a,5} - E_{a,4} = 44.0 \pm 1.2 \text{ kJ mol}^{-1}$ and $\ln(A_5/A_4) = 47.5 \pm 0.5$, see Fig. S5. The determined difference of the Arrhenius activation energy stands mainly for the thermal decomposition step (pathway (5)), i.e. $E_{a,5} \gg E_{a,4}$. It is speculative at the moment what individual, mechanistic step is responsible for the observed temperature dependence (Kroll et al., 2001; Kurten and Donahue, 2012). Nevertheless, the Arrhenius equation allows studying the temperature effect of H_2SO_4 formation for the atmospherically relevant temperature range.

Table 2

Compilation of yields and rate coefficient ratios determined in this study.

	Temperature (K)	sCI yield	sCI + OH yield	$k(\text{dec})/k(\text{sCI} + \text{SO}_2)$ (molecule cm^{-3})	$k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$
Acetaldehyde oxide trans-2-butene	293	0.49 ± 0.22	0.88 ± 0.40	$(1.2 \pm 0.1) \cdot 10^{12}$	$(8.8 \pm 0.4) \cdot 10^{-5}$
Acetone oxide TME	293	0.45 ± 0.20	1.20 ± 0.54	$(4.2 \pm 0.3) \cdot 10^{12}$	$<4 \cdot 10^{-6}$
	283	—	—	$2.3 \cdot 10^{12}$	$<4 \cdot 10^{-6}$
	303	—	—	$8.1 \cdot 10^{12}$	$<4 \cdot 10^{-6}$

A compilation of the determined yields and coefficients from this study is given in Table 2. Values for acetone oxide at 283 and 303 K have been calculated based on the Arrhenius equation.

4. Atmospheric implications

There are a few modelling studies in the literature investigating the effect of H_2SO_4 formation from sCI + SO_2 for the total H_2SO_4 concentration in the atmosphere (Sarwar et al., 2013; Boy et al., 2013). Boy et al. (2013) observed an increase of the H_2SO_4 concentration of 33–46% at two different locations (SMEAR II, Hyytiälä, Finland, and Hohenpeissenberg, Germany) using experimental data for the reactivity of the individual sCI considered. On the other hand, Sarwar et al. (2013) did not find a significant contribution of the sCI + SO_2 reaction for atmospheric H_2SO_4 concentrations considering scenarios for winter and summer time in the USA. The reaction with water vapour was identified as the predominate fate of sCI. Sarwar et al. (2013) used for all sCI the measured rate coefficient from the reaction of formaldehyde oxide (CH_2OO) with SO_2 by Welz et al. (2012) and the ratio $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2) = 6.1 \cdot 10^{-5}$ from Calvert et al. (1978). Our study, however, demonstrates that the rate coefficient ratio $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ strongly depends on the structure of the sCI. Fig. 8 shows the fraction of sCI forming H_2SO_4 according to Equation (II) as a function of SO_2 for acetaldehyde oxide (CH_3CHOO) and acetone oxide ($(\text{CH}_3)_2\text{COO}$) at RH: 50%, kinetic data from Table 2, reaction pathways (3)–(5). For CH_3CHOO , the atmospheric fate is governed by the reaction with water vapour (>0.95) and only a small fraction reacts with SO_2 forming H_2SO_4 (<0.004) even for the highest SO_2 concentration assumed. In the case of $(\text{CH}_3)_2\text{COO}$, the upper limit of $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2) = 4 \cdot 10^{-6}$ was applied in the calculations. $(\text{CH}_3)_2\text{COO}$ is able to produce about a 5-fold H_2SO_4 concentration compared to CH_3CHOO at 293 K and the main atmospheric fate represents the thermal decomposition (>0.78). According to the observed temperature dependence of $k(\text{dec})/k(\text{sCI} + \text{SO}_2)$ there is a distinct increase of formed H_2SO_4 with lowering of the temperature.

It is not clear whether $(\text{CH}_3)_2\text{COO}$ can be generally treated as a model component for sCI with two organic groups bound at the C-atom of the COO-group. More experimental work is needed to get a deeper insight in the structure-dependent reactivity of sCI.

5. Summary

The formation of H_2SO_4 formation from the reaction of stabilized Criegee Intermediates with SO_2 has been studied as a function of the 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). The measurements have been conducted in an atmospheric pressure flow tube using NO_3^- -CI-API-TOF mass spectrometry for H_2SO_4 detection. Formed H_2SO_4 in the presence of the OH radical scavenger was attributed to the reaction of sCI with SO_2 . A H_2SO_4 yield from sCI + SO_2 of unity or close to unity has to conclude as a result of the material balance. The sCI yields at 293 K were measured to be 0.49 ± 0.22 for acetaldehyde oxide from trans-2-butene ozonolysis and 0.45 ± 0.20 for acetone oxide from TME ozonolysis. Total yields of OH radicals and sCI were 0.88 ± 0.40 (trans-2-butene) and 1.20 ± 0.54 (TME). The rate coefficient ratio $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ 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: $<4 \cdot 10^{-6}$. Results of this study point to a preferred formation of anti acetaldehyde oxide from trans-2-butene ozonolysis. The H_2SO_4 formation from sCI decreased with rising temperature.

This fact is very probably due to an enhancement of the thermal decomposition of sCI pushing back the importance of the reaction sCI + SO_2 . The rate coefficient ratio $k(\text{dec})/k(\text{sCI} + \text{SO}_2)$ for acetone oxide increased by a factor of 34 increasing the temperature from 278 to 343 K. Thermal decomposition represents the predominate atmospheric fate of acetone oxide. For acetaldehyde oxide, a strong temperature effect was only visible for relatively low RH. For higher RH, the overall sCI loss was dominated by the reaction with water vapour repressing the thermal decomposition pathway.

This study shows that the reactivity of sCI can be strongly dependent on the sCI structure, especially in the reaction with water vapour. More experimental work is needed in order to provide reliable input parameters for atmospheric modelling.

Acknowledgement

The authors thank K. Pielok, R. Gräfe and A. Rohmer for technical assistance.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2014.02.062>.

References

- Atkinson, R., Lloyd, A.C., 1984. Evaluation and mechanistic data for modeling of photochemical smog. *Journal of Physical and Chemical Reference Data* 13, 315–444.
- Berndt, T., Böge, O., Stratmann, F., 2004. Atmospheric particle formation from the ozonolysis of alkenes in the presence of SO_2 . *Atmospheric Environment* 38, 2145–2153.
- Berndt, T., Jokinen, T., Mauldin III, R.L., Petäjä, T., Herrmann, H., Junninen, H., Paasonen, P., Worsnop, D.R., Sipilä, M., 2012. Gas-Phase ozonolysis of selected olefins: the yield of stabilized Criegee intermediate and the reactivity toward SO_2 . *The Journal of Physical Chemistry Letters* 3, 2892–2896.
- Berresheim, H., Elste, T., Plass-Dülmer, C., Eisele, F.L., Tanner, D.J., 2000. Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H_2SO_4 . *International Journal of Mass Spectrometry* 202, 91–109.
- Boy, M., Mogensen, D., Smolander, S., Zhou, L., Nieminen, T., Paasonen, P., Plass-Dülmer, C., Sipilä, M., Petäjä, T., Mauldin, L., Berresheim, H., Kulmala, M., 2013. Oxidation of SO_2 by stabilized Criegee intermediate (sCI) radicals as a crucial source for atmospheric sulfuric acid concentrations. *Atmospheric Chemistry and Physics* 13, 3865–3879.
- Calvert, J.G., Su, F., Bottenheim, J.W., Strausz, O.P., 1978. Mechanism of the homogeneous oxidation of sulphur dioxide in the troposphere. *Atmospheric Environment* 12, 197–226.
- Calvert, J.G., Atkinson, R., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J., Yarwood, G., 2000. *The Mechanisms of Atmospheric Oxidation of the Alkenes*. Oxford University Press, Oxford.
- Cox, R.A., Penkett, S.A., 1972. Aerosol formation from Sulphur dioxide in the presence of ozone and olefinic hydrocarbons. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 68, 1735–1753.
- Criegee, R., 1975. Mechanism of ozonolysis. *Angewandte Chemie International Edition* 14, 745–752.
- Dusanter, S., Vimal, D., Stevens, P.S., 2008. Technical note: measuring tropospheric OH and HO_2 by laser-induced fluorescence at low pressure. A comparison of calibration techniques. *Atmospheric Chemistry and Physics* 8, 321–340.
- Dzozd, G.T., Donahue, N.M., 2011. Pressure dependence of stabilized Criegee intermediate formation from a sequence of alkenes. *The Journal of Physical Chemistry A* 115, 4381–4387.
- Dzozd, G.T., Kroll, J., Donahue, N.M., 2011. 2,3-Dimethyl-2-butene (TME) ozonolysis: pressure dependence of stabilized Criegee intermediates and evidence of stabilized vinyl hydroperoxides. *The Journal of Physical Chemistry A* 115, 161–166.
- Eisele, F.L., Tanner, D.J., 1993. Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere. *Journal of Geophysical Research* 98, 9001–9010.
- Fenske, J.D., Hasson, A.S., Ho, A.W., Paulson, S.E., 2000. Measurement of absolute unimolecular and bimolecular rate constants for CH_3CHOO generated by the trans-2-butene reaction with ozone in the gas phase. *The Journal of Physical Chemistry* 104, 9921–9932.
- Gäb, S., Hellpointer, E., Turner, W.V., Korte, F., 1985. Hydroxymethyl hydroperoxide and bis(hydroxymethyl) peroxide from gas phase ozonolysis of naturally occurring alkenes. *Nature* 316, 535–536.

- Goff, J.A., 1957. Saturation Pressure of Water on the New Kelvin Temperature Scale. Transactions of the American Society of Heating and Ventilating Engineers, pp. 347–354. Technical report, presented at the semi-annual meeting of the American Society of Heating and Ventilating Engineers, Murray Bay, Que. Canada.
- Hatakeyama, S., Akimoto, H., 1994. Reactions of Criegee intermediates in the gas phase. Research on Chemical Intermediates 20, 503–524.
- Hofzumahaus, A., et al., 1997. Reply. Geophysical Research Letters, 3039–3040.
- Jiang, L., Xu, Y., Ding, A., 2010. Reaction of stabilized Criegee intermediates from ozonolysis of limonene with sulfur dioxide: ab initio and DFT study. The Journal of Physical Chemistry A 114, 12452–12461.
- Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R.L., Kulmala, M., Worsnop, D.R., 2012. Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF. Atmospheric Chemistry and Physics 12, 4117–4125.
- Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostianinen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., Worsnop, D.R., 2010. A high-resolution mass spectrometer to measure atmospheric ion composition. Atmospheric Measurement Techniques 3, 1039–1053.
- Kerr, J.A., Calvert, J.G., 1984. Chemical Transformation Modules for Eulerian Acid Deposition Models, vol. 1. National Center for Atmospheric Research, Boulder, CO.
- Kroll, J.H., Sahay, S.R., Anderson, J.G., Demerjian, K.L., Donahue, N.M., 2001. Mechanism of HO_x formation in the gas-phase ozone-alkene reaction. 2. Prompt versus thermal dissociation of carbonyl oxides to form OH. The Journal of Physical Chemistry A 115, 4446–4457.
- Kurten, T., Lane, J.R., Jorgensen, S., Kjaergaard, H.G., 2011. A computational study of the oxidation of SO₂ to SO₃ by gas-phase organic oxidants. The Journal of Physical Chemistry A 115, 8669–8681.
- Kurten, T., Donahue, N.M., 2012. MRCISD studies of the dissociation of vinyl-hydroperoxide, CH₂CHOOH: there is a saddle point. The Journal of Physical Chemistry A 116, 6823–6830.
- Kuwata, K.T., Hermes, M.R., Carlson, M.J., Zogg, C.K., 2010. Computational studies of the isomerization and hydration of acetaldehyde oxide and methyl vinyl carbonyl oxide. The Journal of Physical Chemistry 114, 9192–9204.
- Lanzendorf, E.J., Hanisco, T.F., Donahue, N.M., Wennberg, P.O., 1997. Comment on: "The measurement of tropospheric OH radicals by laser-induced fluorescence spectroscopy during the POPCORN field campaign" by Hofzumahaus et al. and "Intercomparison of tropospheric OH radical measurements by multiple folded long-path laser absorption and laser induced fluorescence" by Brauers, et al. Geophysical Research Letters 24, 3037–3038.
- Li, J., Ying, Q., Yi, B., Yang, P., 2013. Role of stabilized Criegee intermediates in the formation of atmospheric sulfate in Eastern United States. Atmospheric Environment 79, 442–447.
- Lindinger, W., Hansel, A., Jordan, A., 1998. On-line monitoring of volatile organic compounds at ppt levels by means of Proton-Transfer Reaction Mass Spectrometry (PTR-MS) medical application, food control and environmental research. International Journal of Mass Spectrometry and Ion Processes 173, 191–241.
- Mauldin III, R.L., Frost, G.J., Chen, G., Tanner, D.J., Prevot, A.S.H., Davis, D.D., Eisele, F.L., 1998. OH measurements during ACE-1: observations and model comparisons. Journal of Geophysical Research 103, 16713–16729.
- Mauldin III, R.L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V.-M., Kulmala, M., 2012. A new atmospherically relevant oxidant of sulphur dioxide. Nature 488, 193–197.
- MCM, 2013. Master Chemical Mechanism, MCMv3.2. <http://mcm.leeds.ac.uk/MCM/> (accessed 18.06.13.).
- Ryzhkov, A.B., Ariya, P.A., 2004. A theoretical study of the reactions of parent and substituted Criegee intermediates with water and the water dimer. Physical Chemistry Chemical Physics 6, 5042–5050.
- Sarwar, G., Fahey, K., Kwok, R., Gilliam, R.C., Roselle, S.J., Mathur, R., Xue, J., Yu, J., Carter, W.P.L., 2013. Potential impacts of two SO₂ oxidation pathways on regional sulphate concentrations: aqueous-phase oxidation by NO₂ and gas-phase oxidation by stabilized Criegee intermediate. Atmospheric Environment 68, 186–197.
- Suto, M., Manzanares, E.R., Lee, I.C., 1985. Detection of sulphuric acid aerosols by ultraviolet scattering. Environmental Science & Technology 19, 815–820.
- Taatjes, A.C., et al., 2013. Direct measurement of conformer-dependent reactivity of the Criegee intermediate CH₃CHOO. Science 340, 177–180.
- Treacy, J., El Hag, M., O'Farrell, D., Sidebottom, H., 1992. Reactions of ozone with unsaturated organic compounds. Berichte der Bunsengesellschaft für physikalische Chemie 96, 422–427.
- Vereecken, L., Harder, H., Novelli, A., 2012. The reaction of Criegee intermediates with NO, RO₂, and SO₂, and their fate in the atmosphere. Physical Chemistry Chemical Physics 14, 14682–14695.
- Viggiano, A.A., Perry, R.A., Albritten, D.L., Ferguson, E.E., Fehsenfeld, F.C., 1982. Stratospheric negative-ion reaction rates with H₂SO₄. Journal of Geophysical Research 87 (C9), 7340–7342.
- Welz, O., Savee, J.D., Osborn, D.L., Vasu, S.S., Percival, C.J., Shallcross, D.E., Taatjes, C.A., 2012. Direct kinetic measurements of Criegee intermediate (CH₂OO) formed by reaction of CH₂I with O₂. Science 335, 204–207.
- Witter, M., Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J., 2002. Gas-phase ozonolysis: rate coefficients for a series of terpenes and rate coefficients and OH yields for 2-methyl-3-butene and 2,3-dimethyl-2-butene. International Journal of Chemical Kinetics 34, 394–403.