



Reactivity of sCI from  
isoprene and  
monoterpene  
ozonolysis

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# Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO<sub>2</sub> and organic acids

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## Abstract

Oxidation processes in Earth's atmosphere are tightly connected to many environmental and human health issues and are essential drivers for biogeochemistry. Until the recent discovery of the atmospheric relevance of stabilized Criegee intermediates (sCI), atmospheric oxidation processes were thought to be dominated by few main oxidants: ozone, hydroxyl radicals (OH), nitrate radicals and, e.g. over oceans, halogen atoms such as chlorine. Here, we report results from laboratory experiments at 293 K and atmospheric pressure focusing on sCI formation from the ozonolysis of isoprene and the most abundant monoterpenes ( $\alpha$ -pinene and limonene), and subsequent reactions of the resulting sCIs with  $\text{SO}_2$  producing sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The measured sCI yields were  $(0.15 \pm 0.07)$ ,  $(0.27 \pm 0.12)$  and  $(0.58 \pm 0.26)$  for the ozonolysis of  $\alpha$ -pinene, limonene and isoprene, respectively. The ratio between the rate coefficient for the sCI loss (including thermal decomposition and the reaction with water vapour) and the rate coefficient for the reaction of sCI with  $\text{SO}_2$ ,  $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$ , was determined at relative humidities of 10% and 50%. Observed values represent the average reactivity of all sCIs produced from the individual alkene used in the ozonolysis. For the monoterpene derived sCIs, the relative rate coefficients  $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$  were in the range  $(2.0\text{--}2.4) \times 10^{12} \text{ molecule cm}^{-3}$  and nearly independent on the relative humidity. This fact points to a minor importance of the sCI +  $\text{H}_2\text{O}$  reaction in the case of the sCI arising from  $\alpha$ -pinene and limonene. For the isoprene sCIs, however, the ratio  $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$  was strongly dependent on the relative humidity. To explore whether sCIs could have a more general role in atmospheric oxidation, we investigated as an example the reactivity of acetone oxide (sCI from the ozonolysis of 2,3-dimethyl-2-butene) toward small organic acids, i.e. formic and acetic acid. Acetone oxide was found to react faster with the organic acids than with  $\text{SO}_2$ ;  $k(\text{sCI} + \text{acid})/k(\text{sCI} + \text{SO}_2) = (2.8 \pm 0.3)$  for formic acid and  $k(\text{sCI} + \text{acid})/k(\text{sCI} + \text{SO}_2) = (3.4 \pm 0.2)$  for acetic acid. This finding suggests that sCIs

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can play a role in the formation and loss of several atmospheric constituents besides SO<sub>2</sub>.

## 1 Introduction

Ozone, hydroxyl radicals (OH), nitrate radicals and halogens atoms can initiate the oxidation of hydrocarbons such as biogenic terpenes in the atmosphere (Atkinson, 2000). Although the reactivity of these oxidants toward a large variety of atmospheric trace gases is well-established, ambient observations have revealed major ambiguities in atmospheric oxidation chemistry, especially related to OH in locations having high emissions of biogenic volatile organic compounds (BVOCs) (Di Carlo et al., 2004; Lou et al., 2010; Nölscher et al., 2012; Lelieveld et al., 2008; Hofzumahaus et al., 2009; Taraborrelli, et al., 2012). Recently, two additional major processes contributing to the complexity of atmospheric oxidation have been revealed. Firstly, the yet unknown oxidation mechanism producing highly oxidized condensable organic vapours in the gas phase was observed by Ehn et al. (2012). Such vapours are shown to be essential for formation of secondary organic aerosol (Kulmala et al., 1998; Riipinen et al., 2011, 2012). Secondly, the observation that stabilized Criegee intermediates, formed by ozonolysis of biogenic alkenes (Criegee, 1975), add to the oxidation capacity of the atmosphere – at least from the point of view of SO<sub>2</sub> oxidation and subsequent formation of sulphuric acid, H<sub>2</sub>SO<sub>4</sub> (Mauldin et al., 2012; Berndt et al., 2012). These findings demonstrate the incomplete scientific understanding of atmospheric oxidation chemistry. Here, we focus on the latter of those novel observations.

The sCI formation pathway starts when ozone bridges the double bond of an alkene, producing an energy-rich primary ozonide, which very rapidly decomposes via a concerted ring opening to form a carbonyl oxide, the so-called Criegee intermediate (CI) (Calvert et al., 2000). The energy-rich intermediate, CI, either undergoes unimolecular decomposition on a time scale of 1 ns, yielding OH radicals and other products, or it can be stabilized by collisions with gas molecules (Kroll et al., 2001). The resulting stabi-

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lized Criegee intermediate (sCI) can still undergo unimolecular decomposition, leading again to OH radical formation, but with a thermal lifetime thought to be in the order of 1 s depending on temperature and sCI structure (Kroll et al., 2001). Due to the relatively long lifetime of sCI, bimolecular reactions of sCIs with several compounds like water vapour, SO<sub>2</sub>, carbonyls, etc. are also possible (e.g. Neeb et al., 1996; Johnson, 2001; Weltz et al., 2012; Mauldin et al., 2012; Berndt et al., 2012; Taatjes et al., 2012; 2013). These reactions can potentially be fast enough to contribute significantly to the atmospheric oxidation capacity. Thus, some significant gaps in our understanding of atmospheric oxidation could potentially be filled by sCI-chemistry, once the processes controlling the production and fate of sCIs are properly resolved.

Until recently, the reaction rate coefficients of sCIs with atmospheric compounds, such as SO<sub>2</sub>, were thought to be too small (Johnson, 2001) to cause measurable effects on atmospheric oxidation chemistry, with the exception of the sCI + water vapour reactions (Hasson, 2003). The reaction with water vapour was also thought to be the main fate of sCIs in the atmosphere. However, Mauldin et al. (2012), recently reported ambient and laboratory observations strongly suggesting an atmospherically relevant reaction between sCI and SO<sub>2</sub>. This was qualitatively supported by the laboratory experiment of Welz et al. (2012). Welz et al. (2012) studied the simplest possible Criegee intermediate (formaldehyde oxide, CH<sub>2</sub>OO) in a low-pressure (4 torr) laboratory experiment, finding a rate coefficient for the CH<sub>2</sub>OO + SO<sub>2</sub> reaction of  $3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Mauldin et al. (2012) estimated the reaction rate coefficient to be roughly  $6 \times 10^{-13}$  and  $8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for sCIs from the ozonolysis of  $\alpha$ -pinene and limonene, respectively. Berndt et al. (2012) investigated experimentally the sCI yields, lifetimes, and rate coefficients for reactions with SO<sub>2</sub> for sCIs from the ozonolysis of selected alkenes including 2,3-dimethyl-2-butene (TME), trans-2-butene and 1-methyl-cyclohexene (MCH). They found typical lifetimes at atmospheric pressure and an atmospherically relevant humidity of a few hundreds of milliseconds, and reaction rate coefficients for sCI + SO<sub>2</sub> in the order of  $10^{-13}$ – $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , depending on the structure of the sCI.

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It should be noted that ozonolysis of a single alkene in most cases produces structurally different types of sCI, including syn- and anti-conformers (for sCIs with one H-atom bound at the C-OO carbon) which might have different reactivities. Therefore, the given data for  $\alpha$ -pinene and limonene (Mauldin et al., 2012) and for trans-2-butene and 1-methyl-cyclohexene (Berndt et al., 2012) represent average values for the reactivity of all sCIs arising from the selected alkene.

In summary both the laboratory measurements of Berndt et al. (2012) and field observations of Mauldin et al. (2012) suggest that sCI are roughly a factor of  $\sim 100$  more reactive with  $\text{SO}_2$  than assumed earlier (Johnson, 2001), but approximately two orders of magnitude less reactive than the close-to-collision-limit rate coefficient by Welz et al. (2012). Nevertheless, while recent findings agree on the potential significance of the sCI +  $\text{SO}_2$  reaction, there is still a considerable uncertainty in the absolute and relative rate constants obtained by different experimental approaches.

Understanding the reaction of the sCI +  $\text{SO}_2$  is highly important from the atmospheric chemistry and physics point of view. Sulphuric acid plays a key role in Earth's atmosphere triggering secondary aerosol formation (Kulmala et al., 2004; Berndt et al., 2005, Riipinen et al., 2007; Sipilä et al., 2010; Kerminen et al., 2010), and thus connects natural and anthropogenic  $\text{SO}_2$  emissions to global climate via indirect aerosol effects on radiative forcing. The effect of sCI on  $\text{SO}_2$  oxidation was assessed by Boy et al. (2013), who simulated sulphuric acid production at the SMEAR II boreal forest field station using the reaction rate coefficients suggested by Mauldin et al. (2012). Their results supported the experimental observations by Mauldin et al. (2012), showing that a significant fraction (several tens of percents) of ground-level gas phase sulphuric acid originates from sCI-oxidation of  $\text{SO}_2$ . Pierce et al. (2013) took a step further and studied the role of the sCI +  $\text{SO}_2$  reaction to global aerosol and CCN concentrations by the global climate model. They found, in accordance with Boy et al. (2013) that sCIs can contribute significantly to gas phase  $\text{H}_2\text{SO}_4$  in the lower troposphere above forested areas. However, due to further aerosol dynamical processes during particle growth to CCN sizes, the influence of sCI on sulphuric acid concentration was only

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feebly projected to CCN concentrations, and thus to radiative forcing. However, Pierce et al. (2013) used reaction rate coefficients, including the upper limit for the sCI loss rate (decomposition and reaction with water vapour), obtained by Welz et al. (2012) for CH<sub>2</sub>OO. Furthermore, the sCI reaction rate coefficients may be strongly dependent on the sCI structure. Therefore, a reassessment of the CCN sensitivity, using parameters obtained for atmospherically relevant sCIs in atmospheric conditions, is warranted.

On top of the reaction with SO<sub>2</sub>, a further, mostly unresolved question is whether or not oxidation by sCI has a more general role in atmospheric chemistry. Taatjes et al. (2012, 2013) showed that sCIs – at least the simple sCIs – are reactive toward some other trace gases in addition to SO<sub>2</sub>. Still, the reactions of atmospherically relevant sCIs with compounds other than SO<sub>2</sub> have not been investigated so far.

In the present study, we investigate experimentally the sCI yield and the rate coefficient  $k(\text{sCI} + \text{SO}_2)$  relative to loss coefficient:  $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$ , with loss coefficient incorporating thermal decomposition and the reaction with water vapour,  $k(\text{loss}) = k(\text{dec.}) + k(\text{sCI} + \text{H}_2\text{O}) \times [\text{H}_2\text{O}]$ . This rate coefficient ratio represents (for different temperatures and water vapour concentrations) the important parameter for understanding the sCI controlled oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> in the atmosphere. This study comprises reactions of sCIs produced from the ozonolysis of isoprene and two monoterpenes abundant in the atmosphere:  $\alpha$ -pinene and limonene. To demonstrate the capability of sCIs of playing a more general role in atmospheric chemistry, we investigated the reaction of acetone oxide ((CH<sub>3</sub>)<sub>2</sub>COO, the sCI from TME ozonolysis) with small organic acids.

## 2 Methods

### 2.1 NO<sub>3</sub><sup>-</sup>-chemical ionization-atmospheric pressure interface-time-of-flight mass spectrometer (NO<sub>3</sub><sup>-</sup>-CI-API-TOF)

A NO<sub>3</sub><sup>-</sup>-CI-API-TOF was used in the experiments described here primarily for the detection of sulphuric acid. The NO<sub>3</sub><sup>-</sup>-CI-API-TOF comprises a specially designed inlet for chemical ionization at ambient pressure (CI), and an atmospheric pressure interface (APi) to couple ions to a time-of-flight mass spectrometer (TOF). The instrument is described in detail by Jokinen et al. (2012) but the CI-part of the system will be shortly discussed also here. The APi-TOF is well described elsewhere (Junninen et al., 2010).

The design of the CI-inlet is largely based on the original NCAR-design (Eisele et al., 1993; Kurtén et al., 2011; Jokinen et al., 2012). Ions are produced in a sheath flow concentric to the sample flow by a 10 MBq 241-Am radioactive  $\alpha$ -emitter. Minute quantities of nitric acid vapour are fed into sheath air surrounding the sample inlet flow, resulting in the formation of NO<sub>3</sub><sup>-</sup> (HNO<sub>3</sub>)<sub>n,n=0-2</sub> ions. These ions are pushed into the sample flow, entering the ion-molecule interaction chamber at the centre line, by means of an electric field. The design is virtually wall-less, and sample wall loss occurs only in the sample inlet tube. The sample flow in the system is 10 lpm and the concentric sheath flow where ions are produced is 20 lpm. Sheath gas is air purified with a particle filter and an SO<sub>2</sub> scrubber.

Sample ionization in the CI-system occurs at atmospheric pressure via proton transfer between nitrate ions and sulphuric acid and subsequent HSO<sub>4</sub><sup>-</sup> × HNO<sub>3</sub> adduct formation:



The chemically ionized sample is drawn inside the mass spectrometer through a critical orifice with a flow rate of ~ 0.8 lpm. The ions are then guided through the differentially pumped APi using quadrupoles and eventually to the TOF for  $m/Q$  separation.

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A fraction of  $\text{HSO}_4^- \times \text{HNO}_3$  clusters (Reaction R1) fragment inside the APi-TOF. The sulphuric acid concentration (in  $\text{molec cm}^{-3}$ ) measured with the  $\text{NO}_3^-$ -CI-APi-TOF is calculated from the measured ion signals according to:

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

where  $C$  is the calibration coefficient determined to be  $C = 1.85 \times 10^{10}$  (Jokinen et al., 2012). The detection limit for sulphuric acid monomer is of the order of  $10^4 \text{ molec cm}^{-3}$  and the error in determined sulphuric acid concentration is  $\pm 45\%$  (Berndt et al., 2012). Data were analysed using TofTools software.

## 2.2 Laboratory experiments

Laboratory experiments were conducted in the Leibniz-Institute for Tropospheric Research Laminar Flow Tube (IfT-LFT) at  $T = 293 \pm 0.5 \text{ K}$ ,  $\text{RH} = 10\text{--}50\%$  ( $[\text{H}_2\text{O}] = (0.58 - 2.89) \times 10^{17} \text{ molec cm}^{-3}$ ) and with a flow of  $30 \text{ L min}^{-1}$  (STP) synthetic air as the carrier gas, resulting in a total residence time of 39.5 s. The experimental methods are identical to those reported in Berndt et al. (2013), but will be described briefly here.

In the experiments focusing on sCI yields and the relative reaction rate coefficients, the alkenes,  $\text{SO}_2$  and the OH radical scavenger (propane) premixed with the humidified carrier gas were fed at the top of the flow tube. Ozone diluted with the carrier gas was introduced through an inlet 55 cm downstream the port for the other reactants. The added propane ensured more than 98% scavenging efficiency for OH radicals formed in the ozonolysis. The  $\text{SO}_2$  concentration was varied in the range  $3.2 \times 10^{11} - 2.4 \times 10^{14} \text{ molec cm}^{-3}$ . Concentrations of alkenes, propane, ozone, the reaction rate coefficients used as well as the concentration of reacted alkenes within the residence time of 39.5 s are given in Table 1.

In the experiments focusing on the reactivity of sCI (acetone oxide) toward HCOOH (formic acid) and  $\text{CH}_3\text{COOH}$  (acetic acid), with concentrations ranging between  $3. \times$

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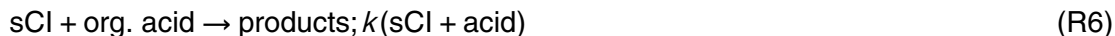
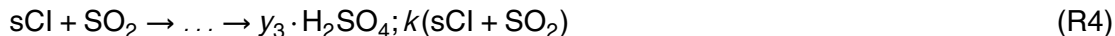
$10^{10}$ – $2. \times 10^{13}$  molecule  $\text{cm}^{-3}$ , were fed together with other reagents at the top of the flow tube. Concentrations of the reagents were (unit: molecule  $\text{cm}^{-3}$ ):  $[\text{TME}] = 4. \times 10^{10}$ ,  $[\text{O}_3] = 2.2 \times 10^{11}$ ,  $[\text{SO}_2] = 3.2 \times 10^{12}$ ,  $[\text{propane}] = 1.64 \times 10^{15}$  and a relative humidity of 10%.

In all experiments sulphuric acid was measured using the  $\text{NO}_3^-$ -CI-APi-TOF and alkene concentrations we measured with the proton transfer reaction mass spectrometer (Ionicon PTR-MS) (Lindinger et al., 1998). The derivation of the parameters of interest from experimental data is described in the Sect. 3.

### 3 Results and discussion

#### 3.1 sCI yields and relative rate coefficients

Figures 1–3 show the sulphuric acid concentration measured at the outflow of IFT-LFT as a function of  $[\text{SO}_2]$  at RH = 10 % and RH = 50 %. In analysing the experimental data the following reaction sequence (R2)–(R6) was considered.



First, ozone, when reacting with alkene, produces Criegee intermediate, CI, which can either rapidly (nanoseconds) decompose and produce OH (with a yield  $y_1$ ) and other products or be stabilized by collisions with the pressure gas resulting in formation of sCI with a yield  $y_2$  (Reaction R2). The sCI can react with water vapour (Reaction R3) or with  $\text{SO}_2$  (Reaction R4). Here we assume that the yield ( $y_3$ ) for reaction (Reaction R4) is unity (see discussion on the validity of assumption below). The sCI can also ther-

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mally decompose before reacting with other molecules, resulting in production of OH and other products (Reaction R5). In addition to unimolecular decomposition and reactions with H<sub>2</sub>O and SO<sub>2</sub>, sCl can, as we will demonstrate, react with organic acids (Reaction R6) and potentially with several other atmospheric constituents.

In absence of organic acid only Reactions (R2)–(R5) are considered. The fraction of sCl that oxidises SO<sub>2</sub> and produce sulphuric acid (sCl<sub>H<sub>2</sub>SO<sub>4</sub></sub>/sCl<sub>TOT</sub>) is equal to the sCl reaction rate with SO<sub>2</sub> (Reaction R4) divided by the sum of all reaction rates (total reaction rate) of sCl (Reactions R3–R5):

$$\frac{sCl_{H_2SO_4}}{sCl_{TOT}} = \frac{k(sCl + SO_2)[SO_2]}{k(sCl + SO_2)[SO_2] + k(dec.) + k(sCl + H_2O)[H_2O]} \quad (2)$$

It follows for a given RH and  $k(loss) = k(dec.) + k(sCl + H_2O) \cdot [H_2O]$  that the total concentration of sulphuric acid produced during the experiment is:

$$[H_2SO_4] = \frac{1}{1 + \frac{k(loss)}{k(sCl+SO_2)[SO_2]}} \cdot [H_2SO_4]_{sCl} \quad (3)$$

where  $[H_2SO_4]_{sCl}$  stands for  $[H_2SO_4]$  from sCl titration, i.e all sCl is converted to H<sub>2</sub>SO<sub>4</sub> in the presence of high SO<sub>2</sub> concentrations via Reaction (R4) making Reactions (R3) and (R5) negligible. In the analysis we assumed 28 % wall loss in total sulphuric acid concentration (Berndt et al., 2013) and the measured values were corrected for the wall loss before used in the data analysis.

The yield  $y_2$  of sCl from Reaction (R2) can be obtained from the knowledge of the reacted alkene and  $[H_2SO_4]_{sCl}$  assuming a H<sub>2</sub>SO<sub>4</sub> yield of unity from Reaction (R4):

$$y_2 = \frac{[H_2SO_4]_{sCl}}{\text{reacted [alkene]}} \quad (4)$$

The amount of reacted alkene and ozone was kept very small (less than 1 % each) allowing us to calculate the reacted alkene concentration according to Eq. (5), see also

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Table 1:

$$\text{reacted [alkene]} = k(\text{O}_3 + \text{alkene}) \cdot [\text{alkene}] \cdot [\text{O}_3] \cdot t \quad (5)$$

The relative rate coefficients  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$  and the sCl yield  $y_2$  were obtained by least square fitting of Eqs. (3) and (4) to the experimental data (Figs. 1–3).

The above approach assumes that all sCl's formed from a selected alkene show a similar reactivity in Reactions (R3)–(R5). Or, in other words, we are able to describe only average effects of all sCl's. Ozonolysis of a single alkene can result in the production of different types of Cl and thus sCl. In case of  $\alpha$ -pinene, possible sCl's include two different isomers, one of which can be either a syn or anti conformer; all in all sCl from  $\alpha$ -pinene ozonolysis can have three different structures. The same applies for limonene. Nevertheless, the “one-sCl” approach seems to work well for  $\alpha$ -pinene and limonene, suggesting that one of the possible sCl structures dominates, or that different sCl's show similar  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$ . With the help of the “single sCl” model, Eq. (3), the experimental data are described reasonably well (Figs. 1 and 2). For isoprene, due to the structure of the parent alkene, four different sCl structures are possible, as we shall show below, the “one-sCl” model is not sufficient for isoprene.

In the flow-tube experiments for monoterpenes, increasing the water-vapour concentration by a factor of five did not change the results within the experimental uncertainties. This indicates that thermal decomposition dominates the loss mechanism of sCl under these conditions and the reaction with water vapour is of less importance, i.e.  $k(\text{dec.}) \gg k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$  for  $[\text{H}_2\text{O}] \leq 2.9 \times 10^{17} \text{ molecule cm}^{-3}$ . The relative rate coefficients and yields from monoterpene ozonolysis experiments are summarized in Table 2.

The experiments with isoprene showed a different behaviour. At low water vapour concentration, RH = 10 %, the above approach of the “one sCl” model fits well to the experimental data. At an elevated water vapour concentration (RH = 50 %) a significant drop in sulphuric acid concentration is observed and the “one sCl” model fails in describing the data. The flaw of the “one sCl” model can be explained by different re-

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activity of different sCIs toward water vapour. To account for the possible differences in the reactivity of different sCIs, Eq. (3) was extended to a “two sCI” model considering different reactivities in Reactions (R3)–(R5):

$$[\text{H}_2\text{SO}_4] = \frac{1}{1 + \frac{k(\text{loss})_{\text{I}}}{k(\text{sCI} + \text{SO}_2)_{\text{I}}[\text{SO}_2]}} \cdot [\text{H}_2\text{SO}_4]_{\text{sCI}_{\text{I}}} + \frac{1}{1 + \frac{k(\text{loss})_{\text{II}}}{k(\text{sCI} + \text{SO}_2)_{\text{II}}[\text{SO}_2]}} \cdot [\text{H}_2\text{SO}_4]_{\text{sCI}_{\text{II}}} \quad (6)$$

5 Non-linear regression analysis to the experimental data suggest that the “first sCI” (type I) is responsible on 85% and the “second sCI” (type II) on 15% of the total measured  $[\text{H}_2\text{SO}_4]_{\text{sCI}}$ . Furthermore, it shows that the relative rates coefficients  $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$  are significantly different between the two sCIs:  $3.3 \times 10^{13}$  molecules  $\text{cm}^{-3}$  for type I and  $2.6 \times 10^{11}$  molecules  $\text{cm}^{-3}$  for type II. From our experiment we cannot draw clear  
10 conclusions on what kind of sCI formed from the isoprene ozonolysis is responsible for type I and type II. It could be speculated that  $\text{CH}_2\text{OO}$  and/or an *anti*-conformer sCI causes the strong RH dependence of produced sulphuric acid due to their efficient reaction with water vapour (Reaction R3) in competition with Reaction (R4). The relative rate coefficients and yields are summarized in Table 2.

15 The relative rate coefficients  $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$  obtained in this study are close to those obtained by Berndt et al. (2013) for sCI from the ozonolysis of trans-2-butene and TME. Berndt et al. (2013) also showed that significant differences in the relative rate coefficients occurred between *syn*- and *anti*-conformers of sCI from trans-2-butene.

Similar to Berndt et al. (2012, 2013), our analysis of the relative rate coefficients and sCI yields incorporates the yield of  $\text{H}_2\text{SO}_4$  from the sCI +  $\text{SO}_2$  reaction – i.e. our investigation is limited to the channel leading to the formation of  $\text{H}_2\text{SO}_4$ . However, the yields cannot be significantly below unity, since otherwise the obtained yields of sCI should be higher by the same factor. As the sCI yield cannot exceed unity, we conclude that the yield of  $\text{H}_2\text{SO}_4$  from sCI +  $\text{SO}_2$  reaction must be, if not unity, at least  $> 0.2$  for monoterpene sCIs and  $> 0.5$  for isoprene sCIs. However, there is reason to believe that  
20 the  $\text{H}_2\text{SO}_4$  yields are much higher than that and thus very close to unity; our measured sCI yield for  $\alpha$ -pinene of  $0.15 \pm 0.07$  assuming an unity  $\text{H}_2\text{SO}_4$  yield from sCI +  $\text{SO}_2$

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is in excellent agreement with a yield of 0.15 recently determined with an sCl-specific scavenger technique (Drozd and Donahue, 2011). These facts also call the stable, non-SO<sub>3</sub> producing, secondary ozonides, theoretically investigated by Kurtén et al. (2011) and Veerecken et al. (2012), as a predominant product from the sCl + SO<sub>2</sub> reaction into question.

Our results on relative rate coefficient can be compared to those calculated from the data reported by Welz et al. (2012) who, as discussed above, studied the simplest possible Criegee, (CH<sub>2</sub>OO) in a low pressure system. They found  $k(\text{sCl} + \text{SO}_2) = 3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , lower end estimation for the lifetime against decomposition of 2 ms – resulting in upper end estimation for  $k(\text{dec.})$  of  $500 \text{ s}^{-1}$  – and the upper end estimation for reaction coefficient with H<sub>2</sub>O of  $k(\text{sCl} + \text{H}_2\text{O}) < 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Using the upper end rate coefficients for CH<sub>2</sub>OO in  $k(\text{loss}) = k(\text{dec.}) + k(\text{sCl} + \text{H}_2\text{O}) \times [\text{H}_2\text{O}]$ , for the relative reaction rate coefficients,  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$ , follow  $< 1.9 \times 10^{13} \text{ molecule cm}^{-3}$  (RH = 10 %) and  $< 4.2 \times 10^{13} \text{ molecule cm}^{-3}$  (RH = 50 %) being qualitatively not in contradiction with our results for the sCIs of the monoterpenes and isoprene, see Table 2. Assuming that the reaction of CH<sub>2</sub>OO with H<sub>2</sub>O dominates the loss process ( $k(\text{dec.}) \ll k(\text{sCl} + \text{H}_2\text{O}) \times [\text{H}_2\text{O}]$ ), the resulting  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$  ratios from Welz et al. (2012) data are  $< 5.9 \times 10^{12} \text{ molecule cm}^{-3}$  (RH = 10 %) and  $< 3. \times 10^{13} \text{ molecule cm}^{-3}$  (RH = 50 %) again not contrarily to our findings. A more detailed comparison is impossible because the study by Welz et al. (2012) yielded only upper limits for the rate coefficients of the sCl decomposition step (Reaction R5) and the reaction of sCl with H<sub>2</sub>O (Reaction R3). It is to be noted also here, that Reactions (R3) and/or (R5) describe the most important, atmospheric loss processes. For a reliable assessment of the importance of H<sub>2</sub>SO<sub>4</sub> formation in the atmosphere via sCl + SO<sub>2</sub>, the sCl main Reactions (R3) and (R5) must be characterized very well.

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### 3.2 Reaction of sCl with organic acids

The reaction of acetone oxide ((CH<sub>3</sub>)<sub>2</sub>COO, sCl from TME ozonolysis) with small organic acids was investigated by a competitive reaction kinetics experiment at constant SO<sub>2</sub> concentration (3.2 × 10<sup>12</sup> molecule cm<sup>-3</sup>) and varying the concentration of the organic acids (Fig. 4).

Berndt et al. (2013) showed that for acetone oxide the reaction with water vapour (Reaction R3) is of less importance compared with the thermal decomposition (Reaction R5) for RH ≤ 50%. Our experiment was conducted at low RH (10%) and thus only the thermal decomposition of sCl was considered together with the reactions of sCl with SO<sub>2</sub> (Reaction R4) and the acids (Reaction R6). From pathways (R4)–(R6) follows:

$$[\text{H}_2\text{SO}_4] = \frac{1}{1 + \frac{k(\text{dec.})}{k(\text{sCl} + \text{SO}_2)[\text{SO}_2]} + \frac{k(\text{sCl} + \text{acid})[\text{acid}]}{k(\text{sCl} + \text{SO}_2)[\text{SO}_2]}} \cdot [\text{H}_2\text{SO}_4]_{\text{sCl}} \quad (7)$$

The relative rate coefficient  $k(\text{dec.})/k(\text{sCl} + \text{SO}_2)$  was determined by Berndt et al. (2013) to be 4.2 × 10<sup>12</sup> molecules cm<sup>-3</sup>. [H<sub>2</sub>SO<sub>4</sub>] stands again for the loss corrected sulphuric acid concentration at the lft-LFT outflow and [H<sub>2</sub>SO<sub>4</sub>]<sub>sCl</sub> for [H<sub>2</sub>SO<sub>4</sub>] from sCl titration. Results from the non-linear regression analysis [H<sub>2</sub>SO<sub>4</sub>] = *f*([acid]) from Eq. (7) yields the free parameters  $k(\text{sCl} + \text{acid})/k(\text{sCl} + \text{SO}_2)$  and [H<sub>2</sub>SO<sub>4</sub>]<sub>sCl</sub>, see Table 3. Our measurements reveal an about three times faster reaction of acetone oxide with the acids compared with the reaction with SO<sub>2</sub>. The reasonably high reactivity of sCl toward small organic acids points toward a more general role of sCl oxidation chemistry in the atmosphere and demonstrates the necessity to investigate the sCl chemistry with a wider scope.

## 4 Conclusions and summary

We investigated experimentally the sCl yield and relative rate coefficient  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$  for the sCl loss reaction,  $k(\text{loss}) = k(\text{dec.}) + k(\text{sCl} + \text{H}_2\text{O}) \times [\text{H}_2\text{O}]$ , and the  $\text{H}_2\text{SO}_4$  producing reaction of sCl with  $\text{SO}_2$ . The values  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$  are the key quantities for an assessment of the role of sCl for the sulphuric acid production in the atmosphere via  $\text{sCl} + \text{SO}_2$ . Investigations probed sCl from the ozonolysis of isoprene and two monoterpenes,  $\alpha$ -pinene and limonene, at ambient-relevant temperature, pressure and humidity. The observed quantities represent average values of all sCl's produced from the individual alkene. The sCl yields were in the range of few tens of % and similar to the yields determined for smaller sCl's using the same approach (Berndt et al., 2013) or another sCl-specific scavenger technique (Drozd and Donahue, 2011). For the studied monoterpenes, the relative rate coefficients  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$  were in the range of  $(2.0\text{--}2.4) \times 10^{12} \text{ molecules cm}^{-3}$  with no measurable effect on the relative humidity (RH = 10 or 50 %). In the case of the isoprene derived sCl's an efficient reaction with water vapour was observed making  $k(\text{loss})/k(\text{sCl} + \text{SO}_2)$  strongly RH-dependent. We also showed that beyond the contribution to sulphuric acid formation, sCl can react rapidly with small organic acids, and thus potentially with several other atmospheric constituents, suggesting that sCl's have a more general role in the atmospheric chemistry than  $\text{SO}_2$  oxidation alone.

Our results demonstrate the necessity to investigate non-OH oxidation especially in the forested areas of the world, where the level of understanding of atmospheric oxidation chemistry is lowest. The most significant open question in atmospheric oxidation still to be answered is related to the enigma of oxidation mechanisms of highly oxidized organics, believed to be crucial for secondary nanoparticle formation (Riipinen et al., 2012; Kulmala et al., 2013) and qualitatively observed by Ehn et al. (2012), as well as their role in atmospheric aerosol formation and global climate.

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**Table 1.** Concentrations of alkenes (initial and reacted within the residence time of 39.5 s), OH-scavenger and O<sub>3</sub>, and the reaction rate coefficients used in the experiments.

Alkene	[alkene] molecule cm <sup>-3</sup>	[propane] molecule cm <sup>-3</sup>	[O <sub>3</sub> ] molecule cm <sup>-3</sup>	<i>k</i> (alkene + O <sub>3</sub> ) cm <sup>3</sup> s <sup>-1</sup>	reacted [alkene] molecule cm <sup>-3</sup>
α-Pinene	8.0 × 10 <sup>11</sup>	(1.64–8.2) × 10 <sup>15</sup>	2.2 × 10 <sup>11</sup>	1.1 × 10 <sup>-16</sup>	7.65 × 10 <sup>8</sup>
Limonene	1.6 × 10 <sup>11</sup>	(1.64–8.2) × 10 <sup>15</sup>	2.2 × 10 <sup>11</sup>	2.5 × 10 <sup>-16</sup>	3.48 × 10 <sup>8</sup>
Isoprene	1.5 × 10 <sup>12</sup>	(1.64–8.2) × 10 <sup>15</sup>	2.2 × 10 <sup>11</sup>	1.29 × 10 <sup>-17</sup>	1.68 × 10 <sup>8</sup>

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**Table 2.** Results according to Eqs. (3) and (4) from nonlinear regression analysis  $[H_2SO_4] = f([SO_2])$ .

Alkene	$k(\text{loss})/k(\text{sCl} + \text{SO}_2)$ molecule $\text{cm}^{-3}$	$[H_2SO_4]_{\text{sCl}}$ molecule $\text{cm}^{-3}$	sCl yield
$\alpha$ -Pinene	$(2.4 \pm 0.2) \times 10^{12}$ RH: 10 % $(2.0 \pm 0.4) \times 10^{12}$ RH: 50 %	$(1.15 \pm 0.02) \times 10^8$ RH: 10 % $(1.13 \pm 0.04) \times 10^8$ RH: 50 %	$0.15 \pm 0.07$
Limonene	$(2.4 \pm 0.2) \times 10^{12}$ RH: 10 % $(2.1 \pm 0.2) \times 10^{12}$ RH: 50 %	$(9.3 \pm 0.1) \times 10^7$ RH: 10 % $(9.3 \pm 0.2) \times 10^7$ RH: 50 %	$0.27 \pm 0.12$
Isoprene	$(2.5 \pm 0.1) \times 10^{12}$ RH: 10 % $(2.1 \pm 0.5) \times 10^{13}$ RH: 50 %*	$(9.9 \pm 0.1) \times 10^7$ RH: 10 % $(9.7 \pm 0.6) \times 10^7$ RH: 50 %	$0.58 \pm 0.26$

\* For a “two sCl” model we get  $3.3 \times 10^{13}$  and  $2.6 \times 10^{11}$  assuming the same total  $[H_2SO_4]_{\text{sCl}}$ , where the first sCl accounts for ~ 85 % and the second for ~ 15 %.

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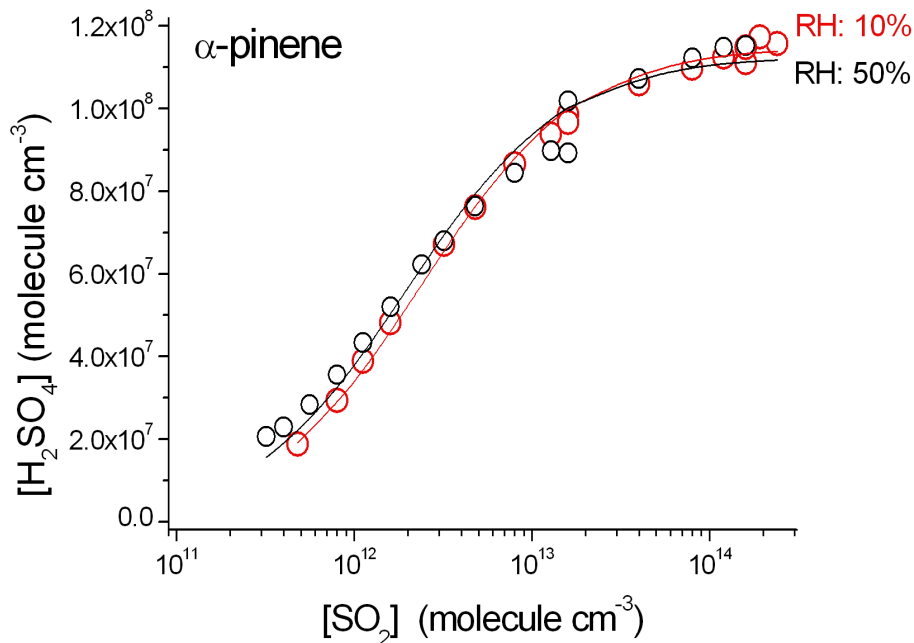
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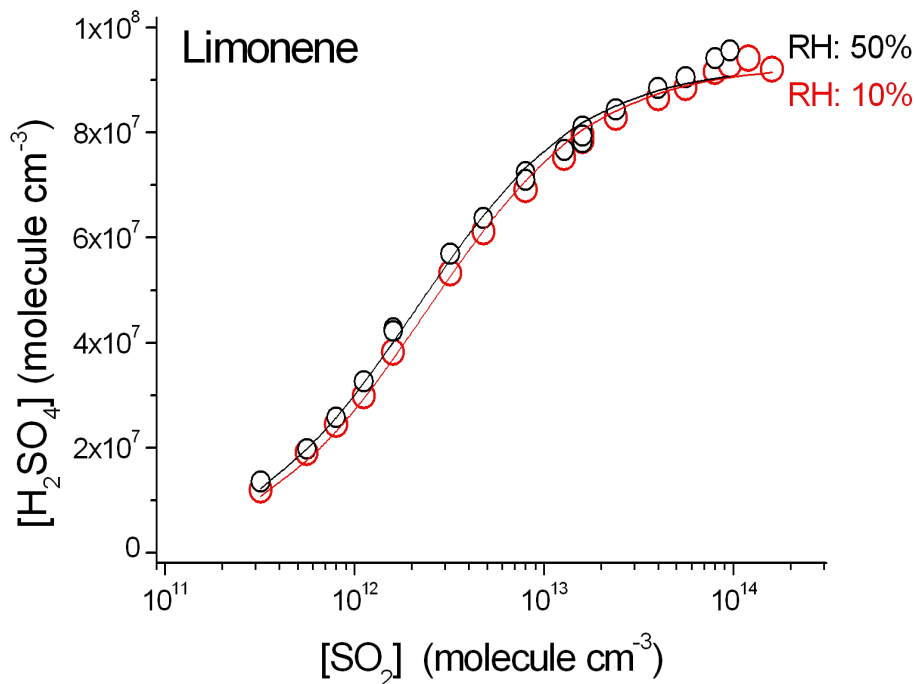
**Table 3.** Relative reaction rate coefficients for reaction of  $(\text{CH}_3)_2\text{COO}$  (sCI from TME ozonolysis) with small organic acids and  $\text{SO}_2$  based on competitive reaction kinetics experiments.

acid	$k(\text{sCI} + \text{acid})/k(\text{sCI} + \text{SO}_2)$	$[\text{H}_2\text{SO}_4]_{\text{sCI}}$ , molecule $\text{cm}^{-3}$
HCOOH, formic acid	$(2.80 \pm 0.32)$	$2.05 \times 10^8$
$\text{CH}_3\text{COOH}$ , acetic acid	$(3.43 \pm 0.22)$	$2.05 \times 10^8$





**Fig. 1.** Loss-corrected measured  $[\text{H}_2\text{SO}_4]$  at the outflow of IFT-LFT in  $\alpha$ -pinene experiments at RH = 10% and RH = 50%. Lines show multivariate least square fittings according to Eq. (3) from which the relative rate coefficients and sCI yield were obtained.



**Fig. 2.** Loss-corrected measured  $[\text{H}_2\text{SO}_4]$  at the outflow of IFT-LFT in limonene ozonolysis experiment at RH = 10% and RH = 50%. Lines show multivariate least square fittings according to Eq. (3).

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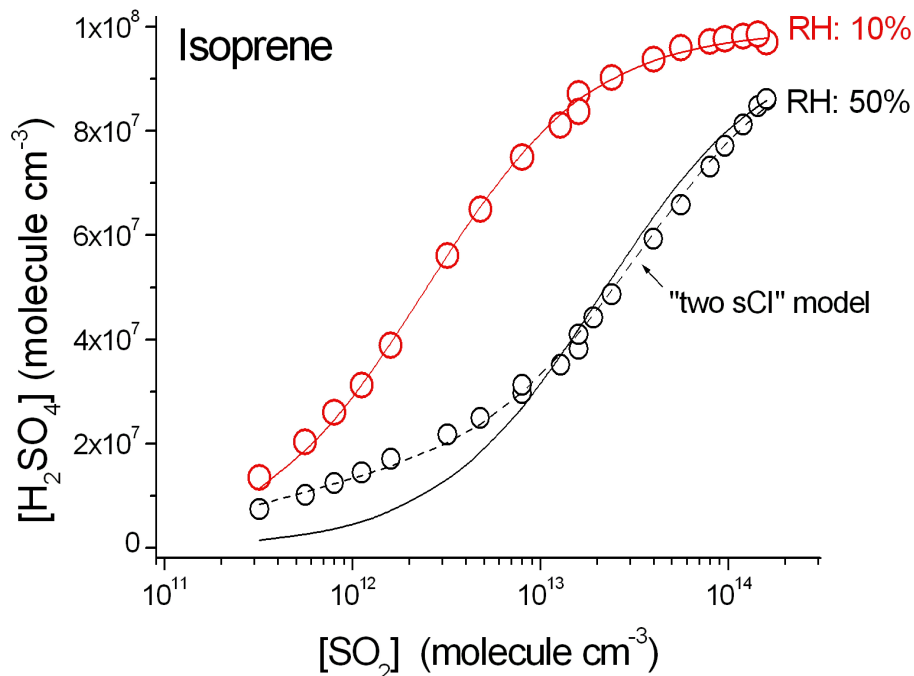
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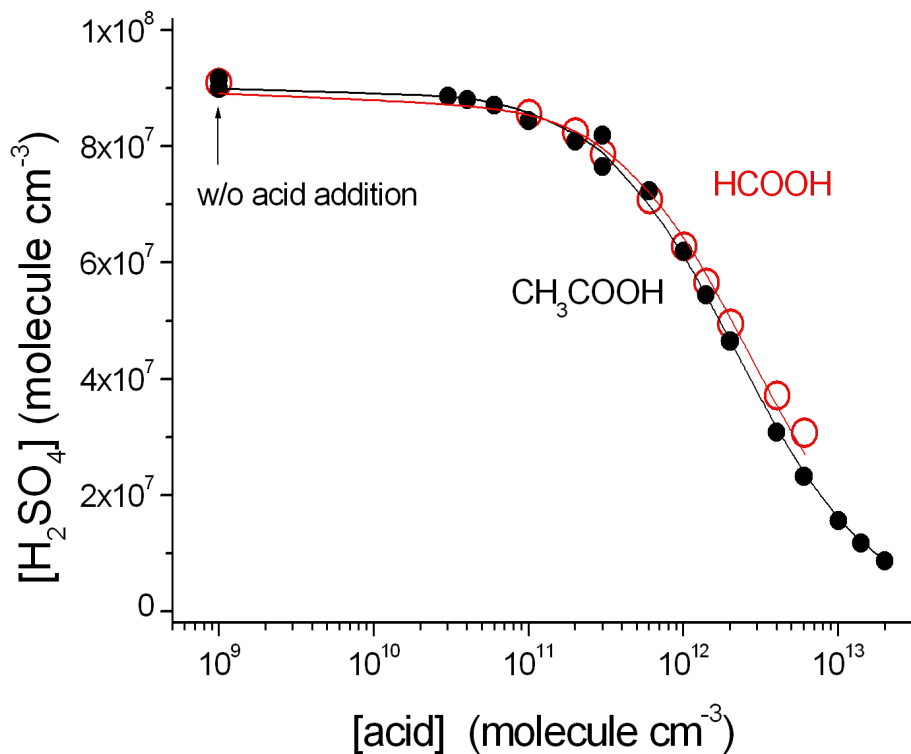
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**Fig. 3.** Loss-corrected measured  $[\text{H}_2\text{SO}_4]$  at the outflow of IFT-LFT in isoprene experiments at  $\text{RH} = 10\%$  and  $\text{RH} = 50\%$ . Solid lines show multivariate least square fittings according to Eq. (3). Dashed line shows the multivariate least square fittings according to Eq. (6) which accounts for the different behaviour of different sCIs.



**Fig. 4.** Experimental data from the competitive reaction kinetics experiments,  $\text{sCl} + \text{SO}_2$  vs.  $\text{sCl} + \text{acid}$ ,  $\text{sCl} \equiv (\text{CH}_3)_2\text{COO}$  (from TME ozonolysis). The lines show the best fit result of the non-linear regression analysis from Eq. (7).