Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO_2 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 the reaction of stabilized Criegee intermediates (sCI) with SO_2, 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 (α-pinene and limonene), and subsequent reactions of the resulting sCIs with SO_2 producing sulphuric acid (H_2SO_4). The measured total sCI yields were (0.15 ± 0.07), (0.27 ± 0.12) and (0.58 ± 0.26) for α-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 SO_2, k(loss) / k(sCI+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(loss) / k(sCI+SO_2) were in the range $(2.0 - 2.4) \cdot 10^{12}$ molecule cm^{-3} and nearly independent on the relative humidity. This fact points to a minor importance of the sCI + H_2O reaction in the case of the sCI arising from α-pinene and limonene. For the isoprene sCIs, however, the ratio k(loss) / k(sCI+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 SO_2; k(sCI+acid) / k(sCI+SO_2) = (2.8 ± 0.3) for formic acid and k(sCI+acid) / k(sCI+SO_2) = (3.4 ± 0.2) for acetic acid. This finding indicates that sCIs can play a role in the formation and loss of other atmospheric constituents besides SO_2.

1 Introduction

Ozone, hydroxyl radicals (OH) and 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 auto-oxidation mechanism producing highly oxidized condensable organic vapours in the gas phase discovered by Ehn et al. (2014). Such vapours are shown to be essential for formation of secondary organic aerosol (Kulmala et al., 1998; Riipinen et al., 2011). Secondly, the suggestion that stabilized Criegee Intermediates, formed by ozonolysis of biogenic alkenes (Criegee, 1975), might add to the oxidation capacity of the atmosphere – at least from the point of view of SO_2 oxidation and subsequent formation of sulphuric acid, H_2SO_4 (Mauldin et al., 2012; Berndt et al., 2012; Welz 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 reacts with 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 stabilized Criegee Intermediate (sCI) can still undergo unimolecular decomposition, leading again to OH radical formation and others, 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_2, carbonyls, organic acids, etc. are also possible (e.g. Neeb et al., 1996, 1997; Johnson, 2001; Welz et al., 2012, 2014; Mauldin et al., 2012; Berndt et al., 2012, 2014a; 2014b; 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_2, 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_2. 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_2OO) in a low-pressure (4 torr) laboratory experiment, finding an absolute rate coefficient for the $CH_2OO + SO_2$ reaction of $3.9 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Mauldin et al. (2012) estimated the reaction rate coefficient to be roughly $6 \cdot 10^{-13}$ and $8 \cdot 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for sCIs from the ozonolysis of α-pinene and limonene, respectively. Berndt et al. (2012) investigated experimentally the sCI yields, lifetimes, and rate coefficients for reactions with SO_2 for sCIs from the ozonolysis of selected alkenes including 2,3-dimethyl-2-butene (TME), trans-2-butene and 1-methyl-cyclohexene (MCH). Using an indirect approach based on H_2SO_4 measurements, 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_2 in the order of 10^{-13} - 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, depending on the structure of the sCI.

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 a different reactivity. Therefore, the given data for α-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 by Berndt et al. (2012) and field observations by Mauldin et al. (2012) suggest that sCI are roughly a factor of ~100 more reactive with SO_2 than suggested 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 + 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 + 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 SO_2 emissions to global climate via indirect aerosol effects on radiative forcing. The effect of sCI on 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 probably from sCI-initiated oxidation of SO_2. Pierce et al. (2013) took a step further and studied the role of the sCI + 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 H_2SO_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 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_2OO. Furthermore, the sCI reaction rate coefficients, including sCI loss in a reaction with water, 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, would be warranted.

On top of the reaction with SO_2, a further, mostly unresolved question is whether or not oxidation by sCI has a more general role in atmospheric chemistry. Earlier studies have probed the reaction of CH_2OO with several atmospheric constituents (see e.g. Fenske et al., 2000). Reaction of CH_2OO with formic acid, HCOOH, yielding to production of hydroperoxymethyl formate was demonstrated by Neeb et al. (1995; 1996) with follow-up studies by Thamm et al. (1996) and Hasson et al. (2001). Neeb et al. (1997) showed that the rate coefficient for the above reaction is relatively large, (14000-fold) in comparison to the reaction rate coefficient for CH_2OO + water. An extremely high reactivity of CH_2OO and CH_3CHOO toward formic (HCOOH) and acetic acid (CH_3COOH) was observed also by Welz et al. (2014) in a low pressure system. Also Taatjes et al. (2012; 2013) showed that sCIs – at least the simple sCIs – are reactive toward other trace gases in addition to SO_2. These observations imply that reactions of sCI with organic acids might have atmospheric importance and further research is urgently required.

In the present study, we investigate experimentally the sCI yield and the rate coefficient ratio k(loss) / k(sCI+SO_2), where the loss coefficient k(loss) incorporates thermal decomposition of sCI and the reaction with water vapour, k(loss) = k(dec.) + k(sCI+H_2O)·[H_2O]. This rate coefficient ratio represents (for different temperatures and water vapour concentrations) the important parameter for understanding the sCI controlled oxidation of SO_2 to H_2SO_4 in the atmosphere. This study comprises reactions of sCIs produced from the ozonolysis of isoprene and two monoterpenes abundant in the atmosphere, i.e. α-pinene and limonene. To demonstrate the capability of sCIs playing a more general role in atmospheric chemistry, we investigated the reaction of acetone oxide (($CH_3)_2COO$, the sCI from TME ozonolysis) with small organic acids.

2 Methods

2.1 NO_3^- - chemical ionization – atmospheric pressure interface – time-of-flight mass spectrometer (NO_3^--CI-APi-TOF)

A NO_3^--CI-APi-TOF was used in the experiments described here primarily for the detection of sulphuric acid. The NO_3^--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 α-emitter. Minute quantities of nitric acid vapour are fed into sheath air surrounding the sample inlet flow, resulting in the formation of $NO_3^-(HNO_3)_{n,n=0-2}$ ions. These ions are pushed into the sample flow, entering the ion-molecule interaction tube 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_2 scrubber.

Sample ionization in the CI-system occurs at atmospheric pressure via proton transfer between nitrate ions and sulphuric acid and subsequent $HSO_4^-\cdot HNO_3$ adduct formation:

$H_2SO_4 + NO_3^-\cdot(HNO_3)_{n,n=0-2} \rightarrow HSO_4^-\cdot HNO_3 + n(HNO_3)$, n=0-2 (R1

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 (mass to charge) separation.

A fraction of $HSO_4^-\cdot HNO_3$ clusters (R1) fragment inside the APi-TOF. The sulphuric acid concentration (in molecule cm^{-3}) measured with the NO_3^--CI-APi-TOF is calculated from the measured ion signals according to:

$$[H_2SO_4] = \frac{HSO_4^- + H_2SO_4NO_3^-}{NO_3^- + HNO_3NO_3^- + HNO_3(HNO_3)NO_3^-} \times C, \quad (1)$$

where C is the calibration coefficient.. The detection limit for sulphuric acid monomer is of the order of 10^4 molecule cm^{-3} and the error in determined sulphuric acid concentration is ±45% (Berndt et al., 2012). Data were analysed using TofTools software.

Neglected in the analysis based on Eq. (1) is the potential effect of water vapour on ion chemistry and thus on the calibration coefficient C. Water vapor can affect the level of hydration of sulphuric acid, thereby affecting the charging, the diffusion coefficient and the collision diameter. Nitrate-water clusters also have different collision diameter than pure nitrate ions and clustering could, potentially, change the proton affinity of the primary ions. Also steric effects may play a role. The CI-APi-TOF technique is relatively new and detailed understanding how RH affects the detection does not exist. Experiments on the RH-dependent H_2SO_4 sensitivity of CI-APi-TOF instruments reveal that the calibration coefficient C is less influenced by RH in the range 2 – 65% and the small changes observed are within the uncertainty of the measurement, see experimental data given in the online discussion of this paper and Berndt et al. (2014a). It is to be noted that the rate coefficient ratios reported here are independent of the absolute H_2SO_4 calibration.

2.2 Laboratory experiments

Laboratory experiments were conducted in the Leibniz-Institute for Tropospheric Research Laminar Flow Tube (IfT-LFT) at T = 293 ± 0.5 K, RH = 10 - 50% ($[H_2O] = (0.58 - 2.89)\cdot 10^{17}$ molecules cm^{-3}) and with a flow of 30 l/min (STP) synthetic air as the carrier gas, resulting in a total residence time of 39.5 sec. The experimental methods are identical to those reported in Berndt et al. (2014a), but will be described briefly here.

In the experiments focusing on sCI yields and the relative reaction rate coefficients, the alkenes, 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 scavenging efficiency of 96.9 – 99.98%, depending on the experimental conditions, for OH radicals formed in the ozonolysis. The SO_2 concentration was varied in the range $3.2\cdot 10^{11} - 2.4\cdot 10^{14}$ molecules 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 CH_3COOH (acetic acid), with concentrations ranging between $3.0\cdot 10^{10} - 2.0\cdot 10^{13}$ molecule cm^{-3}, were fed together with other reagents at the top of the flow tube. Concentrations of the reagents were (unit: molecule cm^{-3}): $[TME] = 4.0\cdot 10^{10}$, $[O_3] = 2.2\cdot 10^{11}$, $[SO_2] = 3.2\cdot 10^{12}$, $[propane] = 1.64\cdot 10^{15}$ and a relative humidity of 10%.

In all experiments sulphuric acid was measured using the 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 Results and Discussion section.

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 $[SO_2]$ at RH = 10% and RH = 50%. In analysing the experimental data the following reaction sequence (R2) – (R6) was considered.

O_3 + alkene → $y_1 \cdot OH + y_2 \cdot sCI$ + others (R2)

sCI + H_2O → products ; k(sCI+H_2O) (R3)

sCI + SO_2 → ... → $y_3 \cdot H_2SO_4$; k(sCI+SO_2) (R4)

sCI → OH + others ; k(dec.) (R5)

sCI + org. acid → products ; k(sCI+acid) (R6)

First, ozone, when reacting with alkene, produces Criegee Intermediate, CI, which can either rapidly (picoseconds) 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 (R2). The sCI can react with water vapour (R3) or with SO_2 (R4). Here we assume that the H_2SO_4 formation yield (y_3) for reaction (R4) is unity (see discussion on the validity of assumption below). The sCI can also thermally decompose before reacting with other molecules, resulting in the production of OH and other products (R5). In addition to the unimolecular decomposition and reactions with H_2O and SO_2, sCI can, as we will demonstrate, react with organic acids (R6) and potentially with several other atmospheric constituents.

Since OH formed in reaction (R5) is efficiently scavenged (>96.9%, at highest [SO_2], see Table 1 for propane concentrations used for different ranges of SO_2), the reaction of remaining (<3.1%) OH with SO_2 can be neglected. Even at highest [SO_2] of $2.4 \cdot 10^{14}$ molecule cm^{-3}, reaction of OH radicals with SO_2 contributes to less than 10% of total [H_2SO_4]. At [SO_2] below $1 \cdot 10^{14}$ molecule cm^{-3}, the OH reaction can be totally neglected.

Another reaction that could be speculated to produce additional H_2SO_4 in our system is the reaction of peroxy radicals, RO_2, with SO_2. However, there are no clear experimental indications in the literature suggesting a fast enough reaction of $RO_2 + SO_2$. For example for the $CH_3O_2 + SO_2$ reaction, the rate coefficient is below $5 \cdot 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} (DeMore et al., 1997). Theoretical findings also suggest a slow reaction (Kurten et al., 2011). Our RO_2 concentrations are in the same order or lower than atmospheric [RO_2] ([RO_2] cannot exceed alkene conversion) and therefore the slow reaction of $RO_2 + SO_2$ can be disregarded in our study. Moreover, if $RO_2 + SO_2$ would be a significant source of [H_2SO_4] in atmospheric OH measurements relying on SO_2 titration (Petäjä et al., 2009 and references therein), these measurements would be wrong.

Also carbonyls or acids formed as products in the ozonolysis reaction or in reaction of OH with propane could affect the results via the reaction of sCI + carbonyl/acid in competition with sCI + SO_2. Carbonyl concentration from alkene ozonolysis cannot exceed the reacted alkene concentration (should be clearly lower). Total OH produced upon ozonolysis cannot exceed reacted alkene concentration and thus also carbonyls resulting from OH + propane cannot exceed reacted alkene concentration. Thus, maximum carbonyl concentrations in our experiment are in the range of few 10^8 molecule cm^{-3}, i.e. 3 – 6 orders of magnitude lower than the SO_2 concentrations used. The relative reactivity, k(sCI + carbonyl) / k(sCI + SO_2), is clearly below one (Taatjes et al., 2012). Therefore, a potential role of the reaction sCI + carbonyl in our experimental system can be completely ruled out. Same applies to the reaction of organic acids with sCI. Acid formation yields are about 5% of reacted alkene, and thus the acid concentrations are in the range of 10^7 molecule cm^{-3} (4 – 7 orders of magnitude lower than the SO_2 concentrations). The relative reactivity, k(sCI + acid) / k(sCI + SO_2), is ~3 as shown later in this work and qualitatively in line with Welz et al. (2014). Thus, sCI + acid cannot be competitive to sCI + SO_2 in this experiment.

Furthermore, the sCI wall loss could be important for the sCI balance. The first-order rate coefficient for the diffusion-limited wall loss of sCI can be estimated according to $k_{wall\text{-}loss} = 3.65 \cdot D/r^2$, where D is the diffusion coefficient of sCI and r stands for the tube radius. As the diffusion coefficient a value of 0.1 $cm^2\ s^{-1}$ was assumed ($D(H_2SO_4) = 0.08\ cm^2\ s^{-1}$) resulting in $k_{wall\ loss} = 0.023\ s^{-1}$. Thermal decomposition of sCI is expected to be much more rapid (Welz et al., 2012; Berndt et al., 2012) making the sCI wall loss negligible in the kinetic analysis.

In absence of organic acid added to the reaction gas only reactions (R2) – (R5) are considered. The fraction of sCI that oxidises SO_2 producing sulphuric acid (sCI_{H2SO4}/sCI_{TOT}) is equal to the sCI reaction rate with SO_2 (R4) divided by the sum of all reaction rates (total reaction rate) of sCI (R3) – (R5):

$$\frac{sCI_{H2SO4}}{sCI_{TOT}} = \frac{k(sCI+SO_2)[\mathrm{SO_2}]}{k(sCI+SO_2)[\mathrm{SO_2}]+k(dec)+k(sCI+H_2O)[\mathrm{H_2O}]} \qquad (2)$$

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

$$[\mathrm{H_2SO_4}] = \frac{1}{1+\frac{k(loss)}{k(sCI+SO_2)[\mathrm{SO_2}]}} \cdot [\mathrm{H_2SO_4}]_{\mathrm{sCI}} \qquad (3)$$

where $[H_2SO_4]_{sCI}$ stands for $[H_2SO_4]$ from sCI titration, i.e all sCI is converted to H_2SO_4 in the presence of high SO_2 concentrations via (R4) making the reactions (R3) and (R5) negligible. In the analysis we assumed 28% wall loss in total sulphuric acid concentration (Berndt et al., 2014a) and the measured values were corrected for the wall loss before used in the data analysis.

The yield y_2 of sCI from the reaction (R2) can be obtained from the knowledge of the reacted alkene and $[H_2SO_4]_{sCI}$ assuming a H_2SO_4 yield of unity from reaction (R4):

$$y_2 = \frac{[\mathrm{H_2SO_4}]_{\mathrm{sCI}}}{\text{reacted [alkene]}} \qquad (4)$$

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 Table 1:

$$\text{reacted [alkene]} = k(O_3+\text{alkene})\cdot[\text{alkene}]\cdot[O_3]\cdot t \qquad (5)$$

The relative rate coefficients k(loss) / $k(sCI+SO_2)$ and the sCI yield y_2 were obtained by least square fitting according to Eqs. 3 and 4 using the experimental data depicted in Figs. 1-3.

The above approach assumes that all sCIs formed from a selected alkene show a similar reactivity in (R3) – (R5), i.e. we are able to describe only average effects of all sCIs. Ozonolysis of a single alkene can result in the production of different types of CI and thus sCI. In case of α-pinene, possible sCIs include two different isomers, one *syn* and one which can be either a *syn* or *anti* conformer, with *syn* having two different structures possible; all in all sCI from α-pinene ozonolysis can have four different structures. The same applies for limonene. Nevertheless, the "one-sCI" approach seems to work well for α-pinene and limonene, suggesting that one of the possible sCI structures dominates, or that different sCIs show similar k(loss) / $k(sCI+SO_2)$. With the help of the "single sCI" model, Eq.3, the experimental data are described reasonably well (Figs. 1 and 2). For isoprene, due to the structure of the parent alkene, five different sCI structures are possible. In this case the "one-sCI" model is too simple for a reliable description of the measurements, see below.

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 sCI under these conditions and the reaction with water vapour is of less importance, i.e. k(dec.) >> $k(sCI+H_2O)\cdot[H_2O]$ for $[H_2O] \leq 2.9 \cdot$

10^{17} 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 sCI" 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 sCI" model fails in describing the measurements. The flaw of the "one sCI" model can be explained by the different reactivity 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 a different reactivity of $\mathrm{sCI_I}$ and $\mathrm{sCI_{II}}$ in the reactions (R3) – (R5):

$$[\mathrm{H_2SO_4}] = \frac{1}{1+\frac{k(loss)_I}{k(sCI+SO_2)_I[\mathrm{SO_2}]}} \cdot [\mathrm{H_2SO_4}]_{\mathrm{sCI}_I} + \frac{1}{1+\frac{k(loss)_{II}}{k(sCI+SO_2)_{II}[\mathrm{SO_2}]}} \cdot [\mathrm{H_2SO_4}]_{\mathrm{sCI}_{II}} \quad (6)$$

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 $[\mathrm{H_2SO_4}]_{\mathrm{sCI}}$. Furthermore, it shows that the relative rates coefficients k(loss) / k(sCI+SO_2) are significantly different between the two sCIs: $3.3 \cdot 10^{13}$ molecules cm^{-3} for type I and $2.6 \cdot 10^{11}$ molecules cm^{-3} for type II. From our experiment we cannot draw clear conclusions on what kind of sCI formed from the isoprene ozonolysis is responsible for type I and type II. It could be speculated that CH_2OO and/or an *anti*-conformer sCI causes the strong RH dependence of produced sulphuric acid due to their efficient reaction with water vapour (R3) in competition with reaction (R4). The relative rate coefficients and yields are summarized in Table 2.

If the fast reaction with water is due to CH_2OO, that might have implications for our understanding of CI chemistry and the inclusion of the results by Welz et al. (2012) in models, including global chemical transport models (Pierce et al., 2013). Stone et al., (2014) suggest a relatively slow water reaction obtained by a technique similar to the approach by Welz et al. (2012) while the older measurements suggest that the water reaction dominates in the atmosphere over 'all' other reactions, see for example Hasson et al. (2001a). Recent work by Berndt et al. (2014b) also suggests that reaction with water (dimer) is relatively fast dominating the atmospheric fate of CH_2OO. The relative rate coefficients k(loss) / k(sCI+SO_2) obtained in this study are close to those obtained by Berndt et al. (2012) for sCI from the ozonolysis of trans-2-butene and TME. Berndt et al. (2014a) also showed that significant differences in the relative rate coefficients k(sCI+H_2O) / k(sCI+SO_2) occurred between *syn*- and *anti*-confomers of sCI from trans-2-butene. Absolute measurements by Taatjes et al. (2012) support this finding as well.

Similar to Berndt et al. (2012; 2014a;b), our analysis of the relative rate coefficients and sCI yields incorporates the yield of H_2SO_4 from the sCI + SO_2 reaction – i.e. our investigation is limited to the channel leading to the formation of H_2SO_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 H_2SO_4 from sCI + 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 the H_2SO_4 yields are much higher than that and thus very close to unity; our measured sCI yield for α-pinene of 0.15 ± 0.07 assuming an unity H_2SO_4 yield from sCI + SO_2 is in excellent agreement with a yield of 0.15 recently determined with an sCI-specific scavenger technique (Drozd and Donahue, 2011). These observations also call into question the stable, non-SO_3 producing, sulphur-bearing secondary ozonides, theoretically investigated by Kurtén et al. (2011) and Veerecken et al. (2012), as a predominant product from the sCI + SO_2 reaction.

Our results on the 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_2OO) in a low pressure system. They found $k(sCI+SO_2) = 3.9\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, lower end estimation for the lifetime against decomposition of 2 ms – resulting in upper end estimation for k(dec) of 500 s^{-1} – and the upper end estimation for reaction coefficient with H_2O of $k(sCI+H_2O) < 4\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. Using the upper end rate coefficients for CH_2OO in $k(loss) = k(dec) + k(sCI+H_2O)\cdot[H_2O]$, for the relative reaction rate coefficients, $k(loss) / k(sCI+SO_2)$, follow $< 1.9\times10^{13}$ molecule cm^{-3} (RH = 10%) and $< 4.2\times10^{13}$ molecule cm^{-3} (RH = 50%) being qualitatively not in contradiction with our results for the sCIs of the monoterpenes and isoprene, see Table 2. If the reaction of CH_2OO with H_2O dominated the loss process ($k(dec) \ll k(sCI+H_2O)\cdot[H_2O]$), the resulting $k(loss) / k(sCI+SO_2)$ ratios from Welz et al. (2012) data would be $< 5.9\times10^{12}$ molecule cm^{-3} (RH = 10%) and $< 3.0\cdot10^{13}$ molecule cm^{-3} (RH = 50%) still not contradicting 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 sCI decomposition step (R5) and the reaction of sCI with H_2O (R3). Since pressures in our work and the study by Welz et al. (2012) were completely different, differences related to pressure effects may arise. It is to be noted also here, that the reactions (R3) and/or (R5) describe the most important, atmospheric loss processes. For a reliable assessment of the importance of H_2SO_4 formation in the atmosphere via sCI + SO_2, the sCI main reactions (R3) and (R5) must be characterized very well.

3.2 Reaction of sCI with organic acids

The reaction of acetone oxide ($(CH_3)_2COO$, sCI from TME ozonolysis) with small organic acids was investigated by a competitive reaction kinetics experiment at constant SO_2 concentration ($3.2\cdot10^{12}$ molecule cm^{-3}) and varying the concentration of the organic acids (Fig. 4).

Berndt et al. (2014a) showed that for acetone oxide the reaction with water vapour (R3) is of less importance compared with the thermal decomposition (R5) for RH $\leq$ 50%. Our experiment was conducted at low RH (10%) and thus only the thermal decomposition of sCI was considered together with the reactions of sCI with SO_2 (R4) and the acids (R6). From pathways (R4) – (R6) follows:

$$[\mathrm{H_2SO_4}] = \frac{1}{1+\frac{k(dec)}{k(sCI+SO_2)[\mathrm{SO_2}]}+\frac{k(sCI+acid)[\mathrm{acid}]}{k(sCI+SO_2)[\mathrm{SO_2}]}} \cdot [\mathrm{H_2SO_4}]_{\mathrm{sCI}} \qquad (7)$$

The relative rate coefficient k(dec) / k(sCI+SO_2) was determined by Berndt et al. (2014a) to be $4.2\cdot10^{12}$ molecules cm^{-3}. [H_2SO_4] stands again for the loss corrected sulphuric acid concentration at the IfT-LFT outflow and $[H_2SO_4]_{sCI}$ for [H_2SO_4] from sCI titration. Results from the non-linear regression analysis [H_2SO_4] = f([acid]) from Eq. 7 yields the free parameters k(sCI+acid) / k(sCI+SO_2) and $[H_2SO_4]_{sCI}$, see Table 3. Our measurements reveal an about three times faster reaction of acetone oxide with the acids compared with the reaction with SO_2.

Neeb et al. (1997) measured rapid reaction of sCI + HCOOH in comparison to sCI + water. However, our results cannot be directly compared to Neeb et al. (1997) due to different water reactivity of CH_2OO (studied by Neeb et al., 1997) and $(CH_3)_2COO$ investigated here (Berndt et al., 2014b). However, our result is very similar to the reaction rate coefficients reported by Welz et al. (2012; 2104) for reactions of CH_2OO with SO_2 and HCOOH/CH_3COOH. Welz et al. (2012; 2014) studies demonstrate the relative reactivity of 2.8 and 3.3 for k(sCI+HCOOH) / k(sCI+SO_2) and for k(sCI+CH_3COOH) / k(sCI+SO_2), respectively. These values are stunningly close to our measured values of 2.8 and 3.4, though it should be kept in mind that our sCI represents $(CH_3)_2COO$ while Welz et al. (2012; 2014) data is for CH_2OO.

Now we discuss on the potential importance of sCI + acid reaction in the atmosphere. Mauldin et al. (2012) estimated the absolute reaction rate coefficient of sCI+SO_2 to be in the range of $6\cdot10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for α-pinene and limonene. Using this value, the absolute reaction rate coefficient for sCI+HCOOH and sCI+ CH_3COOH would be in the range of few 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The reaction rate coefficient for OH + CH_3COOH is $8\cdot10^{-13}$ cm^3 $molecule^{-1}$ $s^{-1}$and for OH+ HCOOH $4\cdot10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. As shown by Mauldin et al. (2012), the summertime sCI concentrations are similar to OH peak concentrations in boreal forest. Therefore, it is possible, that sCI oxidation plays a crucial role for the HCOOH and CH_3COOH budget. However, as stated above, the conformation and structure of sCI propably have major effects on the sCI reactivity toward acids, and therefore, further investigations are required before our observations can be generalized to sCIs other than acetone oxide. On the other hand, Welz et al. (2014) measured for CH_2OO + HCOOH/CH_3COOH rate coefficients exceeding 10^{-10} cm^3 $molecule^{-1}$ s^{-1} suggesting that also this structurally different sCI (CH_2OO) reacts with acids rapidly in comparison to the OH radical reaction.

It is important to notice that even though from sCI point of view SO_2 or organic acids were the minor sinks for sCI, the situation can be completely opposite from point of view of formation of H_2SO_4 (Boy et al., 2013; Pierce et al., 2013) or the loss of organic acids (Welz et al., 2014). Most likely, the dominating reactions controlling the sCI concentrations in natural environments are thermal decomposition and reaction with water vapour. Very high concentrations (several to tens of ppb) of SO_2 or organic acids would be required for altering the sCI budget significantly. However, the reaction with sCI can still be a significant or even the main fate of acid or source of H_2SO_4.

Regarding the role of sCI in atmospheric gas phase H_2SO_4-production, the present study is in a reasonable agreement with the results by Mauldin et al. (2012). Thereby results by Boy et al. (2013) who applied Mauldin et al. (2012) findings in boundary layer modelling can be considered valid as well. Pierce et al. (2013) applied Welz et al. (2012) results in a chemical transport model for studying the role of sCI in global gas phase H_2SO_4 burden. Because our relative rate coefficient between sCI loss and sCI+SO_2 are not conflicting the results by Welz et al (2012), our present results validate, form one side, also the modelling study by Pierce et al. (2013). Thus, our understanding on the role of sCI in atmospheric H_2SO_4 production remains unchanged.

4 Conclusions and Summary

We investigated experimentally the sCI yield and relative rate coefficient k(loss)/ k(sCI+SO_2) for the sCI loss reaction, k(loss) = k(dec.) + k(sCI+H_2O)·[H_2O], and the H_2SO_4 producing reaction of sCI with SO_2. The values k(loss) / k(sCI+SO_2) are the key quantities for an assessment of the role of sCI for the sulphuric acid production in the atmosphere via sCI + SO_2. Investigations probed sCI from the ozonolysis of isoprene and two monoterpenes, α-pinene and limonene, at ambient-relevant temperature, pressure and humidity. The observed quantities represent average values of all sCIs produced from the individual alkene. The sCI yields were in the range of few tens of % and similar to the yields determined for smaller sCIs using the same approach (Berndt et al., 2014a) or another sCI-specific scavenger technique (Drozd and Donahue, 2011). For the studied monoterpenes, the relative rate coefficients k(loss)/ k(sCI+SO_2) were in the range of (2.0 - 2.4) $\cdot 10^{12}$ molecules cm^{-3} with no measurable effect on the relative humidity (RH = 10 or 50%). In the case of the isoprene derived sCIs an efficient reaction with water vapour was observed making k(loss) / k(sCI+SO_2) strongly RH-dependent. We also showed that beyond the contribution to sulphuric acid formation, sCI can react rapidly with small organic acids, and thus potentially with several other atmospheric constituents, suggesting that sCIs have a more general role in the atmospheric oxidation chemistry than SO_2 oxidation alone. Further investigations are necessary for obtaining a holistic and detailed understanding on the sCI chemistry and the role of sCI in the formation and loss of various atmospheric species.

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Tables

Table 1. Concentrations of alkenes (initial and reacted within the residence time of 39.5 s), OH-scavenger and O_3, and the reaction rate coefficients used in the experiments.

Alkene	[alkene] molecule cm^{-3}	[propane] molecule cm^{-3}	[O_3] molecule cm^{-3}	k(alkene+O_3) $cm^3\ s^{-1}$	reacted [alkene] molecule cm^{-3}
α-Pinene	$8.0\cdot10^{11}$	$1.64\cdot10^{15}$ (SO_2: $(3.2\text{-}160)\cdot10^{11}$) $8.2\cdot10^{15}$ (SO_2: $(1.6\text{-}24)\cdot10^{13}$)	$2.2\cdot10^{11}$	$1.1\cdot10^{-16}$	$7.65\cdot10^{8}$
Limonene	$1.6\cdot10^{11}$	$1.64\cdot10^{15}$ (SO_2: $(3.2\text{-}160)\cdot10^{11}$) $8.2\cdot10^{15}$ (SO_2: $(1.6\text{-}16)\cdot10^{13}$)	$2.2\cdot10^{11}$	$2.5\cdot10^{-16}$	$3.48\cdot10^{8}$
Isoprene	$1.5\cdot10^{12}$	$1.64\cdot10^{15}$ (SO_2: $(3.2\text{-}160)\cdot10^{11}$) $8.2\cdot10^{15}$ (SO_2: $(1.6\text{-}16)\cdot10^{13}$)	$2.2\cdot10^{11}$	$1.29\cdot10^{-17}$	$1.68\cdot10^{8}$

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

Alkene	k(loss) / k(sCI+SO_2) molecule cm^{-3}	$[H_2SO_4]_{sCI}$ molecule cm^{-3}	sCI yield
α-Pinene	$(2.4 \pm 0.2)\cdot 10^{12}$ RH: 10% $(2.0 \pm 0.4)\cdot 10^{12}$ RH: 50%	$(1.15 \pm 0.02)\cdot 10^{8}$ RH: 10% $(1.13 \pm 0.04)\cdot 10^{8}$ RH: 50%	0.15 ± 0.07
Limonene	$(2.4 \pm 0.2)\cdot 10^{12}$ RH: 10% $(2.1 \pm 0.2)\cdot 10^{12}$ RH: 50%	$(9.3 \pm 0.1)\cdot 10^{7}$ RH: 10% $(9.3 \pm 0.2)\cdot 10^{7}$ RH: 50%	0.27 ± 0.12
Isoprene	$(2.5 \pm 0.1)\cdot 10^{12}$ RH: 10% $(2.1 \pm 0.5)\cdot 10^{13}$ RH: 50%*	$(9.9 \pm 0.1)\cdot 10^{7}$ RH: 10% $(9.7 \pm 0.6)\cdot 10^{7}$ RH: 50%	0.58 ± 0.26

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

Table 3. Relative reaction rate coefficients for reaction of $(CH_3)_2COO$ (sCI from TME ozonolysis) with small organic acids and SO_2 based on competitive reaction kinetics experiments.

acid	k(sCI+acid)/k(sCI+SO_2)	$[H_2SO_4]_{sCI}$, molecule cm^{-3}
HCOOH, formic acid	(2.80±0.32)	$2.05 \cdot 10^8$
CH_3COOH, acetic acid	(3.43±0.22)	$2.05 \cdot 10^8$

Figure captions

Figure 1: Loss-corrected measured [H_2SO_4] at the outflow of IfT-LFT in α-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.

Figure 2: Loss-corrected measured [H_2SO_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).

Figure 3: Loss-corrected measured [H_2SO_4] at the outflow of IfT-LFT in α-pinene experiments at RH=10% and 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.

Figure 4: Experimental data from the competitive reaction kinetics experiments, sCI + SO_2 vs. sCI + acid, sCI ≡ $(CH_3)_2COO$ (from TME ozonolysis). The lines show the best fit result of the non-linear regression analysis from Eq. 7.

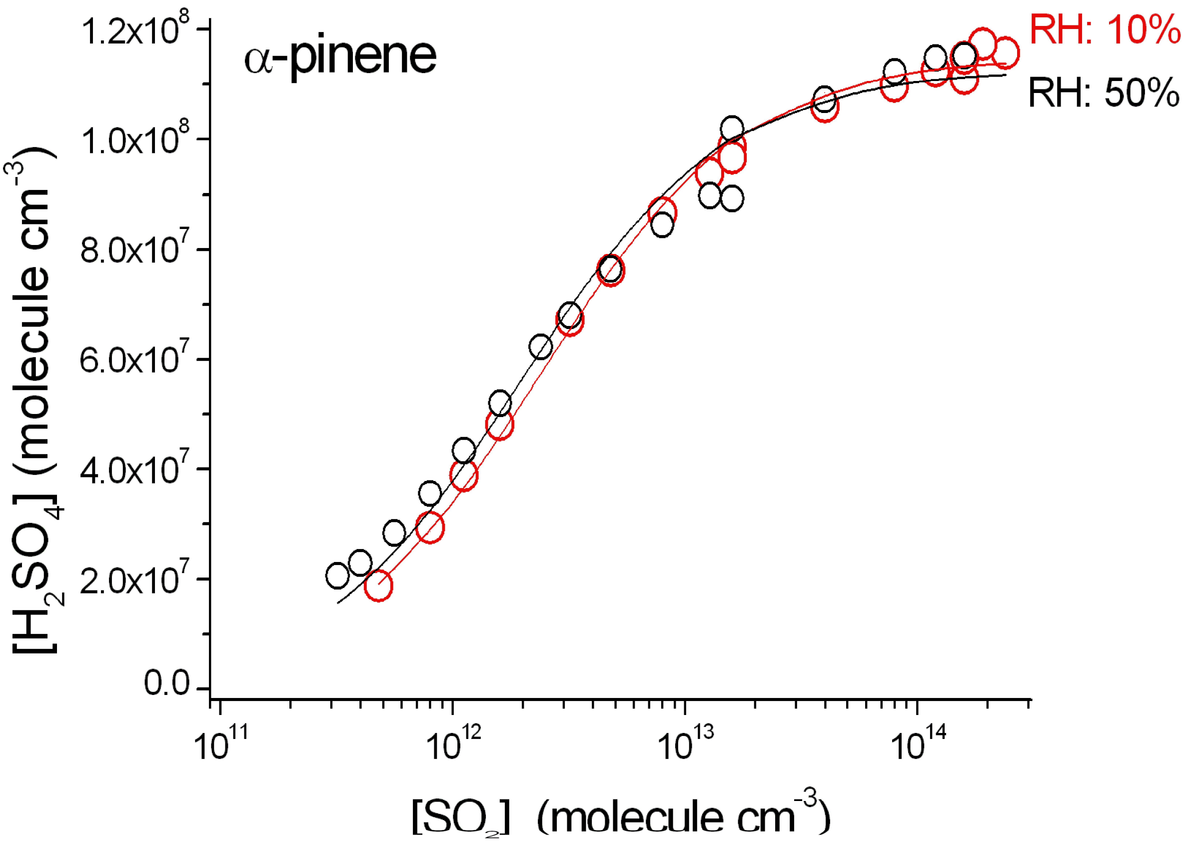
α-pinene
RH: 10%
RH: 50%
[H2SO4] (molecule cm-3)
1.2x10^8
1.0x10^8
8.0x10^7
6.0x10^7
4.0x10^7
2.0x10^7
0.0
10^11
10^12
10^13
10^14
[SO2] (molecule cm-3)

Figure 1

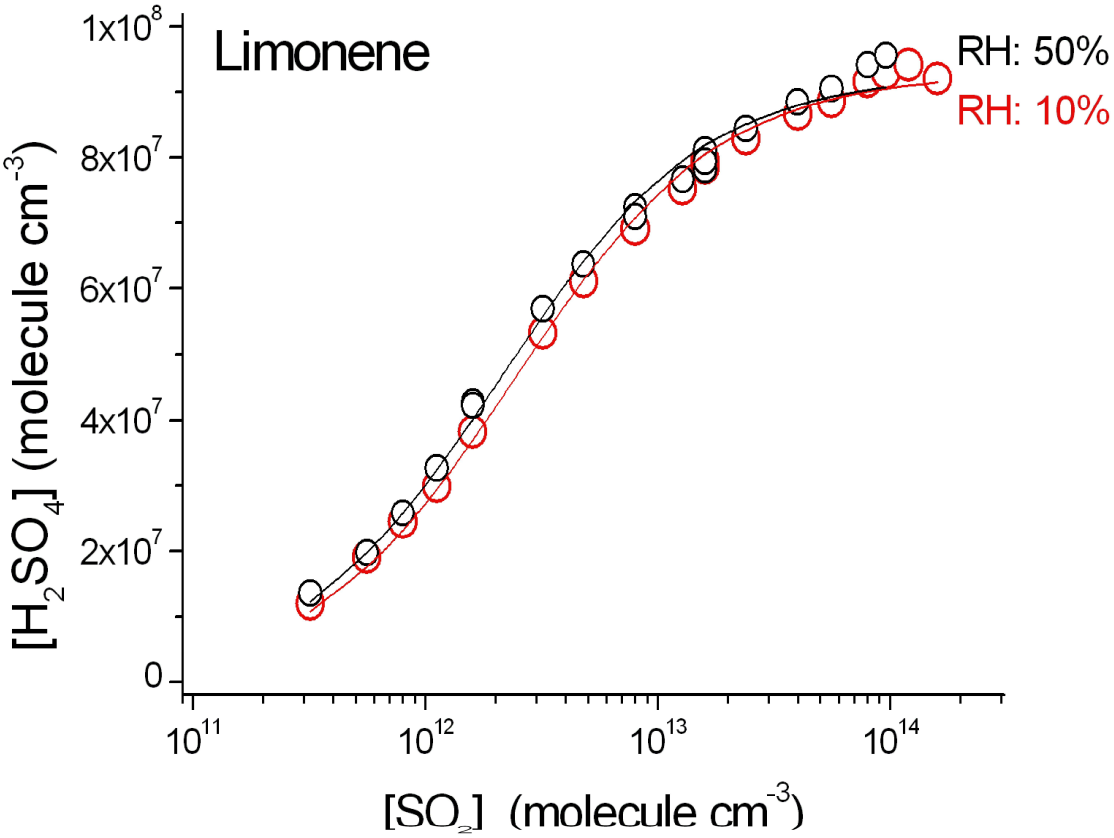
Limonene
RH: 50%
RH: 10%
1x10^8
8x10^7
6x10^7
4x10^7
2x10^7
0
[H2SO4] (molecule cm^-3)
10^11
10^12
10^13
10^14
[SO2] (molecule cm^-3)

Figure 2

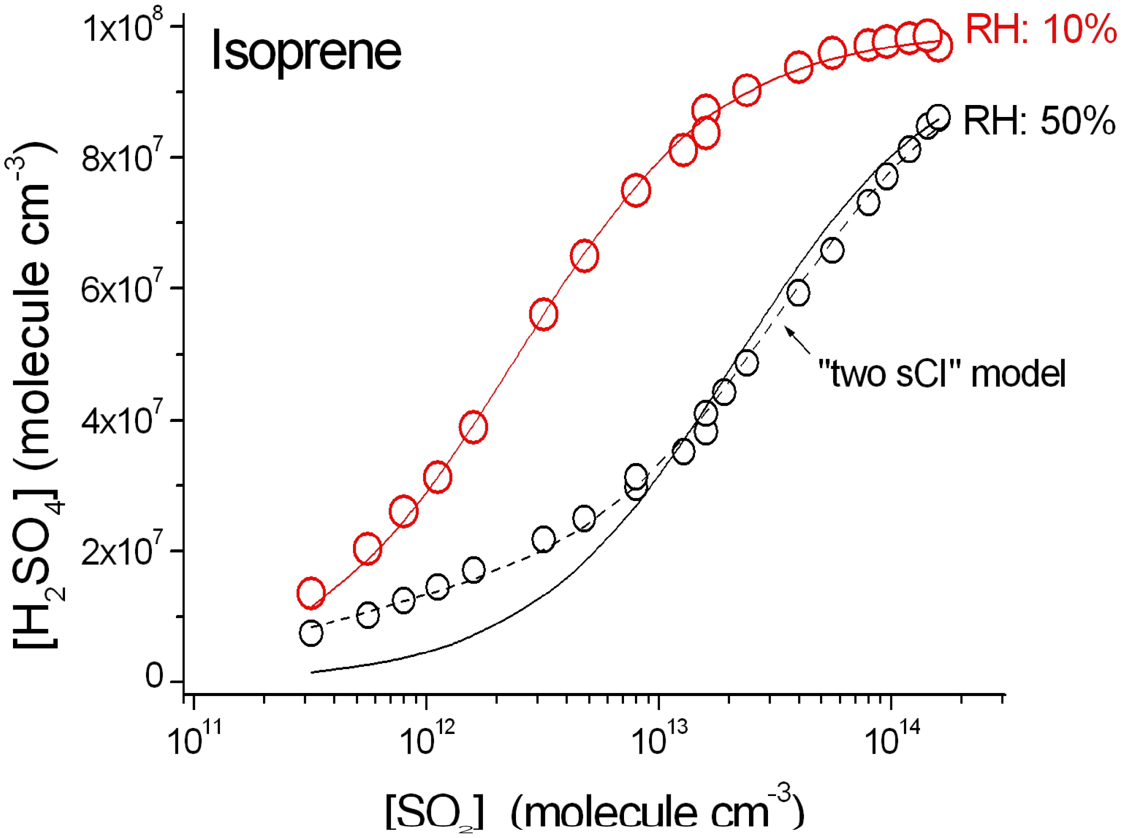
Isoprene
RH: 10%
RH: 50%
"two sCI" model
1x10^8
8x10^7
6x10^7
4x10^7
2x10^7
0
10^11
10^12
10^13
10^14
[H2SO4] (molecule cm-3)
[SO2] (molecule cm-3)

Figure 3

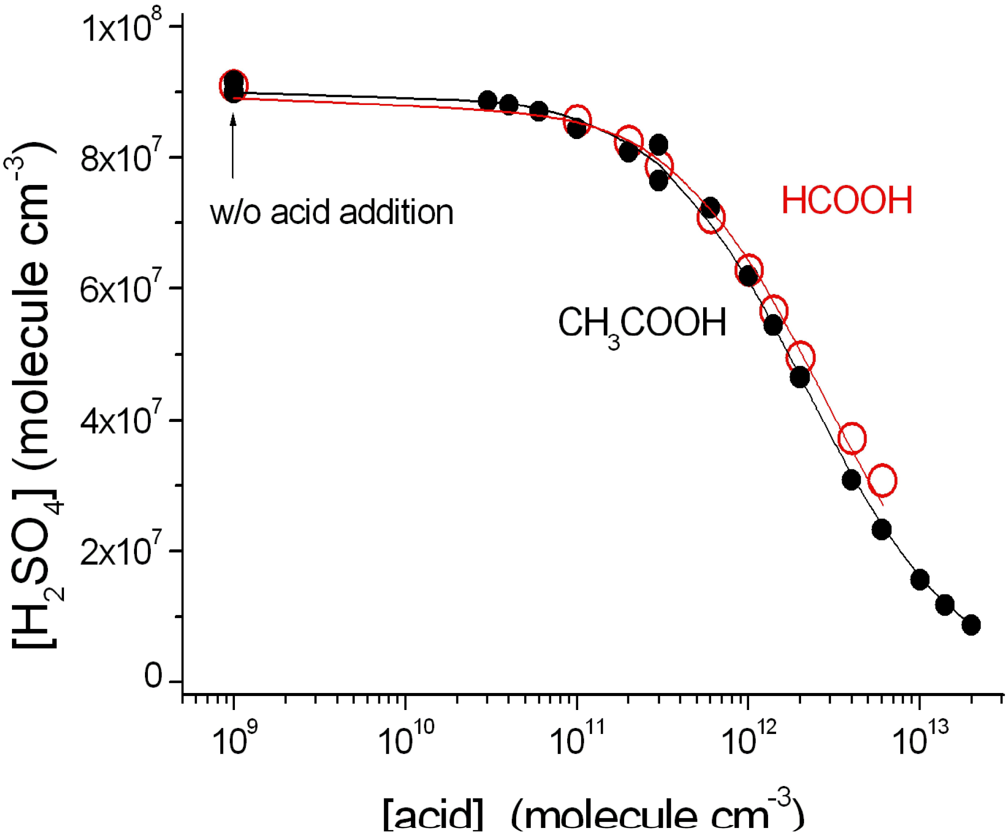
1x10^8
8x10^7
6x10^7
4x10^7
2x10^7
0
[H2SO4] (molecule cm-3)
10^9
10^10
10^11
10^12
10^13
[acid] (molecule cm-3)
w/o acid addition
HCOOH
CH3COOH

Figure 4