



Reactivity of sCI from
isoprene and
monoterpene
ozonolysis

M. Sipilä et al.

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Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO₂ and organic acids

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 (α -pinene and limonene), and subsequent reactions of the resulting sCIs with SO_2 producing sulphuric acid (H_2SO_4). The measured sCI yields were (0.15 ± 0.07) , (0.27 ± 0.12) and (0.58 ± 0.26) for the ozonolysis of 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 , $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$, 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 + H_2O reaction in the case of the sCI arising from α -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 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

Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



can play a role in the formation and loss of several atmospheric constituents besides SO₂.

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 SO₂ oxidation and subsequent formation of sulphuric acid, H₂SO₄ (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-

Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 CH₂OO. 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 SO₂, 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 SO₂. Still, the reactions of atmospherically relevant sCIs with compounds other than SO₂ 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 SO₂ to H₂SO₄ in the atmosphere. This study comprises reactions of sCIs produced from the ozonolysis of isoprene and two monoterpenes abundant in the atmosphere: α -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 ((CH₃)₂COO, the sCI from TME ozonolysis) with small organic acids.

2 Methods

2.1 NO₃⁻-chemical ionization-atmospheric pressure interface-time-of-flight mass spectrometer (NO₃⁻-CI-API-TOF)

A NO₃⁻-CI-API-TOF was used in the experiments described here primarily for the detection of sulphuric acid. The NO₃⁻-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 NO₃⁻ (HNO₃)_{n,n=0-2} 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 SO₂ scrubber.

Sample ionization in the CI-system occurs at atmospheric pressure via proton transfer between nitrate ions and sulphuric acid and subsequent HSO₄⁻ × HNO₃ 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.

Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A fraction of $\text{HSO}_4^- \times \text{HNO}_3$ clusters (Reaction R1) fragment inside the APi-TOF. The sulphuric acid concentration (in molec cm^{-3}) measured with the 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 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, 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 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 CH_3COOH (acetic acid), with concentrations ranging between $3. \times$

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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 H₂O and SO₂, 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 SO₂ and produce sulphuric acid (sCl_{H₂SO₄}/sCl_{TOT}) is equal to the sCl reaction rate with SO₂ (Reaction R4) divided by the sum of all reaction rates (total reaction rate) of sCl (Reactions R3–R5):

$$\frac{\text{sCl}_{\text{H}_2\text{SO}_4}}{\text{sCl}_{\text{TOT}}} = \frac{k(\text{sCl} + \text{SO}_2)[\text{SO}_2]}{k(\text{sCl} + \text{SO}_2)[\text{SO}_2] + k(\text{dec.}) + k(\text{sCl} + \text{H}_2\text{O})[\text{H}_2\text{O}]} \quad (2)$$

It follows for a given RH and $k(\text{loss}) = k(\text{dec.}) + k(\text{sCl} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$ that the total concentration of sulphuric acid produced during the experiment is:

$$[\text{H}_2\text{SO}_4] = \frac{1}{1 + \frac{k(\text{loss})}{k(\text{sCl} + \text{SO}_2)[\text{SO}_2]}} \cdot [\text{H}_2\text{SO}_4]_{\text{sCl}} \quad (3)$$

where $[\text{H}_2\text{SO}_4]_{\text{sCl}}$ stands for $[\text{H}_2\text{SO}_4]$ from sCl titration, i.e all sCl is converted to H₂SO₄ in the presence of high SO₂ 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 $[\text{H}_2\text{SO}_4]_{\text{sCl}}$ assuming a H₂SO₄ yield of unity from Reaction (R4):

$$y_2 = \frac{[\text{H}_2\text{SO}_4]_{\text{sCl}}}{\text{reacted [alkene]}} \quad (4)$$

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

Reactivity of sCl from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 α -pinene, possible sCl_s include two different isomers, one of which can be either a syn or anti conformer; all in all sCl from α -pinene ozonolysis can have three different structures. The same applies for limonene. Nevertheless, the “one-sCl” approach seems to work well for α -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-

Reactivity of sCl from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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: 3.3×10^{13} molecules cm^{-3} for type I and 2.6×10^{11} molecules 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 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 (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 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
 20 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

Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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-SO₃ producing, secondary ozonides, theoretically investigated by Kurtén et al. (2011) and Veerecken et al. (2012), as a predominant product from the sCl + SO₂ 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, (CH₂OO) 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 s^{-1} – and the upper end estimation for reaction coefficient with H₂O 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 CH₂OO 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 CH₂OO with H₂O 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 H₂O (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 H₂SO₄ formation in the atmosphere via sCl + SO₂, the sCl main Reactions (R3) and (R5) must be characterized very well.

Reactivity of sCl from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Reaction of sCl with organic acids

The reaction of acetone oxide ((CH₃)₂COO, sCl from TME ozonolysis) with small organic acids was investigated by a competitive reaction kinetics experiment at constant SO₂ concentration (3.2 × 10¹² molecule cm⁻³) 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 SO₂ (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 × 10¹² molecules cm⁻³. [H₂SO₄] stands again for the loss corrected sulphuric acid concentration at the lft-LFT outflow and [H₂SO₄]_{sCl} for [H₂SO₄] from sCl titration. Results from the non-linear regression analysis [H₂SO₄] = *f*([acid]) from Eq. (7) yields the free parameters $k(\text{sCl} + \text{acid})/k(\text{sCl} + \text{SO}_2)$ and [H₂SO₄]_{sCl}, see Table 3. Our measurements reveal an about three times faster reaction of acetone oxide with the acids compared with the reaction with SO₂. 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.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Conclusions and summary

We investigated experimentally the sCI yield and relative rate coefficient $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$ for the sCI loss reaction, $k(\text{loss}) = k(\text{dec.}) + k(\text{sCI} + \text{H}_2\text{O}) \times [\text{H}_2\text{O}]$, and the H_2SO_4 producing reaction of sCI with SO_2 . The values $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$ are the key quantities for an assessment of the role of sCI for the sulphuric acid production in the atmosphere via $\text{sCI} + \text{SO}_2$. 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., 2013) or another sCI-specific scavenger technique (Drozd and Donahue, 2011). For the studied monoterpenes, the relative rate coefficients $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$ 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 sCIs an efficient reaction with water vapour was observed making $k(\text{loss})/k(\text{sCI} + \text{SO}_2)$ 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 chemistry than 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.

ACPD

14, 3071–3098, 2014

Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Acknowledgements. Support of Academy of Finland (251427, 139656, Finnish center of excellence 141135), PEGASOS project funded by the European Commission under the Framework Program 7 (FP7-ENV-2010-265148), the European Research Council (ATMNUCLE) and NASA/ROSES is acknowledged. We thank Ari Asmi for useful discussions.

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ACPD

14, 3071–3098, 2014

Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Reactivity of sCl from
isoprene and
monoterpene
ozonolysis**

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Reactivity of sCI from
isoprene and
monoterpene
ozonolysis**

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Reactivity of sCI from
isoprene and
monoterpene
ozonolysis**

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Mauldin III, R. L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V.-M., and Kulmala, M.: A new atmospherically relevant oxidant, *Nature*, 488, 193–196, doi:10.1038/nature11278, 2012.

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**Reactivity of sCI from
isoprene and
monoterpene
ozonolysis**

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Taatjes, C. A., Welz, O., Eskola, A. J., Savee, J. D., Scheer, A. M., Shallcross, D. E., Rotavera, B., Lee, E. P. F., Dyke, J. M., Mok, D. K. W., Osborn, D. L., and Percival, C. J.: Direct measurements of conformer-dependent reactivity of the Criegee intermediate CH_3CHOO , *Science*, 340, 177–180, 2013.
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Reactivity of sCI from isoprene and monoterpene ozonolysis

M. Sipilä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Concentrations of alkenes (initial and reacted within the residence time of 39.5 s), OH-scavenger and O₃, and the reaction rate coefficients used in the experiments.

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

Reactivity of sCl from isoprene and monoterpene ozonolysis

M. Sipilä et al.

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 cm^{-3}	$[H_2SO_4]_{\text{sCl}}$ molecule cm^{-3}	sCl yield
α -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 ± 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 ± 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 ± 0.26

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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Reactivity of sCI from
isoprene and
monoterpene
ozonolysis**

M. Sipilä et al.

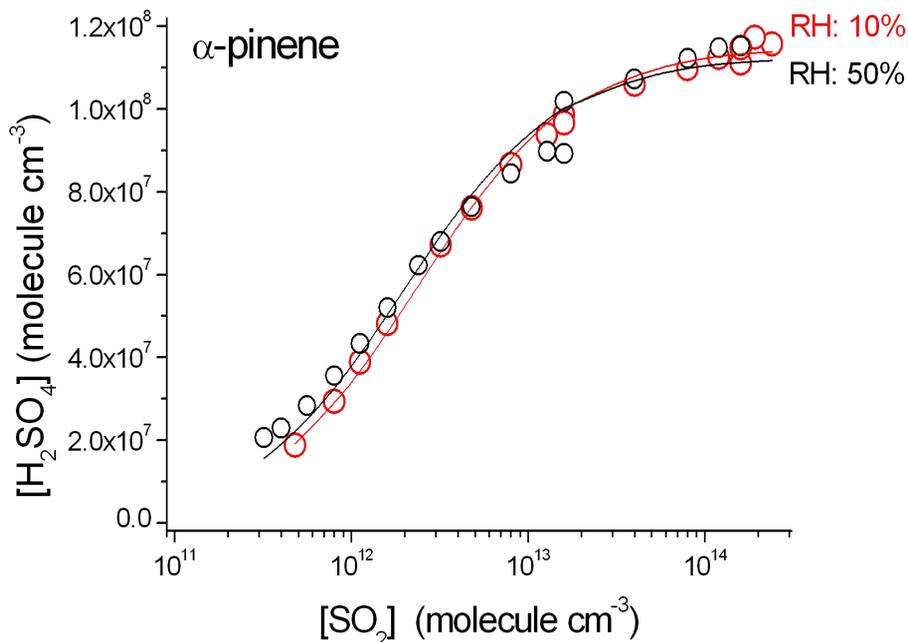


Fig. 1. Loss-corrected measured $[\text{H}_2\text{SO}_4]$ at the outflow of IFT-LFT in α -pinene experiments at RH = 10% and RH = 50%. Lines show multivariate least square fittings according to Eq. (3) from which the relative rate coefficients and sCI yield were obtained.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[⏴](#)[⏵](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

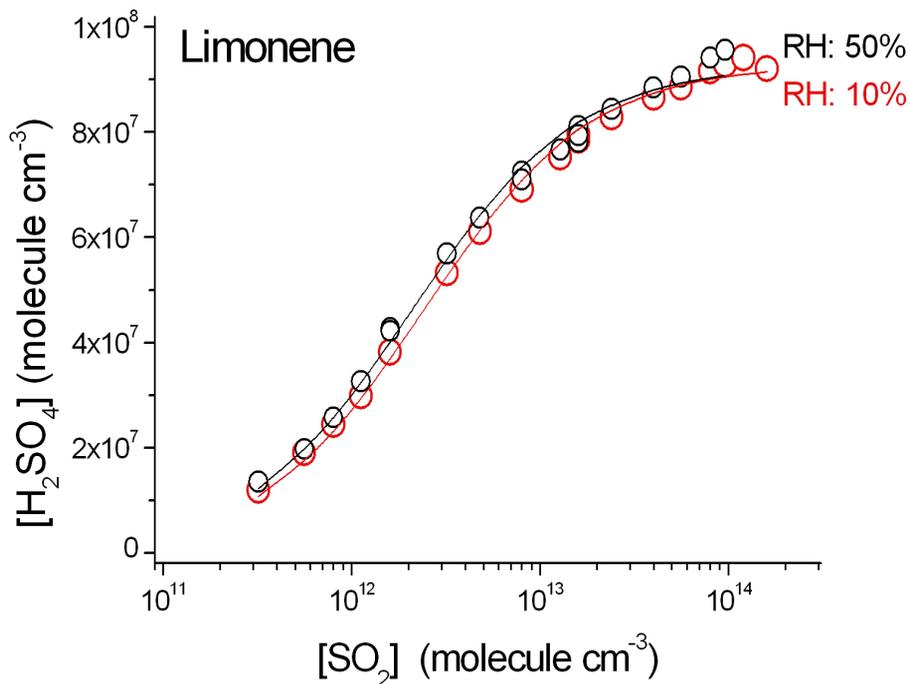


Fig. 2. Loss-corrected measured $[\text{H}_2\text{SO}_4]$ at the outflow of IFT-LFT in limonene ozonolysis experiment at RH = 10% and RH = 50%. Lines show multivariate least square fittings according to Eq. (3).

Reactivity of sCI from
isoprene and
monoterpene
ozonolysis

M. Sipilä et al.

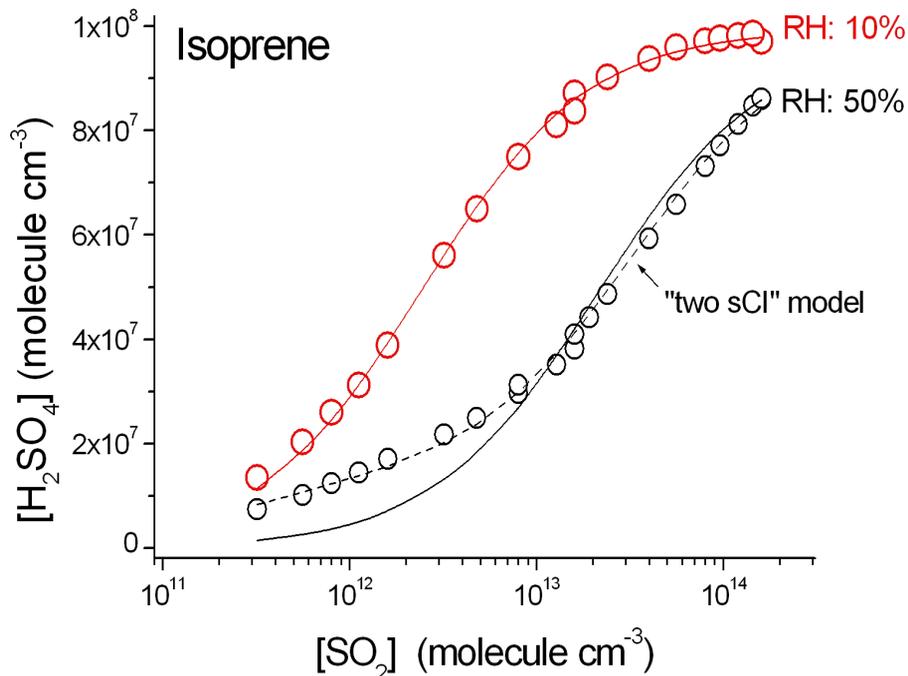


Fig. 3. Loss-corrected measured $[H_2SO_4]$ at the outflow of IFT-LFT in isoprene experiments at RH = 10% and RH = 50%. Solid lines show multivariate least square fittings according to Eq. (3). Dashed line shows the multivariate least square fittings according to Eq. (6) which accounts for the different behaviour of different sCIs.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

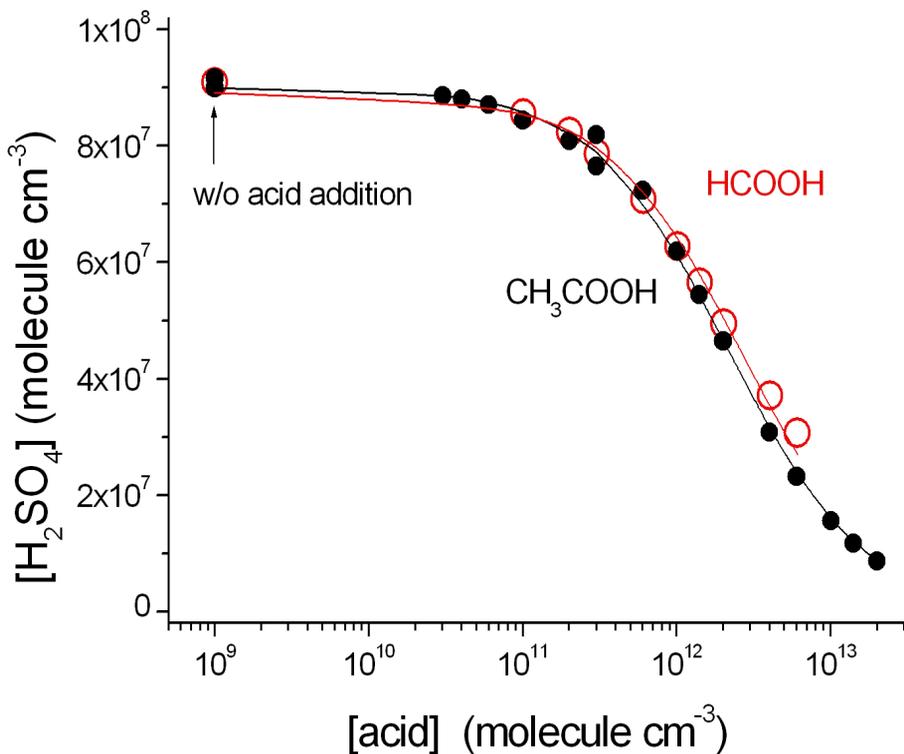


Fig. 4. Experimental data from the competitive reaction kinetics experiments, $\text{sCl} + \text{SO}_2$ vs. $\text{sCl} + \text{acid}$, $\text{sCl} \equiv (\text{CH}_3)_2\text{COO}$ (from TME ozonolysis). The lines show the best fit result of the non-linear regression analysis from Eq. (7).