Response to referees of submission of:
The atmospheric impacts of monoterpane ozonolysis on global stabilised Criegee intermediate budgets and SO2 oxidation: experiment, theory and modelling by Newland et al., 2017, submitted to ACP

General Response

We thank the referees for giving their time to make insightful comments, helping to clarify and further improve our manuscript. All 3 referee’s recognise the importance of the results presented, and recommend publication in ACP.

A couple of significant changes to note are:

(i) The removal of part of Section 5.2.4, ‘Experimental Summary’ and all of Section 7, ‘Discussion and Atmospheric Implications’, as requested by reviewer #3. No information has been lost from the manuscript, these sections were, as pointed out by reviewer #3, somewhat repeating previous sections, a little of Section 7 has been merged into the Conclusions.

(ii) The use of the IUPAC recommended rate coefficient for the decomposition rate of (CH3)2COO, as recommended by R. Chhantyal-Pun in a Comment. This has tended to increase the burden of SCI-B in our global modelling study, and increase the removal of SO2 by SCI by ~ 20%.

See the replies to the specific reviewer for further details of these changes.

Responses to specific points raised by each reviewer are given separately beneath that point.

Anonymous Referee #1

First, the authors should clarify the difference between the real atmospheric environment and their chamber. The real atmospheric environment has a range of temperature, relative humidity, and pressure; they should say which temperature, humidity, pressure range can be attained in their chamber.

We agree that we could be clearer that the results are applicable to the atmospheric boundary layer (i.e. surface pressure). This is where the chemistry is important as alkene concentrations are low outside the boundary layer due to their short atmospheric lifetimes. We have clarified this in the abstract by amending the fifth sentence (P2, L2-6) to read:

“We have investigated the removal of SO2 by SCI formed from the ozonolysis of three atmospherically important monoterpenes (a-pinene, b-pinene and limonene) in the...
presence of varying amounts of water vapour in large-scale simulation chamber
experiments, representative of boundary layer conditions.”

EUPHORE is an outdoor environmental chamber and as such we have no control over
the temperature. It is stated that temperature varied between 287 – 302 K across the
experiments (p10, I28).

We clearly state the relative humidity of each experiment (as is required - the whole
point of the experiments is to determine the effect of RH), as well as giving the overall
range in the experimental section (p11, I12).

Second, on page 22, lines 13-16, the authors mention the issues concerning the non-linear
results for the limonene results in Figure 2. Can the authors cool the limonene before
entering the chamber to decrease the ozonolysis rate? Or can they try an experiment at
lower temperatures, to obtain cleaner data for low humidity?

Unfortunately we are unable to perform further experiments at EUPHORE as they
were a part of the REACT-SCI campaign in 2013. The possible issue with the non-
linearity of the limonene loss is not the reaction rate per se, but more the low volatility
of the limonene precursor, meaning that a period of a few minutes is required to add
the compound to the chamber. Cooling the sample would only exacerbate this effect.

As stated above, EUPHORE is an outdoor environmental chamber and hence we have
no control over the chamber temperature.

Third, cyclohexane is used as an OH scavenger. Is the SCI reaction with cyclohexane slow
that it will not interfere with their analysis?

Reaction rates of SCI with alkanes are thought to be very slow. Recent theoretical work
(Xu et al., 2017) has calculated reaction rates of CH₂OO with cyclohexane to be 5.7 x
10⁻²² cm³ s⁻¹. At 75 ppmv cyclohexane, as employed in our experiments, this would lead
to loss rates for CH₂OO to the alkane on the order of 1 x 10⁻¹⁶ s⁻¹, eight orders of
magnitude lower than typical loss rates to decomposition or reaction with water.

Small points that can be fixed are as follows:

In page 13 lines 11-13, the authors mention that water dimer reaction will be negligible at
atmospherically accessible [H₂O]. However, it has already been shown experimentally that
for anti-CH₃CHOO water vapor reaction, water dimer reaction will dominate the room
temperature reaction at a relative humidity (RH) above 30%. (PCCP, 18, 28189-, 2016) On
the other hand, the present chamber experiments were done at RH 0.1 to 28%. Therefore,
the authors should change this part to “For the analysis of the present chamber results the
water dimer reaction can be ignored.”
The referee is right to point out the work of Lin et al. (2016) on anti-CH3OO + (H2O)2.

We have altered this paragraph in response to this comment. We have moved the first part of the paragraph to the introduction in response to a comment from referee #2.

We now include the following paragraph in the introduction:

“To date, the effects of the water dimer, (H2O)2 on SCI removal have only been determined experimentally for CH2OO (Berndt et al., 2014; Chao et al., 2015; Lewis et al., 2015; Newland et al., 2015a; Sheps et al., 2017; Liu et al., 2017) and anti-CH3CHOO (Lin et al., 2016). Theoretical calculations (Vereecken et al., 2017) have predicted the ratio of the SCI + (H2O)2 : SCI + H2O rate constants, k5/k3, of larger, and more substituted SCI, to be of a similar order of magnitude as for CH2OO (i.e. 1.5–2.5 × 103).”

The referee is also right that the dimer reaction will have a negligible impact on the water reaction rates determined in this work because the RH is relatively low and because at the RH where the dimer begins to become a significant loss for anti-SCI, almost all of the anti-SCI is already being removed by the monomer. Hence there is a negligible effect on the SO2 loss. The paragraph in Section 2.2 now reads:

“The water dimer reactions of non-CH2OO SCI are not considered in our analysis. The effect of the water dimer reaction with C10 and C9 SCI (rather than the monomer) is expected to be minor at the maximum [H2O] (2 × 1017 cm−3) used in these experiments (< 30 % RH). Further, with analogy to the syn/anti-CH3CHOO system, for syn-SCI loss to the dimer (and monomer) will not become competitive at the highest [H2O] used here; for anti-SCI, the water monomer will already be removing the majority of the SCI at the [H2O] at which the dimer would become a significant loss process, hence the dimer reaction is deemed unimportant. For CH2OO, the reaction rates with water and the water dimer have been quantified in recent EUPHORE experimental studies, and the values from Newland et al. (2015a) are used in our analysis.”

In Page 21 lines 23-24, they mention the effective rates for the SCI water vapour reaction at RH 75%, 298 K, and discuss results, but their experimental chamber results are up to RH 28%, so I am not sure it is relevant to mention the results for such high RH.

We agree with the referee, while the aim of the work is to determine the impact of the SCI under boundary layer conditions, this comment perhaps doesn’t belong in the experimental section but instead in a discussion section. We have changed these lines to reflect the experimental conditions from:

“SCI-3 is expected to undergo unimolecular reactions at least an order of magnitude faster than SCI-4 (Nguyen et al., 2009; Ahrens et al., 2014). The reaction of SCI-3 with water is expected to be slow based on the calculations presented in Table 4, with a pseudo first order reaction rate of 1.0 s−1 at 75 % RH, 298 K, whereas the water reaction with SCI-4 is expected to be considerably faster with a pseudo first order reaction rate of 240 s−1 at 75 % RH, 298 K. This reaction will thus likely be the dominant fate of SCI-4
at typical atmospheric RH. This is in agreement with the observations of Ma and Marston (2008), that show a clear dependence of nopinone formation on RH (presumed to be formed from SCI + H₂O). Fitting Equation E4 to the data determines values of γ⁺ = 0.41 and γ⁻ = 0.59 (Figure 4).”

To:

“SCI-3 is expected to undergo unimolecular reactions at least an order of magnitude faster than SCI-4 (Nguyen et al., 2009; Ahrens et al., 2014). The reaction of SCI-3 with water is expected to be slow based on the calculations presented in Table 4, with a pseudo first order reaction rate of 0.3 s⁻¹ at the highest [H₂O] used here, 2 × 10¹⁷ cm⁻³, 298 K, whereas the water reaction with SCI-4 is expected to be considerably faster with a pseudo first order reaction rate of 85 s⁻¹ at [H₂O] = 2 × 10¹⁷ cm⁻³, 298 K. This reaction would thus be expected to be competitive with reaction with SO₂ for SCI-4 under the experimental conditions employed. This is in agreement with the observations of Ma and Marston (2008), that show a clear dependence of nopinone formation on RH (presumed to be formed from SCI + H₂O). Fitting Equation E4 to the data determines values of γ⁺ = 0.41 and γ⁻ = 0.59 (Figure 4).”

Anonymous Referee #2

Provide more information how it was done and what’s the accuracy, detection limit etc.

We have added the following information on instrumental precision to the experimental section:

“SO₂ and O₃ abundance were measured using conventional fluorescence (reported precision ± 1.0 ppbv) and UV absorption monitors (reported precision ± 4.5 ppbv), respectively;”

Experimental procedure is detailed clearly in Section 2.1 (p.10, l.23 – p.11, l.14).

Scavenged the majority of the SCI.” Why the authors did not chose perfect experimental conditions for these titration experiments allowing a direct determination of the SCI fraction without any further processing of the primary data?

It is impossible to scavenge 100 % of the SCI, rates of decomposition of many of the SCI studied are on the order of hundreds per second. There is a limit to how much SO₂ we can safely and practically use in the large EUPHORE chamber (with the lab situated directly below it).

p.17/18 and table 1: Finally stated SCI yields have a quite low range of uncertainty. Does the uncertainty really reflect the overall precision of this experimental approach?

We have added a sub-section to Section 2 – Experimental uncertainties which contains the following text:
"The uncertainty in $k_3/k_2$ was calculated by combining the mean relative errors from the precision associated with the SO$_2$ and ozone measurements (given in Section 2.1) with the $2\sigma$ error and the relative error in $\phi$, using the root of the sum of the squares of these four sources of error. The uncertainty in $k_4/k_2$ was calculated in the same way.

The uncertainty in $\phi_{\text{min}}$ was calculated by combining the uncertainty in $\Delta$SO$_2$ and $\Delta$O$_3$, as above. The uncertainty in $\phi$ was calculated by applying the $k_3/k_2$ uncertainties and combining these with the uncertainties in $\phi_{\text{min}}$, using the root of the sum of the squares."

Rate coefficients to set their relative values on an absolute scale, Sheps et al., PCCP (2014). Especially by Taatjes et al., Science (2013). Is there a special reason using the Sheps et al. values? What are the consequences if the Taatjes et al. data are used instead of those by Sheps et al.?

The difference between the Sheps and the Taatjes measured rate constants for the anti-CH$_3$CHO + SO$_2$ reaction is likely owing to differences in the detection techniques used (UV-cavity enhanced absorption spectroscopy vs. Photo-Ionization Mass Spectrometry), with the broadband UV-cavity enhanced absorption technique affording superior sensitivity and selectivity over PIMS (also note that the yield of stabilised anti-CH$_3$CHO from the CH$_3$CHI + O$_3$ reaction is only between 10-30% of the total stabilised CH$_3$CHO yield). Therefore, it was decided to put our chamber relative rate measurements on an absolute basis using the Sheps measurements. However, it is important to point out here that our relative rate measurements can be placed on an absolute basis using new and improved evaluated SO$_2$ rate constants as new measurements become available.
Scholarly presentation: The text on monoterpene ozonolysis in the early part of the manuscript is a very nice and thorough summary but when read the reader is asking himself: ‘And what is the outcome of the present paper for this?’ - this is then treated in the results section. Maybe some on the contents of the introductory text can be shortened and be used when the results are actually presented. That would also compact the paper to some extent. Shortening certain sections and avoiding doubling of text appears advisable as the manuscript reads kind of lengthy at times. There is the danger to loose the reader. The theoretical chemistry section of the paper might be problematic, but I am not an expert in this.

Details:
Page 4, line 4: The population of CIs is formed...pls check sentence.

Changed to, "The population of CIs is formed ..."

p12, l6: This equation looks strangely formatted. Pls check.

We're not sure what looks strange about it, but it will in any case be formatted to the ACP style during typesetting.

p13-15: I feel this is partly repeating material already given in the introductory overview. That should be avoided. Please check and discuss the state-of-the-art regarding the water reaction, the roles of the water dimer and the difference of syn- and anti-conformers once in the manuscript and then work with internal referencing.

We have moved the 'literature review' part of this paragraph to the introduction and included all up to date references. This section now reads:

"To date, the effects of the water dimer, $(H_2O)_2$ on SCI removal have only been determined experimentally for $CH_2OO$ (Berndt et al., 2014; Chao et al., 2015; Lewis et al., 2015; Newland et al., 2015a; Sheps et al., 2017; Liu et al., 2017) and anti-$CH_2CHOO$ (Lin et al., 2016). Theoretical calculations (Vereecken et al., 2017) have predicted the ratio of the SCI + $(H_2O)_2$ : SCI + $H_2O$ rate constants, $k_5/k_3$, of larger, and more substituted SCI, to be of a similar order of magnitude as for $CH_2OO$ (i.e. $1.5-2.5 \times 10^3$)."

p16: If it has been shown, that post-CCSD(T) calculations are needed but these cannot be performed for technical reason, what is then the use of this? It is difficult to judge how valid such calculations could be. Certain journals do not accept theoretical chemistry calculation not being performed with the best available techniques. The authors should deal with this. Maybe it is better to outsource this part and do the bigger calculations separately.
Like experimental measurements, all theoretical predictions are subject to an uncertainty margin, where one aims to reduce the uncertainty by applying the highest possible levels of theory. The methodology used in this work is generally considered high-level and reliable, and the data presented here required well over half a million cpu core hours (>>50 years), and include CCSD(T) calculations with over 1000 basis functions. It is doubtful that any journal would consider these calculations not state-of-the-art for the molecules studied. Going beyond these methodologies is not obvious, and it is not a matter of outsourcing post-CCSD(T) calculations, but rather the question whether anyone is able to do them at all with current computational resources, and can/wants to afford the cost, especially as the empirical corrections described in Vereecken et al. 2017 are expected to recover a large part of the bias on the barrier height. Further improvement could perhaps be made by the kinetic analysis but this, too, requires significant additional computational resources.

As shown in Vereecken et al. 2017, the final rate coefficient predictions for unimolecular reactions are expected to be accurate within a factor of 5. For the CI + H$_2$O reaction, rate predictions are estimated to be accurate within an order of magnitude. While it would be useful to further reduce the uncertainty on these predictions, they are already sufficiently accurate to have useful predictive value, and the computational cost of reducing the uncertainty may suffer from diminishing returns.

The use of these predictions is that we now have two studies with very different methodologies, experimental and theoretical, which agree quantitatively within the respective uncertainties, suggesting that the conclusions presented in the paper are reliable. Furthermore, the theoretical data allows one to identify the molecular identity of the CI groups used in the experimental analysis; this data is not readily available otherwise.

We have changed the first paragraph of Section 3 to read:

"The rovibrational characteristics of all conformers of the CI formed from α-pinene and β-pinene, the transition states for their unimolecular reaction, and for their reaction with H$_2$O, were characterized quantum chemically, first using the M06-2X/cc-pVDZ level of theory, and subsequently refined at the M06-2X/aug-cc-pVTZ level. To obtain the most accurate barrier heights for reaction, it has been shown (Berndt et al., 2015; Chhantyal-Pun et al., 2017; Fang et al., 2016a, 2016b; Long et al., 2016; Nguyen et al., 2015) that post-CCSD(T) calculations are necessary. Performing such calculations for the SCI discussed in this paper, with up to 14 non-hydrogen atoms, is well outside our computational resources. Instead, we base our predictions on high-level CCSD(T)/aug-cc-pVTZ single point energy calculations, performed for the reactions of nopinone oxides and the most relevant subset of pinonaldehyde oxides. These data are reliable for relative rate estimates, but it remains useful to further improve the absolute barrier height predictions, as described by Vereecken et al. (2017) based on a data set with a large number of systematic calculations on smaller CI, allowing empirical corrections to estimate the post-CCSD(T) barrier heights. Briefly, they compare rate coefficient
calculations against available harmonized experimental and very-high level theoretical kinetic rate predictions, and adjusts the barrier heights by 0.4 to 2.6 kcal mol⁻¹ (depending on the base methodology and the reaction type) to obtain best agreement with these benchmark results."

p18,l29: Pls check sentence
Checked.

p23, Is that section 5.2.4. really needed? I think it should be skipped in order to streamline the whole paper.
We agree that much of this section is repeated in the conclusions and that parts of the section could be removed to shorten the paper, but also feel that it is useful to provide a summary of the experimental numbers from the previous sections. As such, we have significantly shortened this section, removing the first 15 lines and the final paragraph.

p24, section 5.3: See general comment on this. Is it necessary to give all the structural data in the SI?
It is not clear whether the referee is requesting more structural data in the main manuscript, or less in the SI. If it is the latter, then we would suggest that this is exactly what the SI is for. We would hope that the information will be useful for those looking to further understand the theoretical work.

p26, Why is section 6 separate from the 'results' section - these are also results, so it might be sensible to make this a sub-point of the results section 5 rather than a new section 6
We agree that the current grouping of the experimental and theoretical results, but separation of the modelling is somewhat illogical. The three separate techniques: experiment, theory, and modelling are now placed in separate sections. This seems to us a logical and useful way of setting out the paper. In order to clarify the differences between these sections we have renamed Section 5, Experimental Results. Theoretical results and comparison to experiments is now Section 6. And Global modeling study is now Section 7.

p29, l14: Oceanic MT emissions are expected to be small compared to the continental ones.
This may be the case, but we clearly reference two studies which provide values for oceanic MT emissions and then discuss the implication of these studies with reference to our work.

p30, sections 7 & 8: Maybe these sections can be combined.
We agree with the referee, Section 7 has been removed and the following sentence has been added to the conclusion (with reference to using a 2-species system for modelling SCI chemistry).

"Moreover such an approach is required to accurately predict SCI concentrations, which will be underestimated if a simple average of the properties of the two different SCI classes is used."
Comment – Rabi Chhantyal-Pun

Please could the authors clarify why a value of 819 (±190) s⁻¹ is being used for (CH₃)₂COO unimolecular reaction rate coefficient? The recent IUPAC task group on atmospheric chemical kinetic data evaluation’s preferred value is 397 s⁻¹ at 298 K. Is the author’s global modelling study affected if more accurate rate coefficients are used?

The value originally used for the (CH₃)₂COO decomposition rate (819 s⁻¹) comes from ozonolysis experiments (Newland et al., 2015) that used the same experimental conditions as those used in the monoterpene experiments reported in the manuscript. The relative rate from Newland et al. (2015) was scaled to the k((CH₃)₂COO+SO₂) rate determined by Huang et al. (2015). This values lies within the uncertainty limits of the recommended IUPAC value.

However, we agree with R. Chhantyal-Pun that the modelling should be done with the IUPAC recommended value (which was not available when the modelling was originally done!). We have repeated the global modeling using the temperature dependent decomposition value from IUPAC (http://iupac.pole-ether.fr/htdocs/datasheets/pdf/CGI_14_(CH3)2COO+M.pdf) and will include this revised model output in the final manuscript.

As expected, using this slower unimolecular rate increases the concentrations of the SCI-B from ocimene and myrcene, for which the acetone oxide kinetics are used. These increased concentrations lead to an increased relative importance of these SCI compared to other SCI and increased removal of SO₂.

The relative contributions of myrcene and ocimene to total [SCI-B] increase from 1.2 % and 5.4 % to 2.7 % and 11% respectively, with commensurate decreases in the relative contributions of the other monoterpenes. Peak annually averaged [SCI] (in the tropics) increases from 1.2 × 10⁶ cm⁻³ to 1.4 × 10⁶ cm⁻³.

The contribution of SCI to annual gas phase SO₂ oxidation in the terrestrial tropics increases from 1.1% – 1.2%. Globally, the annual contribution of SCI to gas phase SO₂ oxidation increases from 0.5% to 0.7%, and the total annual SO₂ removal increases from 6.8 to 8.1 Gg.

All relevant values have been updated throughout the manuscript. The modelling using the Blitz updated k(SO₂+OH) rate constant in the SI has also been updated.

As expected, using this slower unimolecular rate increases the concentrations of the SCI-B from ocimene and myrcene, for which the acetone oxide kinetics are used. These increased concentrations lead to an increased relative importance of these SCI compared to other SCI and increased removal of SO₂.

The relative contributions of myrcene and ocimene to total [SCI-B] increase from 1.2 % and 5.4 % to 2.7 % and 11% respectively, with commensurate decreases in the relative contributions of the other monoterpenes. Peak annually averaged [SCI] (in the tropics) increases from 1.2 × 10⁶ cm⁻³ to 1.4 × 10⁶ cm⁻³.

The contribution of SCI to annual gas phase SO₂ oxidation in the terrestrial tropics increases from 1.1% – 1.2%. Globally, the annual contribution of SCI to gas phase SO₂ oxidation increases from 0.5% to 0.7%, and the total annual SO₂ removal increases from 6.8 to 8.1 Gg.

All relevant values have been updated throughout the manuscript. The modelling using the Blitz updated k(SO₂+OH) rate constant in the SI has also been updated.
The atmospheric impacts of monoterpane ozonolysis on global stabilised Criegee intermediate budgets and SO$_2$ oxidation: experiment, theory and modelling

Mike J. Newland$^{1,3}$, Andrew R. Rickard$^{2,3}$, Tomás Sherwen$^5$, Mathew J. Evans$^{2,3}$, Luc Vereecken$^{4,5}$, Amalia Muñoz$^6$, Milagros Ródenas$^6$, William J. Bloss$^1$

[1] University of Birmingham, School of Geography, Earth and Environmental Sciences, Birmingham, UK
[2] National Centre for Atmospheric Science (NCAS), University of York, York, UK
[3] Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, UK
[4] Max Planck Institute for Chemistry, Atmospheric Sciences, Hahn-Meitner-Weg 1, Mainz, Germany
[5] Institute for Energy and Climate Research, Forschungszentrum Jülich GmbH, Jülich, Germany

Correspondence to: M. J. Newland (mike.newland@york.ac.uk)
A. R. Rickard (andrew.rickard@york.ac.uk)

Abstract

The gas-phase reaction of alkenes with ozone is known to produce stabilised Criegee intermediates (SCIs). These biradical/zwitterionic species have the potential to act as atmospheric oxidants for trace pollutants such as SO$_2$, enhancing the formation of sulfate aerosol with impacts on air quality and health, radiative transfer and climate. However, the importance of this chemistry is uncertain as a consequence of limited understanding of the abundance and atmospheric fate of SCIs. In this work we apply experimental, theoretical and numerical modelling methods to quantify the atmospheric impacts, abundance, and fate, of the
structurally diverse SCIs derived from the ozonolysis of monoterpenes, the second most abundant group of unsaturated hydrocarbons in the atmosphere. We have investigated the removal of SO$_2$ by SCI formed from the ozonolysis of three atmospheric important monoterpenes ($\alpha$-pinene, $\beta$-pinene and limonene) in the presence of varying amounts of water vapour in large-scale simulation chamber experiments, representative of boundary layer conditions. The SO$_2$ removal displays a clear dependence on water vapour concentration, but this dependence is not linear across the range of [H$_2$O] explored. At low [H$_2$O] a strong dependence of SO$_2$ removal on [H$_2$O] is observed, while at higher [H$_2$O] this dependence becomes much weaker. This is interpreted as being caused by the production of a variety of structurally (and hence chemically) different SCI in each of the systems studied, each displaying different rates of reaction with water and of unimolecular rearrangement/decomposition. The determined rate constants, $k$(SCI+H$_2$O), for those SCI that react primarily with H$_2$O range from $4 \times 10^{-15}$ cm$^3$ s$^{-1}$. For those SCI that predominantly react unimolecularly, determined rates range from 130 – 240 s$^{-1}$. These values are in line with previous results for the (analogous) stereo-specific SCI system of syn/anti-CH$_3$CHO. The experimental results are interpreted through theoretical studies of the SCI unimolecular reactions and bimolecular reactions with H$_2$O, characterised for $\alpha$-pinene and $\beta$-pinene at the M06-2X/aug-cc-pVTZ level of theory. The theoretically derived rates agree with the experimental results within the uncertainties. A global modelling study, applying the experimental results within the GEOS-Chem chemical transport model, suggests that > 97% of the total monoterpenes derived global SCI burden is comprised of SCI whose structure determines that they react slowly with water, and whose atmospheric fate is dominated by unimolecular reactions. Seasonally averaged boundary layer concentrations of monoterpened-derived SCI reach up to $1.4 \times 10^4$ cm$^{-3}$ in regions of elevated monoterpenes emissions in the tropics. Reactions of monoterpenes derived SCI with SO$_2$ account for < 1% globally but may account for up to 60% of the gas-phase SO$_2$ removal over areas of tropical forests, with significant localised impacts on the formation of sulfate aerosol, and hence the lifetime and distribution of SO$_2$.

1 Introduction

Chemical oxidation processes in the atmosphere exert a major influence on atmospheric composition, leading to the removal of primary emitted species, and the formation of secondary
products. In many cases either the emitted species or their oxidation products negatively impact air quality and climate (e.g. ozone, which is also a potent greenhouse gas). These reactions can also transform gas-phase species to the condensed phase, forming secondary aerosol that again can be harmful to health and can both directly and indirectly influence radiative transfer and hence climate (e.g. SO$_2$ oxidation leading to the formation of sulfate aerosol).

Tropospheric gas-phase oxidants include the OH radical, ozone, the NO$_x$ radical, and halogen atoms. Stabilised Criegee intermediates (SCIs), or carbonyl oxides, have been identified as another potentially important oxidant in the troposphere (e.g. Cox and Penkett, 1971; Mauldin et al., 2012). SCIs are thought to be formed in the atmosphere predominantly from the reaction of ozone with unsaturated hydrocarbons, though other processes may be important under certain conditions, e.g. alkyl iodide photolysis (Gravestock et al., 2010), dissociation of the DMSO peroxy radical (Asatryan and Bozzelli, 2008). Laboratory experiments and theoretical calculations have shown SCI to oxidise SO$_2$ (e.g. Cox and Penkett, 1971; Welz et al., 2012; Taatjes et al., 2013), organic (Welz et al., 2014) and inorganic (Foreman et al., 2016) acids (Vereecken et al., 2017), and a number of other important trace gases found in the atmosphere, as well as forming adducts with NO$_2$ (Taatjes et al., 2014; Vereecken et al., 2017; Caravan et al., 2017). Measurements in a boreal forest (Mauldin et al., 2012) and at a coastal site (Berresheim et al., 2014) have both identified a ‘missing’ process (in addition to reaction with OH) oxidising SO$_2$ to H$_2$SO$_4$, potentially arising from SCI reactions.

Here, we present results from a series of experimental studies into SCI formation and reactions, carried out under atmospheric boundary layer conditions in the European Photochemical Reactor facility (EUPHORE), Valencia, Spain. We examine the ozonolysis of three monoterpenes with very different structures (and hence reactivities with OH and ozone): $\alpha$-pinene (with an endocyclic double bond), $\beta$-pinene (with an exocyclic double bond) and limonene (with both an endo and exo cyclic double bond). We observe the removal of SO$_2$ in the presence of each alkene-ozone system as a function of water vapour concentration. This allows us to derive relative SCI kinetics for reaction with H$_2$O, SO$_2$, and unimolecular decomposition. Further, we calculate absolute unimolecular rates and bimolecular reaction rates with H$_2$O for all $\alpha$-pinene and $\beta$-pinene derived SCI at the M06-2X/aug-cc-pVTZ level of theory. A global modelling study, using the GEOS-Chem global chemical transport model, is
performed to assess global and regional impacts of the chemical kinetics of monoterpenes SCI
determined in this study.

1.1 Stabilised Criegee Intermediate Kinetics

Ozonolysis of an unsaturated hydrocarbon produces a primary ozonide that rapidly
decomposes to yield pairs of Criegee intermediates (CIs) and carbonyls (Johnson and
Marston 2008). The population of CIs are formed with a broad internal energy distribution
giving both chemically activated and stabilised forms. Chemically activated CIs may
undergo collisional stabilisation to an SCI, unimolecular decomposition or isomerisation.
SCIs can have sufficiently long lifetimes to undergo bimolecular reactions (Scheme 1).

The predominant atmospheric fate for the simplest SCI, CH$_2$OO, is reaction with water vapour (likely with the dimer ((H$_2$O)$_2$) (e.g. Berndt et al., 2014; Newland et al., 2015a;
Chao et al., 2015; Lewis et al., 2015; Lin et al., 2016a). For larger SCI, both experimental
(Taatjes et al., 2013; Sheps et al., 2014; Newland et al., 2015a; Huang et al., 2015) and
theoretical (Kuwata et al., 2010; Anglada et al., 2011; Anglada and Sole, 2016, Vereecken
et al., 2017) studies have shown that their kinetics, in particular reaction with water, are
highly structure dependent. The significant double bond character exhibited in the
zwitterionic configurations of mono-substituted SCI leads to two distinct chemical forms:
syn-SCI (i.e. those where an alkyl-substituent group is on the same side as the terminal
oxygen of the carbonyl oxide moiety), and anti-SCI (i.e. with the terminal oxygen of the
carbonyl oxide moiety on the same side as a hydrogen group). The two conformers of
CH$_3$CHOO, which are both mono-substituted, display these properties. This difference in
conformer reactivities has been predicted theoretically (Ryzhkov and Ariya, 2004, Kuwata
et al., 2010; Anglada et al., 2011; Lin et al., 2016a) and was subsequently confirmed
experimentally (Taatjes et al., 2013; Sheps et al., 2014) for the two CH$_3$CHOO conformers.
The significantly faster reaction of anti-CH$_3$CHOO with water is driven by the higher
potential energy of this isomer, while more stable SCI, with a methyl group in syn-position,
such as syn-CH$_3$CHOO or (CH$_3$)$_2$COO, react orders of magnitude more slowly with water.

To date, the effects of the water dimer, (H$_2$O)$_2$, on SCI removal have only been determined
experimentally for CH$_2$OO (Berndt et al., 2014; Chao et al., 2015; Lewis et al., 2015;
Newland et al., 2015a; Sheps et al., 2017; Liu et al., 2017) and anti-CH$_3$CHOO (Lin et al.,
2016b). Theoretical calculations (Vereecken et al., 2017) have predicted the ratio of the SCI +
SCI can also undergo unimolecular isomerisation/decomposition in competition with bimolecular reactions. This is likely to be a significant atmospheric sink for syn-SCI because of their slow reaction with water vapour (e.g. Huang et al., 2015). Unimolecular reactions of syn-Cl/SCI are dominated by a 1,4-H-shift, forming a vinyl hydroperoxide (VHP) intermediate (Niki et al., 1987; Rickard et al., 1999; Martinez and Herron, 1987; Johnson and Marston, 2008; Kidwell et al., 2016). Decomposition of the VHP formed in this process is an important non-photolytic source of OH, HO₂, and RO₂ in the atmosphere (Niki et al., 1987; Alam et al., 2013; Kidwell et al., 2016), which can also lead to secondary organic aerosol formation (Ehn et al., 2014). Unimolecular reactions of the anti-Cl/SCI are thought to be dominated by a 1,3-ring closure, the “acid/ester channel”, in which the CI/SCI decomposes, through a rearrangement to a dioxirane intermediate, producing a range of daughter products and contributing to the observed overall HOₓ radical yield (Kroll et al., 2002; Johnson and Marston, 2008; Alam et al., 2013).

Decomposition of the simplest SCI, CH₂OO, is slow (< 10 s⁻¹) and is not likely to be an important sink in the troposphere (e.g. Newland et al., 2015a; Chhantyal-Pun et al., 2015). This decomposition occurs primarily via rearrangement through a ‘hot’ acid species, which represents the lowest accessible decomposition channel (Gutbrod et al., 1996; Alam et al., 2011; Chen et al., 2016). However, recently determined unimolecular reaction rates of larger syn-SCI are considerably faster. Newland et al. (2015a) reported unimolecular reaction rate constants for syn-CH₃CHOO of 348 (± 332) s⁻¹ and for (CH₃)₂COO of 819 (± 190) s⁻¹ (assuming k(syn-CH₃CHOO+SO₂) = 2.9 × 10⁻¹³ cm³ s⁻¹ (Sheps et al., 2014) and k((CH₃)₂COO+SO₂) = 1.3 × 10⁻¹³ cm³ s⁻¹.)
16 \text{ cm}^3 \text{s}^{-1} \) (Huang et al., 2015), respectively. Smith et al. (2016) measured the unimolecular decomposition rate of \((\text{CH}_3)\text{COO}\) to be 269 (± 82) \text{s}^{-1} at 283 K, suggesting the rate to be fast and highly temperature dependent. Novelli et al. (2014), respectively estimated a significantly slower decomposition rate for \(\text{syn-CH}_3\text{CHOO}\) of 20 (3-30) \text{s}^{-1} from direct observations of OH formation, while Fenske et al. (2000), estimated the decomposition rate of \(\text{CH}_3\text{CHOO}\) (i.e. a mix of \text{syn} and \text{anti} conformers) produced from ozonolysis of \(\text{trans-2-but-2-ene}\) to be 76 \text{s}^{-1} (accurate to within a factor of three).

1.2 Monoterpene Ozonolysis

Monoterpenes are volatile organic compounds (VOCs) with the general formula \(\text{C}_{10}\text{H}_{16}\), which are emitted by a wide range of vegetation, particularly from boreal forests. Total global monoterpene emissions are estimated to be 95 (± 3) Tg yr$^{-1}$ (Sindelarova et al., 2014) - roughly 13 % of total non-methane biogenic VOC emissions. Monoterpene emissions are dominated by \(\alpha\)-pinene, which accounts for roughly 34 % of the total global emissions, while \(\beta\)-pinene and limonene account for 17 % and 9 % respectively (Sindelarova et al., 2014). Monoterpenes (mainly \(\alpha\)-pinene and limonene) are also present in indoor environments, in significant amounts where cleaning products and air fresheners are in routine use (on the order of 100s of ppbv) (e.g. Singer et al., 2006; Sarwar and Corsi, 2007), where their ozonolysis products can affect indoor chemistry and health (e.g. Rossignol et al., 2013; Shallcross et al., 2014).

Monoterpenes are highly reactive due to the presence of (often multiple) double bonds. The oxidation of monoterpenes yields a wide range of multi-functional gas-phase and aerosol products. This process can be initiated by OH and NO$_3$ radicals or by O$_3$, with ozonolysis having been shown to be particularly efficient at generating low volatility products that can form SOA, even in the absence of sulfuric acid (e.g. Ehn et al., 2014; Kirkby et al., 2016). These highly oxygenated secondary products have received considerable attention in recent years because of their role in affecting the climate through absorption and scattering of solar radiation (the direct aerosol effect). They can also increase cloud condensation nuclei concentrations, which can change cloud properties and lifetimes (the indirect aerosol effect). They have also been shown to have a wide range of deleterious effects on human health (e.g. Pöschl and Shiraiwa, 2015).

The ozonolysis reaction for monoterpenes is expected to follow a similar initial process to that
of smaller alkenes, with cyclo-addition at a double bond giving a primary ozonide (POZ),
followed by rapid decomposition of the POZ to yield a CI and a carbonyl (Scheme 1).
Stabilisation of the large POZs formed in monoterpene ozonolysis is expected to be
negligible (Nguyen et al., 2009). However, a major difference in ozonolysis at endocyclic bonds
is that, on decomposition of the POZ, the carbonyl oxide and carbonyl moieties are tethered as
part of the same molecule, providing the potential for further interaction of the two. These can
react together to form secondary ozonides (SOZ), which may be stable for several hours (Beck
et al., 2011). However, while this has been shown to be potentially the major fate in the
atmosphere for SCI derived from sesquiterpenes (C_{15}H_{24}) (e.g. Nguyen et al., 2009b; Beck et
al., 2011; Yao et al., 2014), formation of SOZ is predicted to be small for monoterpene derived
SCI because of the high ring strain caused by the tight cyclisation (e.g. Nguyen et al., 2009b).
Chuong et al. (2004) predicted formation of a SOZ to become the dominant atmospheric fate
for SCI formed in the ozonolysis of endo-cyclic alkenes with a carbon number between 8 and
15, while Vereecken and Francisco (2012) suggested that internal SOZ formation is likely to
be limited to product rings containing six or more carbons due to ring strain.
No studies have yet directly determined the reaction rates of the large SCI produced from
monoterpene ozonolysis with SO_{2} (or any other trace gases). This is owing to the complexities
of synthesising and measuring large SCI. However, Ahrens et al. (2014) concluded that the
reaction of the C9-SCI formed in β-pinene ozonolysis with SO_{2} is as fast as that determined by
Welz et al. (2012) and Taatjes et al. (2013) for CH_{2}OO and CH_{3}CHOO respectively (ca. 4 ×
10^{-13} \text{cm}^{3} \text{s}^{-1}) by fitting to the decay of SO_{2} in the presence of the ozonolysis reaction. Mauldin
et al. (2012) calculated significantly slower reaction rates for an additional oxidant (assumed to
be SCI) derived from α-pinene and limonene ozonolysis, with k(\text{SCI+SO}_{2}) determined to be 6
× 10^{-13} \text{cm}^{3} \text{s}^{-1} and 8 × 10^{-13} \text{cm}^{3} \text{s}^{-1} for α-pinene and limonene derived SCI respectively.
However, it seems likely that the rates calculated by Mauldin et al. (2012) may be substantially
underestimated due to the assumption of a very long SCI lifetime (0.2 s) in experiments that
were performed at 50 % RH. The calculated rates scale linearly with SCI lifetime and based on
reaction rates of smaller SCI with H_{2}O (reported since the Mauldin et al. work, e.g. Taatjes et
al., 2013) it seems likely that the lifetime of the SCI in their experiments would have been more
like 0.1 – 2 × 10^{-2}s, increasing the calculated rate constants by more than an order of magnitude,
bringing them into much closer agreement with the rates reported by Ahrens et al. (2014).
Unimolecular reactions of the monoterpene SCI are expected to proceed rapidly through the
VHP route if a hydrogen is available for a 1,4 H-shift. Those SCI that cannot undergo this
rearrangement may undergo unimolecular reactions via the formation of the dioxirane intermediate, but this is expected to be a much slower process (Nguyen et al., 2009). In contrast to smaller SCI, it has been observed experimentally, and predicted theoretically, that the VHP route will mainly lead to rearrangement to an acid (also yielding an OH radical) rather than decomposition of the molecule (e.g. Ma et al., 2008, Ma and Marston, 2008). As for the smaller alkenes, monoterpene ozonolysis has been shown to be a source of HOx (e.g. Paulson et al., 1997; Alam et al., 2013), predominantly via the VHP rearrangement. The MCMv3.3.1 (Jenkin et al., 2015) applies OH yields of 0.80, 0.35 and 0.87 for α-pinenes, β-pinene and limonene respectively.

1.2.1 α-pinene derived SCI

Decomposition of the α-pinene POZ yields four different $C_{10}$ Criegee intermediates (Scheme 2: CI-1a, 1b, 2a, 2b), with the carbonyl oxide moiety at one end and a carbonyl group at the other. Here, CI-1 is a mono-substituted CI for which both syn (1a) and anti (1b) conformers exist, while the other, CI-2, is di-substituted, for which two syn-conformers (2a and 2b) exist. Ma et al. (2008) infer a relative yield of 50 % for the two basic CI formed, based on the observation that norpinonic acid yields from the ozonolysis of α-pinene and an enone, upon ozonolysis yields CI-1, are almost indistinguishable. The total SCI yield from α-pinene was determined to be 0.15 (± 0.07) by Sipilä et al. (2014) in indirect experiments measuring the production of $H_2SO_4$ from $SO_2$ oxidation in the α-pinene ozonolysis system. Drozd and Donahue (2011) also determined a total SCI yield of about 0.15 at 740 Torr, from measuring the loss of hydrofluoroacetone in ozonolysis experiments in a high pressure flow system. The MCMv3.3.1 (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2015) applies a value of 0.20 based on stabilisation of only the mono-substituted CI-1.

1.2.2 β-pinene derived SCI

β-pinene ozonolysis yields two distinct conformers of the nopinone C9-CI (Scheme 3: CI-3 and CI-4), which differ in orientation of the carbonyl oxide group, and $CH_2OO$. CI-3 and CI-4 are formed in roughly equal proportions with very little inter-conversion between the two (Nguyen et al., 2009). The difference in the chemical behaviour of CI-3 and CI-4, which were often not distinguished in earlier studies, arises from the inability of the carbon attached to the four-membered ring to undergo the 1,4-H-shift that allows unimolecular decomposition via the VHP channel. This was noted in Rickard et al. (1999) as being a reason for the considerably lower...
OH yield (obtained via the VHP route) from β-pinene ozonolysis compared to that of α-pinene. This difference leads to contrasting unimolecular decomposition rates for the two CI, with Nguyen et al. (2009) predicting a loss rate of ca. 50 s\(^{-1}\) for CI-3 (via a VHP) and ca. 1 s\(^{-1}\) for CI-4 (via ring closure to a dioxirane). This result is qualitatively consistent with the experimental work of Ahrens et al. (2014), who determine a ratio of 85:15 for the abundance of SCI-4:SCI-3 about 10 s after the initiation of the ozonolysis reaction, as a consequence of the much faster decomposition rate of SCI-3. Thus the potential for bimolecular reactions to compete with decomposition of SCI-3 and SCI-4 in the atmosphere is very different. Nguyen et al. (2009) theoretically calculate a total SCI yield from β-pinene ozonolysis of 42 %, consisting of 16.2 % SCI-3, 20.6 % SCI-4, and 5.1 % CH\(_2\)OO. Ahrens et al. (2014) assume an equal yield of CI-3 and CI-4 (45 %) with a 10 % yield of CH\(_2\)OO; 40 % of the total C9-CI are calculated to be stabilised at 1 atm. If all of the CH\(_2\)OO is assumed to be formed stabilised (e.g. Nguyen et al., 2009) then this gives a total SCI yield of 46 %. Earlier experimental studies have tended to determine lower total SCI yields with Hasson et al. (2001) reporting a total SCI yield of 0.27 from measured product yields (almost entirely nopinone) and Hatakeyama et al. (1984) reporting a total SCI yield of 0.25. Winterhalter et al. (2000) determined a yield of 0.16 (± 0.04) for excited CH\(_2\)OO from β-pinene ozonolysis, obtained via the nopinone yield and 0.35 for the stabilised C9-CI, giving a total SCI yield of 0.51 of all the CH\(_2\)OO is assumed to be stabilised. Also, experimental studies have tended to report higher CH\(_2\)OO yields (determined from measured nopinone yields) than theoretical studies. Nguyen et al. (2009) note that this could be because nopinone can also be formed in bimolecular reactions of SCI-4, hence experimental studies may overestimate CH\(_2\)OO production. The MCMv3.3.1 incorporates a total SCI yield of 0.25 from β-pinene ozonolysis, with a yield of stabilised C9-CI of 0.102 and a CH\(_2\)OO yield of 0.148.

### 1.2.3 Limonene derived SCI

Limonene has two double bonds at which ozone can react. Theory suggests that reaction at the endocyclic bond is more likely; Baptista et al. (2011) calculate reaction at the endo-cyclic bond to be 84 – 94 % (dependent on the level of theory applied). Zhang et al. (2006) suggest the reaction at the endo-cyclic double bond to be roughly 25 times faster than at the exo-cyclic bond, i.e. leading to a branching ratio of ca. 96 % reaction at the endo bond and the current IUPAC recommendation (IUPAC, 2013) suggests about 95 % of the primary ozone reaction to be at the endo bond. Leungsakul et al. (2005) reported a best fit to measurements from chamber...
experiments by assuming an 85% reaction at the endo-cyclic bond and 15% at the exo-cyclic bond.

Ozone reaction at the endo-cyclic bond of limonene produces four different C\(_{10}\) CI (Scheme 4: CI-5a, 5b, 6a, 6b). Similar to CI-1 and CI-2 from α-pinene, CI-5 is a mono-substituted CI for which both syn (5a) and anti (5b) conformers exist, while the other, CI-6, is di-substituted, for which two syn-conformers (6a and 6b) exist. Leungsakul et al. (2005) determined a total SCI yield from limonene ozonolysis of 0.34, consisting of CH\(_2\)OO (0.05), CI-7 (0.04), CI-5 (0.15) and CI-6 (0.11). Sipilä et al. (2014) determined a total SCI yield of 0.27 (± 0.12) from indirect experiments measuring the production of H\(_2\)SO\(_4\) from SO\(_2\) oxidation in the presence of the limonene-ozone system. The MCMv3.3.1 describes only reaction with ozone at the endocyclic double bond and recommends a total SCI yield of 0.135 with stabilisation of only the mono-substituted CI-5.

2 Experimental

2.1 Experimental Approach

The EUPHORE facility is a 200 m\(^3\) simulation chamber used primarily for studying reaction mechanisms under atmospheric boundary layer conditions. Further details of the chamber setup and instrumentation are available elsewhere (Becker, 1996; Alam et al., 2011), and a detailed account of the experimental procedure, summarised below, is given in Newland et al (2015a).

Experiments comprised time-resolved measurement of the removal of SO\(_2\) in the presence of the monoterpene-ozone system, as a function of humidity. SO\(_2\) and O\(_3\) abundance were measured using conventional fluorescence (reported precision ± 1.0 ppbv) and UV absorption monitors (reported precision ± 4.5 ppbv), respectively; alkene abundance was determined via FTIR spectroscopy. Experiments were performed in the dark (i.e. with the chamber housing closed; \(j(\text{NO}_2) \leq 10^{-6}\) s\(^{-1}\)), at atmospheric pressure (ca. 1000 mbar) and temperatures between 287 and 302 K. The chamber is fitted with large horizontal and vertical fans to ensure rapid mixing (ca. 2 minutes). Chamber dilution was monitored via the first order decay of an aliquot of SF\(_6\), added prior to each experiment. Cyclohexane (ca. 75 ppmv) was added at the beginning of each experiment to act as an OH scavenger, such that SO\(_2\) reaction with OH was calculated to be ≤ 1% of the total chemical SO\(_2\) removal in all experiments.
Experimental procedure, starting with the chamber filled with clean scrubbed air, comprised addition of SF₆ and cyclohexane, followed by water vapour, O₃ (ca. 500 ppbv) and SO₂ (ca. 50 ppbv). A gap of five minutes was left prior to addition of the monoterpene, to allow complete mixing. The reaction was then initiated by addition of the monoterpene (ca. 400 ppbv for α-pinene and β-pinene, ca. 200 ppbv for limonene), and reagent concentrations followed for roughly 30 - 60 minutes; ca. 30 – 90 % of the monoterpene was consumed after this time, dependent on the reaction rate with ozone. Four α-pinene + O₃, five β-pinene + O₃, and five limonene + O₃ experiments, as a function of [H₂O], were performed in total. Each individual run was performed at a constant humidity, with humidity varied to cover the range of [H₂O] = 0.1 – 19 × 10¹⁶ molecules cm⁻³, corresponding to an RH range of 0.1 – 28 % (at 298 K).

Measured increases in [SO₂] agreed with measured volumetric additions across the SO₂ and humidity ranges used in the experiments (Newland et al., 2015a).

2.2 Analysis
A range of different SCI are produced from the ozonolysis of each of the three monoterpenes (see Schemes 2 – 4), each with their own distinct chemical behaviour (i.e. yields, reaction rates); it is therefore not feasible (from these experiments) to obtain data for each SCI independently; consequently, for analytical purposes we necessarily treat the SCI population in a simplified (lumped) manner – see Section 2.2.2.

SCI are assumed to be formed in the ozonolysis reaction with a yield φ (Reaction R1). They can then react with SO₂, with H₂O, with acids formed in the ozonolysis reaction, with other species present, or undergo unimolecular decomposition, under the experimental conditions applied (Reactions R2 – R5). A fraction of the SCI produced reacts with SO₂. This fraction (f) is the loss rate of the SCI to SO₂ (k₂[SO₂]) compared to the sum of the total loss processes for the SCI (Equation E1):

\[ f = \frac{k_2[SO_2]}{k_3[SO_2] + k_4[H_2O] + k_5[acid] + L} \]  

(E1)

Here, L accounts for the sum of any other chemical loss processes for SCI in the chamber, with the exception of reaction with acids these loss processes are expected to be negligible, as discussed later. After correction for dilution, and neglecting other (non-alkene) chemical sinks for O₃, such as reaction with HO₂ (also produced directly during alkene ozonolysis (Alam et
al., 2013; Malkin et al., 2010)), which was indicated through model calculations to account for < 0.5 % of ozone loss under all the experimental conditions, the following equation is derived:

\[
\frac{d\text{SO}_2}{d\text{O}_3} = \phi_f
\]  

(E2)

From Equation E2, regression of the loss of ozone (\(d\text{O}_3\)) against the loss of SO\(_2\) (\(d\text{SO}_2\)) for an experiment at a given RH determines the product \(\phi_f\) at a given point in time. This quantity will vary through the experiment as SO\(_2\) is consumed, and other potential SCI co-reactants are produced, as predicted by Equation E1. A smoothed fit was applied to the experimental data for the cumulative consumption of SO\(_2\) and O\(_3\), \(\Delta\text{SO}_2\) and \(\Delta\text{O}_3\), (as shown in Figure 2) to determine \(\frac{d\text{SO}_2}{d\text{O}_3}\) (and hence \(\phi_f\)) at the start of each experiment, for use in Equation E2. The start of each experiment (i.e. when \([\text{SO}_2]\) ~ 50 ppbv) was used as this corresponds to the greatest rate of production of the SCI, and hence largest experimental signals (i.e. greatest O\(_3\) and SO\(_2\) rate of change; greatest precision) and is the point at which the SCI + SO\(_2\) reaction has the greatest magnitude compared with any other potential loss processes for either reactant species (see discussion below).

Other potential fates for SCIs include reaction with ozone (Kjaergaard et al., 2013; Vereecken et al., 2014; Wei et al., 2014; Vereecken et al., 2015; Chang et al., 2018), with other SCI (Su et al., 2014; Vereecken et al., 2014), carbonyl products (Taatjes et al., 2012), acids (Welz et al., 2014), or with the parent alkene (Vereecken et al., 2014; Decker et al., 2017). Sensitivity analyses using the most recent theoretical predictions (Vereecken et al., 2015) indicate that the reaction with ozone is not significant under any of our experimental, accounting for less than 1.5% of SCI loss for anti-SCI (based on anti-\(\text{CH}_3\text{CHOO}\)) at the lowest RH (worst case) experiment. Generally, SCI loss to ozone is calculated to be < 1% for all SCI. Summed losses from reaction with SCI (self-reaction), carbonyls and alkenes are likewise calculated to account for < 1 % of the total SCI loss under the experimental conditions applied.

CH\(_2\text{OO}\) and CH\(_3\text{CHOO}\) have been shown to react rapidly (\(k = 1 - 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\)) with formic and acetic acid (Welz et al., 2014). In ozonolysis experiments, Sipilä et al. (2014) determined the relative reaction rate of acetic and formic acids with (\(\text{CH}_3\text{c})\text{COO}\) (i.e. \(k_3/k_2\)) to be roughly three. Organic acid mixing ratios in this work, as measured by FTIR, reached up to a few hundreds of ppbv, suggesting these will likely be a significant SCI sink in our experiments. We have therefore explicitly included reaction with organic acids in our analysis, incorporating the
uncertainty arising from the (unknown) acid reaction rate constant, as described in Section 2.2.1.

The water dimer reactions of non-CH$_3$OO SCI are not considered in our analysis. The effect of the water dimer reaction with C$_4$H and C$_3$H SCI (rather than the monomer) is expected to be minor at the maximum [H$_2$O] (2 \times 10^{17} \text{ cm}^{-3}) used in these experiments (< 30 % RH). Further, with analogy to the syn/anti-CH$_3$CHOO system, for syn-SCI loss to the dimer (and monomer) will not become competitive at the highest [H$_2$O] used here; for anti-SCI, the water monomer will already be removing the majority of the SCI at the [H$_2$O] at which the dimer would become a significant loss process, hence the dimer reaction is deemed unimportant. For CH$_3$OO, the reaction rates with water and the water dimer have been quantified in recent EUPHORE experimental studies, and the values from Newland et al. (2015a) are used in our analysis.

2.2.1 Derivation of $k$(SCI+H$_2$O)/$k$(SCI+SO$_2$) and $k_d$/k(SCI+SO$_2$)

As noted above, a range of different SCI are produced from the ozonolysis of the three monoterpenes (see Schemes 2 – 4), each with their own distinct chemical behaviour, which treated individually, introduce too many unknowns (i.e. yields, reaction rates) for explicit analysis. Consequently for analytical purposes we treat the SCI population in a simplified (lumped) manner:

Firstly, we use the simplest model possible, assuming that a single SCI is formed in each ozonolysis reaction (Equation E3).

$$f = \left( \frac{[\text{SO}_2]}{[\text{SO}_2]} \right) = \left( \frac{k_3}{k_2} \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]} + \frac{k_2}{k_2} + \frac{k_5}{k_2} [\text{acid}] \right)^4$$

(E3)

In a second model, for each monoterpenene, the SCI produced are assumed to belong to one of two populations, denoted SCI-A and SCI-B. These two populations are split according to the observation that the decomposition rates and reaction rates with water for the smaller SCI (CH$_3$CHOO) have been predicted theoretically (Ryzhkov and Ariya, 2004; Kuwata et al., 2010; Anglada et al., 2011) and shown experimentally (Taatjes et al., 2013; Sheps et al., 2014; Newland et al., 2015a) to exhibit a strong dependence on the structure of the molecule. The syn-CH$_3$CHOO conformer, which has the terminal oxygen of the carbonyl oxide moiety in the syn position to the methyl group, has been shown to react very slowly with water and to readily decompose, via the hydroperoxide mechanism; whereas the anti-CH$_3$CHOO conformer, with
the terminal oxygen of the carbonyl oxide moiety in the anti-position to the methyl group, has
been shown to react fast with water and is not able to decompose via the hydroperoxide
mechanism. Vereecken and Francisco (2012) have shown that all SCI studied theoretically with
an alkyl group in the syn position have reaction rates with H2O of $k < 4 \times 10^{-17}$ molecule cm$^{-3}$ s$^{-1}$ (and for SCI larger than acetone oxide, $k < 8 \times 10^{-18}$ molecule cm$^{-3}$ s$^{-1}$).

We thus define two populations, assuming SCI-A (i.e. SCI that exhibit chemical properties of
the anti-type SCI) to react fast with water and not to undergo unimolecular reactions, and SCI-B (i.e. SCI that exhibit chemical properties of the syn type SCI) to not react with water but to
undergo unimolecular reactions. This simplification allows us to fit to the measurements using
Equations E4 and E5, as shown below. The total SCI yields are determined by our experiments
at high SO$_2$, and the relative yields of SCI-A and SCI-B are determined from fitting to Equation
E5. These relative yields are then compared to those predicted from the literature.

In this model, $f = \gamma_A^f + \gamma_B^f$, where $\gamma$ is the fraction of the total SCI yield (i.e. $\gamma_A + \gamma_B = 1$), $f^A$ and $f^B$ are the fractional losses of SCI-A and SCI-B to reaction with SO$_2$. Adapting Equation
E1 to include the two SCI species gives Equation E4, where $k_{acid}$ accounts for the SCI +
acid reaction (see discussion of reaction rate constants below).

$$f = \frac{\gamma_A k_A^f [SO_2]}{k_A^f [SO_2] + k_3 [H_2O] + k_5^A [acid]} + \frac{\gamma_B k_B^f [SO_2]}{k_B^f [SO_2] + k_d + k_5^B [acid]} \quad \text{(E4)}$$

Equation E4 can be rearranged to Equation E5 and fitted according to $f/[SO_2]$ derived from the
measurements.

$$\frac{f}{[SO_2]} = \frac{\gamma_A}{k_2^A + k_3^A [H_2O] + k_5^A [acid]} + \frac{\gamma_B}{k_2^B + k_5^B [acid]} \quad \text{(E5)}$$

Using values for $\gamma_A$ and $\gamma_B$ from the literature and varying the assumed values of the reaction of
SCI with acid ($k_5$) allows us to determine $k_3/k_2^A$ and $k_5/k_2^B$.

The assumptions made here allow analysis of a very complex system. However, a key
consequence is that the relative rate constants obtained from the analysis presented here are not
representative of the elementary reactions of any single specific SCI isomer formed, but rather
represent a quantitative ensemble description of the integrated system, under atmospheric
boundary layer conditions, which may be appropriate for atmospheric modelling. Additionally
our experimental approach cannot determine absolute rate constants (i.e. values of $k_2, k_3, k_d$ in isolation, but is limited to assessing their relative values, measured under atmospheric conditions, which may be placed on an absolute basis through use of an external reference value (here the SCI + SO$_2$ rate constant).

2.2.2 SCI yield calculation

The value for the total SCI yield of each monoterpene, $\phi_{SCI-TOT}$, was determined from an experiment performed under dry conditions (RH < 1%) in the presence of excess SO$_2$ (ca. 1000 ppbv), such that SO$_2$ scavenged the majority of the SCI. From Equation E2, regressing $d$SO$_2$ against $d$O$_3$ (corrected for chamber dilution), assuming $f$ to be unity (i.e. all the SCI produced reacts with SO$_2$), determines the value of $\phi_{min}$, a lower limit to the SCI yield. Figure 1 shows the experimental data, from which $\phi_{min}$ was derived.

In reality $f$ will be less than one, at experimentally accessible SO$_2$ levels, as a fraction of the SCI may still react with trace H$_2$O present, or undergo unimolecular reaction. The actual yield, $\phi_{SCI}$, was determined by combining the result from the excess-SO$_2$ experiment with those from the series of experiments performed at lower SO$_2$, as a function of [H$_2$O], to obtain $k_d/k_2$ and $k_3/k_2$ (see Section 2.2.1), through an iterative process to determine the single unique value of $\phi_{SCI}$ which fits both datasets, as described in Newland et al. (2015a), but taking into account the proposed model in this paper of there being two SCI produced. In this model, $f = \gamma_A^f + \gamma_B^f$. Where $\gamma^f_A = [SO_2] / ([SO_2] + k_3[H_2O]/k_2)$ and $\gamma^f_B = [SO_2] / ([SO_2] + k_d/k_2)$ – other possible SCI sinks are assumed to be negligible. In these excess-SO$_2$ experiments, $f_A \approx 1$ but $f_B < 1$ since $k_d$ still represents a significant sink.

$\gamma$ (and hence $\gamma^f_H$, since $\gamma^f_H = 1 - \gamma^f_A$) is derived from fitting Equation E4 to the data from the experiments performed at lower SO$_2$ for a given $\phi$. Using a range of $\phi$, gives a range of $\gamma$. These different values of $\gamma$ are used with the respective values of $\phi$ in fitting to Equation E4 to determine values of $k_d/k_2$ and $k_3/k_2$.

2.2.3 Experimental uncertainties

The uncertainty in $k_d/k_2$ was calculated by combining the mean relative errors from the precision associated with the SO$_2$ and ozone measurements (given in Section 2.1) with the 2$\sigma$ error and the relative error in $\phi$, using the root of the sum of the squares of these four sources of error.

The uncertainty in $k_3/k_2$ was calculated in the same way.
The uncertainty in $\phi_{\text{min}}$ was calculated by combining the uncertainty in $\Delta S \text{O}_2$ and $\Delta S \text{O}_3$, as above.

The uncertainty in $\phi$ was calculated by applying the $k_3/k_2$ uncertainties and combining these with the uncertainties in $\phi_{\text{min}}$, using the root of the sum of the squares.

3 Theoretical calculations

The rovibrational characteristics of all conformers of the CI formed from $\alpha$-pinene and $\beta$-pinene, the transition states for their unimolecular reaction, and for their reaction with $\text{H}_2\text{O}$, were characterized quantum chemically, first using the M06-2X/cc-pVDZ level of theory, and subsequently refined at the M06-2X/aug-cc-pVTZ level. To obtain the most accurate barrier heights for reaction, it has been shown (Berndt et al., 2015; Chhantyal-Pun et al., 2017; Fang et al., 2016a, 2016b; Long et al., 2016; Nguyen et al., 2015) that post-CCSD(T) calculations are necessary. Performing such calculations for the SCI discussed in this paper, with up to 14 non-hydrogen atoms, is well outside our computational resources. Instead, we base our predictions on high-level CCSD(T)/aug-cc-pVTZ single point energy calculations, performed for the reactions of nopinone oxides and the most relevant subset of pinonaldehyde oxides. These data are reliable for relative rate estimates, but it remains useful to further improve the absolute barrier height predictions, as described by Vereecken et al. (2017) based on a data set with a large number of systematic calculations on smaller CI, allowing empirical corrections to estimate the post-CCSD(T) barrier heights. Briefly, they compare rate coefficient calculations against available harmonized experimental and very-high level theoretical kinetic rate predictions, and adjusts the barrier heights by 0.4 to 2.6 kcal mol$^{-1}$ (depending on the base methodology and the reaction type) to obtain best agreement with these benchmark results.

Using the energetic and rovibrational data thus obtained, multi-conformer transition state theory (MC-TST) calculations (Truhlar et al., 1996; Vereecken and Peeters, 2003) were performed to obtain the rate coefficient at 298K at the high pressure limit. All rate predictions incorporate tunnelling corrections using an asymmetric Eckart barrier (Eckart, 1930; Johnston and Heicklen, 1962). For the reaction of CI + $\text{H}_2\text{O}$, a pre-reactive complex is postulated at 7 kcal mol$^{-1}$ below the free reactants, while the CI + (H$_2$O) reaction is taken to have a pre-reactive complex of 11 kcal mol$^{-1}$ stability. This pre-reactive complex affects tunnelling corrections; it is assumed that this pre-reactive complex is always in equilibrium with the free reactants.
In view of the high number of rotamers and the resulting computational cost, only a single
limonene-derived CI isomer was studied, where the TS for the CI + H2O reaction was analyzed
at the M06-2X/cc-pVDZ level of theory with only a partial conformational analysis; a limited
number of the energetically most stable TS conformers thus discovered were re-optimized at
the M06-2X/aug-cc-pVTZ level of theory. These data will only be used for qualitative
assessments. However, we apply the structure-activity relationships (SARs) presented by
Vereecken et al. (Vereecken et al., 2017) to obtain an estimate of the rate coefficients, and
assess the role of the individual SCI isomers in limonene ozonolysis.

All quantum chemical calculations were performed using Gaussian-09 (Frisch et al., 2010).

4 GEOS-Chem Model Simulation

The global chemical transport model GEOS-Chem (v9-02, www.geos-chem.org, Bey et al.,
2002) is used to explore the spatial and temporal variability of the atmospheric impacts of the
experimentally derived chemistry. The model includes HOx-NOx-VOC-O3-BrOx chemistry
(Mao et al., 2010; Parrella et al., 2012) and a mass-based aerosol scheme. Biogenic
monoterpene emissions are taken from the Model of Emissions of Gases and Aerosols from
Nature (MEGAN) v2.1 inventory (Guenther et al., 2006; 2012). Transport is driven by
assimilated meteorology (GEOS-5) from NASA's Global Modelling and Assimilation Office
(GMAO). The model is run at 4°×5° resolution, with the second year (2005) used for analysis
and first year discarded as spin up.

In this study, the standard simulation was expanded to include emissions of seven monoterpene
species (α-pinene, β-pinene, limonene, myrcene, ocimene, carene, and sabinene) from MEGAN
v2.1. The ozonolysis scheme for each monoterpene, detailed in Section 7.1, considers the
formation of one or two types of SCI, and their subsequent reaction with SO2, H2O, or
unimolecular decomposition. The reaction rates of the monoterpenes with OH, O3 and NO3 are
detailed in Table S1.
5 Experimental Results

5.1 SCI Yield

Figure 1 shows the lower limit to the SCI yield, \( \phi_{\text{min}} \), for the three monoterpenes, determined from fitting Equation E5 to the experimental data. This gives values of 0.16 (± 0.01) for \( \alpha \)-pinene, 0.53 (± 0.01) for \( \beta \)-pinene and 0.20 (± 0.01) for limonene. These \( \phi_{\text{min}} \) values were then corrected as described in Section 2.2 using the \( k_3/k_2 \) and \( k_d/k_2 \) values determined from the measurements shown in Figures 3 – 5 using Equation E4. The corrected yields, \( \phi_{\text{SCI}} \), are 0.19 (± 0.01) for \( \alpha \)-pinene, 0.60 (± 0.03) for \( \beta \)-pinene and 0.23 (± 0.01) for limonene. Uncertainties are ± 2\( \sigma \), and represent the combined systematic (estimated measurement uncertainty) and precision components. Literature yields for SCI production from monoterpene ozonolysis are summarised in Table 1.

The value derived for the total SCI yield from \( \alpha \)-pinene in this work of 0.19 agrees, within the uncertainties, with the value of 0.15 (± 0.07) reported by Sipilä et al. (2014) and the value of 0.20 applied in the MCMv3.3.1.

The total SCI yield from \( \beta \)-pinene derived in this work, 0.60, agrees reasonably well with the recent experimental work of Ahrens et al. (2014) who derived a total SCI yield of 0.50 (0.40 for the sum of CI-1 and CI-2 and 0.10 for CH\(_2\)OO, which is assumed to be formed almost completely stabilised). The MCMv3.3.1 applies a total SCI yield of 0.25, of which 0.10 is a C9-CI and 0.15 is CH\(_2\)OO. Earlier studies also tended to derive lower total SCI yields ranging from 0.25 – 0.27 (Hasson et al., 2001; Hatakeyama et al., 1984).

The total SCI yield from limonene derived in this work, 0.23 (± 0.01) agrees with the recently determined yield from Sipilä et al. (2014) of 0.27 (± 0.12). Leungsakul et al. (2005) derived a somewhat higher yield of 0.34, while the MCMv3.3.1 applies a lower yield of 0.135.

5.2 \( k_d(\text{SCI}+\text{H}_2\text{O})/k_d(\text{SCI}+\text{SO}_2) \) and \( k_d/k_d(\text{SCI}+\text{SO}_2) \) Analysis

Figure 2 shows the loss of SO\(_2\) as ozone is consumed by reaction with the monoterpene for each of the three systems. Box modelling results suggest that > 99 % of this SO\(_2\) removal is caused by reaction with SCI produced in the alkene-ozone reaction (rather than e.g. reaction with OH, which is scavenged by cyclohexane). When the experiments are repeated at higher relative humidity, the rate of loss of SO\(_2\) decreases. This is as expected from Equation E1 and suggests
that there is competition between SO$_2$ and H$_2$O for reaction with the SCI produced, in agreement with observations of smaller SCI, which demonstrate the same competition under atmospherically relevant conditions (Newland et al., 2015a; Newland et al., 2015b).

However, as the relative humidity is increased further, the SO$_2$ loss does not fall to (near) zero as would be expected from Equation E1. This suggests that at high [H$_2$O] the amount of SO$_2$ loss becomes less sensitive to [H$_2$O]. This is most likely due to there being at least two chemically distinct SCI species present. This behaviour was previously observed for CH$_3$CHOO by Newland et al. (2015a) and fits with the current understanding that the reactivity of SCI is structure dependent.

To recap Section 2.2.1, the analysis presented here considers two models to fit the observations. The first of these (Equation E3) assumes the formation of a single SCI species, which, in addition to reacting with SO$_2$, can react with water, undergo unimolecular reaction or react with acid. It is clearly evident from Figures 3 – 5 that this model does not give a good fit to the observations for any of the monoterpane systems studied. Therefore, the results from this (single SCI) approach are not discussed explicitly hereafter. The second of the models (Equation E5) assumes the formation of two lumped, chemically distinct, populations of SCI, denoted SCI-A and SCI-B. SCI-A is assumed to react fast with H$_2$O and to have minimal decomposition. Conversely, SCI-B is assumed to have a negligible reaction with water under the experimental conditions applied but to undergo rearrangement via a VHP. We use a least-squares fit of Equation E5 to the data to determine the values of $k_3/k_2$ and $k_d/k_2$. This approach fits the data well (Figures 3 - 5) for all 3 monoterpene and represents the overall attributes of the SCI formed - but as noted, does not represent an explicit determination of individual conformer-dependent rate constants.

5.2.1 α-pinene

The α-pinene system is sensitive to water vapour at the low H$_2$O range, with the SO$_2$ loss falling dramatically when the RH is increased from 0.1 to 2.5 % (Figure 2). However, at higher RH the SO$_2$ loss appears to be rather insensitive to [H$_2$O].

CI-1 can be formed in either a syn (1a) or anti (1b) configuration, whereas both CI-2 conformers formed are in a syn configuration (see Scheme 2). For one of the two conformers of CI-2 (CI-2b), the hydrogen atom available for abstraction by the terminal oxygen of the carbonyl oxide group is attached to the carbon on the four-membered ring. This has been shown in the β-pinene
system to make a large difference with respect to the ability of the hydrogen to be abstracted and to undergo the VHP mechanism (Rickard et al., 1999; Nguyen et al., 2009). This therefore suggests that CI-2b may exhibit characteristics of both SCI-A and SCI-B. Ma et al. (2008) infer a probable equal yield of the two basic CI structures. This would suggest a relative yield for SCI-A of 0.25 – 0.50 (depending on the precise nature of CI-2b). Fitting Equation E4 to the data and allowing lambda to vary determines values of \( \gamma^A = 0.40 \) and \( \gamma^B = 0.60 \) (Figure 3).

In Figure 3, Equation E4 is fitted to the \( \alpha \)-pinene measurements, assuming \( k(\text{SCI+acid})/k(\text{SCI+SO}_2) = 0 \). This derives a minimum value for \( k(\text{SCI-A+H}_2\text{O})/k(\text{SCI-A+SO}_2) \), the water dependent fraction of the SCI, and a maximum value for \( k(\text{decomposition:SCI-B})/k(\text{SCI-B+SO}_2) \), the water independent fraction of the SCI. The kinetic parameters derived from the fitting are displayed in Table 2.

Figure 6 shows the variation of the derived \( k_3/k_2 \) and \( k_2/k_2 \) values as the ratio \( k_3/k_2 \), \( k(\text{SCI+acid})/k(\text{SCI+SO}_2) \), is varied from zero to one. The derived \( k_3/k_2 \) increases by about 40\% from 1.4 (± 0.34) \( \times 10^{-3} \) to 2.0 (± 0.49) \( \times 10^{-3} \). The derived \( k_2/k_2 \) value decreases, again by about 40\%, from 8.2 (± 1.5) \( \times 10^{12} \text{ cm}^{-3} \) to 5.1 (± 0.93) \( \times 10^{12} \text{ cm}^{-3} \).

The derived limits to the relative rate constants can be put on an absolute scale using the \( k(\text{SCI+SO}_2) \) values for \( \text{CH}_3\text{CHOO} \) from Sheps et al. (2014) for the \( \text{syn} \) and \( \text{anti} \) conformers. These are, \( \text{syn} \): 2.9 \( \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \) and \( \text{anti} \): 2.2 \( \times 10^{-10} \text{ cm}^{-3} \text{ s}^{-1} \). The \( \text{syn} \) rate constant is applied to the derived \( k(\text{decomposition:SCI-B})/k(\text{SCI-B+SO}_2) \) value and the \( \text{anti} \) rate constant to the \( k(\text{SCI-A+H}_2\text{O})/k(\text{SCI-A+SO}_2) \) value. It should be noted that the \( k_2 \) values are for quite different SCI to those formed in this study and to our knowledge no structure specific \( k(\text{SCI+SO}_2) \) have been reported for monoterpane derived SCI, though Ahrens et al. (2014) determine an average \( k_2 \) of 4 \( \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \) for SCI derived from \( \beta \)-pinene, i.e. a value within an order of magnitude of those determined for the smaller SCI \( \text{CH}_3\text{OO}, \text{CH}_3\text{CHOO} \) and \( (\text{CH}_3)_2\text{COO} \) (e.g. Welz et al., 2012; Taatjes et al., 2013; Sheps et al., 2014; Huang et al., 2015). Using the Sheps et al. (2014) values yields \( k(\text{SCI-A+H}_2\text{O}) > 3.1 (± 0.75) \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1} \) and \( k(\text{decomposition:SCI-B}) < 240 (± 44) \text{ s}^{-1} \) (using the values derived for \( k(\text{SCI-A+acid})/k(\text{SCI-A+SO}_2) = 0 \). This \( k_2 \) value is an order of magnitude larger than the rate constants determined for the smaller \( \text{anti} \)-\( \text{CH}_3\text{CHOO} \) in the direct studies of Sheps et al. (2014) (2.4 \( \times 10^{-14} \text{ cm}^{-3} \text{ s}^{-1} \)) and Taatjes et al. (2013) (1.0 \( \times 10^{-14} \text{ cm}^{-3} \text{ s}^{-1} \)). The decomposition value derived for SCI-B is of the same order of magnitude as that for \( \text{syn}-\text{CH}_3\text{CHOO} \) (348 ± 332 s\(^{-1}\)) and \( (\text{CH}_3)_2\text{COO} \) (819 ± 190 s\(^{-1}\)) from Newland et al., (2015a) (using updated direct measurement values of \( k_2 \) from Sheps et al. (2014) and Huang et
al. (2015) for syn-CH$_3$CHO and (CH$_3$)$_2$COO respectively and within the range from the recent paper by Smith et al. (2016) which derives a decomposition rate for (CH$_3$)$_2$COO of 269 (± 82) s$^{-1}$ at 283 K increasing to 916 (± 56) s$^{-1}$ at 323 K. Sipilä et al. (2014) applied a single-SCI analysis approach to the formation of H$_2$SO$_4$ from SO$_2$ oxidation in the presence of the α-pinene ozonolysis system. They determined that for α-pinene, $k_d >> k$(SCI+H$_2$O)[H$_2$O] for [H$_2$O] < 2.9 × 10$^{17}$ cm$^{-3}$, i.e. that the fate of SCI formed in the system is rather insensitive to [H$_2$O]. Across the [SO$_2$] and RH ranges used in their study, the results obtained here would indicate H$_2$O to always be the dominant sink for SCI-A, i.e. the fact that Sipilä et al. (2014) see similar H$_2$SO$_4$ production across the RH range in their study is consistent with these results.

5.2.2 β-pinene

Two recent studies (Nguyen et al., 2009; Ahrens et al., 2014) have suggested yields of the two C$_9$-CI (CI-3 and CI-4, see Scheme 3) obtained from β-pinene ozonolysis to be roughly equal. In these studies Ahrens et al. (2014) assume a CH$_2$OO yield of 0.10 while Nguyen et al. (2009) determine theoretically the yield of CH$_2$OO to be 0.05. Another theoretical study (Zhang and Zhang, 2005) predicted a CH$_2$OO yield of 0.08. In experimental studies, Winterhalter et al. (2000) determined the CH$_2$OO yield to be 0.16 (± 0.04) from measuring the nopinone yield and assuming it to be entirely a primary ozonolysis product (i.e. the co-product of CH$_2$OO formation) and Ma and Marston (2008) determine a summed contribution of 84 % (± 0.03) for the two C$_9$-CI (i.e. a 16 % CH$_2$OO yield). The theoretical studies are somewhat lower than the experimental but Nguyen et al. (2009) note that CI-4 is likely to form additional nopinone in bimolecular reactions. The CH$_2$OO is assumed to all be formed stabilised (e.g. Nguyen et al. 2009).

SCI-3 is expected to undergo unimolecular reactions at least an order of magnitude faster than SCI-4 (Nguyen et al., 2009; Ahrens et al., 2014). The reaction of SCI-3 with water is expected to be slow based on the calculations presented in Table 4, with a pseudo first order reaction rate of 0.3 s$^{-1}$ at the highest [H$_2$O] used here, 2 × 10$^{17}$ cm$^{-3}$, 298 K, whereas the water reaction with SCI-4 is expected to be considerably faster with a pseudo first order reaction rate of 85 s$^{-1}$ at [H$_2$O] = 2 × 10$^{17}$ cm$^{-3}$, 298 K. This reaction would thus be expected to be competitive with reaction with SO$_2$ for SCI-4 under the experimental conditions employed. This is in agreement with...
with the observations of Ma and Marston (2008), which show a clear dependence of nopinone formation on RH (presumed to be formed from SCI + H₂O). Fitting Equation E4 to the data determines values of \( \gamma^A = 0.41 \) and \( \gamma^B = 0.59 \) (Figure 4).

Using these values, and assuming \( k(SCI+\text{acid})/k(SCI+SO_2) = 0 \), yields a \( k(SCI-A+H_2O)/k(SCI-A+SO_2) \) value of > 1.0 \((\pm 0.27) \times 10^{-4}\) and a \( k(\text{decomposition:SCI-B})/k(SCI-B+SO_2) \) value of < 6.0 \((\pm 1.3) \times 10^{-12}\) cm³ (Figure 4).

As shown in Figure 6, increasing \( k_5/k_2 \), \( k(SCI+\text{acid})/k(SCI+SO_2) \), from zero to one, decreases the derived \( k_5/k_2 \) from 6.0 \((\pm 1.3) \times 10^{-12}\) cm³ to 1.8 \((\pm 0.39) \times 10^{-12}\) cm³. The derived \( k_5/k_2 \) increases by a factor of four from 1.0 \((\pm 0.27) \times 10^{-4}\) to 3.7 \((\pm 1.0) \times 10^{-4}\).

These values can be put on an absolute scale (using the values derived above for \( k_5/k_2 = 0 \)). For SCI-A, \( k(SCI+SO_2) \) is taken as the experimentally determined value of \( 4 \times 10^{-11}\) cm³ s⁻¹ from Ahrens et al. (2014). For SCI-B, the syn-\( CH_3CHOO k(SCI+SO_2) \) value determined by Sheps et al. (2014) is used. This gives values of \( k(SCI-A+H_2O) > 4 \times 10^{-15}\) \((\pm 1)\) cm³ s⁻¹ and \( k(\text{decomposition:SCI-B}) < 170 \((\pm 38)\) s⁻¹.

### 5.2.3 Limonene

For the limonene measurements presented in Figure 2, \((dSO_2/dO_3)/dt\) appears to be non-linear, with a jump in \( dSO_2/dO_3 \) between 120 and 150 ppbv of ozone consumed. This is most evident in the two lowest RH runs (0.2 and 2.0 %). Limonene is the fastest reacting of the systems presented here, with the alkene reaction having consumed 100 ppbv of ozone within the first five minutes. The limonene sample required about five minutes of heating before the entire sample was volatized and injected into the chamber. This therefore may account for the apparent non-linear nature of \( dSO_2/dO_3 \) in Figure 2.

The SO₂ loss in the limonene-ozone system is less affected by increasing H₂O than for either α or β-pinene (Figure 5), with the values of \( f/\text{[SO}_2\text{]} \) (y-axis) varying by roughly a factor of two over the RH range applied compared to more than a factor of three variation for the other two systems. Hence it might be expected that there is little formation of H₂O dependent SCI or that it has a rather slow reaction rate with water.

Fitting Equation E4 to the data determines values of \( \gamma^A = 0.22 \) and \( \gamma^B = 0.78 \) (Figure 5). This is broadly in line with the ratio recommended in the MCMv3.3.1 of 0.27:0.73, and with that proposed in Leungsakul et al. (2005) who use a CI-A:CI-B ratio of 0.35:0.65, but also include some stabilisation of CH₂OO and C₉-CI from ozone reaction at the exo-cyclic bond. This yields
a \( k(\text{SCI}-\text{A}+\text{H}_2\text{O})/k(\text{SCI}-\text{A}+\text{SO}_2) \) value of \(< 3.5 \times 10^{-3} \) and a \( k(\text{decomposition}:\text{SCI-B})/k(\text{SCI-B}+\text{SO}_2) \) value of \(> 4.5 \times 10^{-12} \) cm\(^3\) s\(^{-1}\).

Figure 6 shows that the derived \( k_3/k_2 \) increases by about 7 % as \( k(\text{SCI+acid})/k(\text{SCI+SO}_2) \) ranges from 0.0 to 0.8. The derived \( k_3/k_2 \) becomes negative at \( k(\text{SCI+acid})/k(\text{SCI+SO}_2) > 0.8 \), putting an upper limit on this ratio, i.e. \( k_3/k_2 < 0.8 \), for the limonene system.

Putting these values on an absolute scale (using the values derived for \( k_3/k_2 = 0 \), using the CH\(_3\)CHOO syn and anti \( k(\text{SCI+SO}_2) \) determined by Sheps et al. (2014), yields values of \(< 7.7 \times 10^{-15} \) cm\(^3\) s\(^{-1}\) and \(> 130 \pm 3 \) s\(^{-1}\) for \( k_3 \) and \( k_2 \) respectively. These values are similar to those derived for the SCI-A and SCI-B formed from \( \beta \)-pinene. The \( k_1 \) value is a factor of three smaller than that determined by Sheps et al. (2014) for \( k(\text{anti-CH}_3\text{CHOO}+\text{H}_2\text{O}) \), \( 2.4 \times 10^{-14} \) cm\(^3\) s\(^{-1}\).

Sipilä et al. (2014) applied a single-SCI analysis approach to the formation of \( \text{H}_2\text{SO}_4 \) from \( \text{SO}_2 \) oxidation by the limonene ozonolysis system and determined that, similarly to \( \alpha \)-pinene, \( k(\text{decomp.}) >> k(\text{SCI+H}_2\text{O}|\text{H}_2\text{O}) \) for \( [\text{H}_2\text{O}] < 2.9 \times 10^{17} \) cm\(^{-3}\), i.e. that the system is rather insensitive to \( \text{H}_2\text{O} \). Our data are consistent with the limonene system being less sensitive to \( \text{H}_2\text{O} \) than the SCI populations derived from the other two monoterpenes reported here.

5.2.4 Experimental Summary

The reaction rates of SCI-A (i.e. SCI that exhibit chemical properties of the anti-type SCI) derived from the three different monoterpenes with water range from \(< 0.8 \) to \(> 31 \times 10^{-14} \) cm\(^3\) s\(^{-1}\), broadly in line with the derived rates of Sheps et al. (2014) for \( \text{anti-CH}_3\text{CHOO of } 2.4 \times 10^{-14} \) cm\(^3\) s\(^{-1}\). The decomposition rates of SCI-B (i.e. SCI that exhibit chemical properties of the syn-type SCI) are on the order of 100 - 250 s\(^{-1}\). This is in line with those derived for syn-CH\(_3\)CHOO from cis and trans-but-2-ene ozonolysis and (CH\(_3\))\(_2\)COO by Newland et al. (2015a) of \(3.48 \pm 3.32 \) s\(^{-1}\) and \(819 \pm 190 \) s\(^{-1}\) respectively (assuming \( k(\text{syn-CH}_3\text{CHOO}+\text{SO}_2) = 2.9 \times 10^{-11} \) cm\(^3\) s\(^{-1}\) (Sheps et al., 2014) and \( k((\text{CH}_3)\text{COO}+\text{SO}_2) = 2.9 \times 10^{-10} \) cm\(^3\) s\(^{-1}\) (Huang et al., 2015)) and recent results from Smith et al. (2016) of 269 – 916 s\(^{-1}\) (strongly dependent on temperature) for (CH\(_3\))\(_2\)COO decomposition. In this work we only derive relative rates, but the similarity of the \( k_1 \) and \( k_2 \) values derived when the \( k_2 \) values for syn and anti-CH\(_3\)CHOO from Sheps et al. (2014) are applied is consistent with the recent work of Ahrens et al. (2014), suggesting that large SCI, derived from monoterpenes, demonstrate a similar reactivity towards \( \text{SO}_2 \) as smaller SCI. One uncertainty in the derivation of the kinetics presented herein is the.

Deleted: The removal of \( \text{SO}_2 \) in the presence of ozonolysis reactions of \( \alpha \)-pinene, \( \beta \)-pinene and limonene has been studied as a function of water vapour concentration, and analysed following the approximation that the SCI population can be represented through a two-species model, with contrasting unimolecular decomposition rates and reactivity to water. The results presented in this work suggest that all three monoterpenes studied produce range of SCI that have differing reactivities towards water and decomposition. This is in agreement with current theoretical understanding but is the first experimental demonstration for large SCI derived from monoterpenes ozonolysis. The complexity of the SCI system is further highlighted by the fact that the experimental data are not fitted well by the assumption of the formation of a single SCI species. While the behaviour of large SCI derived from monoterpenes are likely to be significantly more complicated than is accounted for by simply considering the differing kinetics of syn and anti SCI conformers, this approach provides a reasonable description of the experimental behaviour observed, and the results presented here are broadly in line with experimental results from the smaller SCI and from theoretical results.
6 Theoretical results and comparison to experiments

The theoretically predicted rate coefficients for unimolecular reactions of the monoterpene SCI are listed in Table 3, while those for the reaction with H₂O are listed in Table 4. These data can be compared against the experimental data obtained in this work.

6.1.1 α-pinene

The theory-based rate coefficients show one pinonaldehyde oxide, CI-1b, with a rate of reaction with water that is significantly faster than the remaining α-pinene-derived CI. Comparing this rate to the experimental data suggests that CI-1b corresponds to SCI-A, with matching rate coefficients within an order of magnitude, i.e. within the expected uncertainty. We thus deduce that SCI-A is CI-1b. The remaining pinonaldehyde oxides, CI-1a, CI-2a and CI-2b, react predominantly through unimolecular reactions, where theory-based rate coefficients range from 60 to 600 s⁻¹, all within a factor of 4 of the experimentally derived population-averaged rate of 240 ± 44 s⁻¹, i.e. matching within the uncertainty margins. The unimolecular rate coefficients of this set of CI are sufficiently close that it is not feasible to separate these in the experimental data, so we can only conclude that SCI-B in the α-pinene ozonolysis experiments may consist of a mixture of C-1a, CI-2a and CI-2b.

6.1.2 β-pinene

The theoretical analysis for nopinone oxides shows one isomer, SCI-4, that has a fast rate of reaction with water, but a slow unimolecular isomerisation, while the other isomer, SCI-3, shows a fast unimolecular decomposition. These can thus be unequivocally equated to the experimentally obtained SCI-A and SCI-B, respectively, inasmuch as the yield of CH₂OO is minor. The predicted rate coefficients are within the expected uncertainty intervals of the theoretical data, a factor of 5 for the unimolecular rates, and an order of magnitude for the reaction with H₂O.

The experimental rate measurements are defined relative to the reaction rate with SO₂; the value adopted for the k(SCI+SO₂) reaction therefore influences the derived rate coefficient values.
Ahrens et al. (2014) directly measured the SO$_2$ rate coefficient of the longest-lived SCI (SCI-4) to be $\sim 4 \times 10^{-11}$ cm$^3$ s$^{-1}$, but for SCI-3 we assume a similar rate coefficient as syn-CH$_3$CHOO + SO$_2$ determined by Sheps et al. (2014) of $2.9 \times 10^{-11}$ cm$^3$ s$^{-1}$. Nopinone oxides are bicyclic compounds, with a bulky dimethyl-substituted 4-membered ring adjacent to the carbonyl oxide moiety. To examine the potential impact of steric hindrance on the SCI + SO$_2$ reaction, we characterized all sulfur-substituted secondary ozonides (S-SOZ) formed in this reaction (Kuwata et al., 2015; Vereecken et al., 2012). We find that the tri-cyclic S-SOZ shows very little interaction between the sulfur-bearing ring and the $\beta$-pinene substituents, and little change in ring strain. The energies of the S-SOZ adducts relative to the SCI + SO$_2$ reactants thus remains very similar to that of CH$_2$OO, CH$_3$CHOO or (CH$_3$)$_2$COO, confirming the quality of our selection of reference rate coefficients.

6.1.3 Limonene

Of the six non-CH$_2$OO CI formed in limonene ozonolysis, CI-5b was predicted to have a fast reaction rate with H$_2$O; its oxide substitution patterns is similar to pinonaldehyde oxide CI-1b. The SAR-predicted rate coefficient of CI-5b + H$_2$O is within a factor of 2 of the experimentally derived $k_3$ value for SCI-A, such that we can equate SCI-A to CI-5b with confidence. The SCI-B set of Criegee intermediates then contains the summed population of the remaining five CI, all of which react slowly with H$_2$O. The SAR-predicted unimolecular decay rate coefficients range from 15 to 700 s$^{-1}$, all within a factor of 9 of the experimentally obtained $k_d = 130$ s$^{-1}$; it should be noted that for limonene-derived CI, no explicit theoretical calculations are available, and the SAR-predictions carry a somewhat larger uncertainty. We have performed an exhaustive characterisation of the conformers of CI-5b. The most stable conformers show an internal complex formation between the oxide moiety and the carbonyl group, similar to those characterized for the bimolecular reaction of CI with carbonyl compounds (Jalan et al., 2013; Wei et al., 2015). The theoretical study by Jiang et al. (2013) on limonene ozonolysis appears to have omitted internal rotation and cannot be compared directly. It seems likely that the limonene-derived CI can thus easily undergo internal SOZ formation, which is thought (Vereecken and Francisco, 2012) to be entropically unfavourable, but to have a low barrier to reaction. For $\alpha$-pinene, a similar internal complex formation and SOZ ring closure is not as favourable due to the geometric limitations enforced by the 4-membered ring.

A large number of transition state conformers for CI-5b + H$_2$O were characterized, though no exhaustive search was completed. The energetically most favourable structures show
interaction between the carbonyl group, and the H₂O co-reactant as it adds onto the carbonyl oxide moiety. Similar stabilising interactions between the carbonyl moiety and the carbonyl oxide moiety were reported recently in cyclohexene-derived CI (Berndt et al., 2017). This interaction thus lowers the barrier to reaction though it is currently unclear whether it enhances the reaction rate compared to e.g. the α-pinene-derived CI-1b, as these hydrogen-bonded structures are entropically not very favourable. The intra-molecular interactions with heterosubstituents could be investigated in future work.

7 Global modelling study

7.1 SCI Chemistry

A global atmospheric modelling study was performed using the GEOS-Chem chemical transport model (as described in Section 4) to examine the global monoterpenes derived SCI budget and the contribution of these SCI to gas-phase SO₂ oxidation. The existing chemistry scheme in the model is supplemented with monoterpenes SCI chemistry based on the experimental results described in Section 5 and in Table 5. It should be noted here that this modelling study focuses on the chemical impacts of monoterpenes SCI formed from ozonolysis reactions only. No chemistry for other SCIs derived from isoprene and/or other (smaller) alkenes are incorporated in the adapted model chemical scheme used.

The monoterpenes emissions in GEOS-Chem are taken from MEGAN v2.1 (Guenther et al., 2012). The scheme emits seven monoterpenes: α-pinene, β-pinene, limonene, myrcene, ocimene, 3-carene, and sabinene. The monoterpenes are oxidised within the model by OH, NO₃ and O₃ at rates shown in Table S1. Reaction with O₃ leads to the production of monoterpenes specific SCI. Reactions with OH and NO₃ does not lead to the formation of any products, with the reactions only acting as a sink for the monoterpenes and the respective oxidant. The SCI yields from the ozonolysis of α-pinene, β-pinene, and limonene are derived from the experimental work presented here. SCI from each monoterpenes are split into SCI-A and SCI-B as defined in previous sections. For the other four monoterpenes emitted, the SCI yields, and kinetics are derived based on similarity of structure to one of the species studied here or previously in the literature. The main SCI produced in the ozonolysis of myrcene and ocimene are expected to be acetone oxide ((CH₃)₂COO) or 4-vinyl-5-hexenal oxide (CH₂CHC(CH₃)CH₂CH₂CHOO), since ozone has been suggested to react predominantly at the
The SCI yield is taken to be 0.30, similar to that of \( (\text{CH}_3)_2\text{COO} \) from 2,3-dimethyl-but-2-ene ozonolysis (Newland et al., 2015a). However, this may be an underestimate since it has been predicted that stabilisation of small CI increases with an increasing size of carbonyl co-product, as this co-product can take more of the nascent energy of the primary ozonide on decomposition due to a greater number of degrees of freedom available (Nguyen et al., 2009, Newland et al., 2015b). Sabinene is a bicyclic monoterpene with an external double bond and hence is treated like β-pinene. This assumption is backed up by recent theoretical work (Wang and Wang, 2017), who predict similar behaviour of sabinene derived SCI to the predicted behaviour of β-pinene SCI by Nguyen et al. (2009a). They predict a SCI yield between 24% - 64%. 3-carene is a bicyclic monoterpene with an internal double bond and is treated like α-pinene.

### 7.2 Modelling Results

Figure 7 shows the annually averaged total SCI burden from monoterpene ozonolysis in the surface layer in the GEOS-Chem simulation. A number of interesting features are apparent from this figure and the associated information given in Table 6:

(i) The highest annually averaged monoterpene SCI concentrations are found above tropical forests.

(ii) Peak annually averaged monoterpene SCI concentrations are ~ \( 1.4 \times 10^4 \text{ cm}^{-3} \).

(iii) > 97% of the total monoterpene SCI burden is SCI-B.

Annual global monoterpene emissions are dominated by the tropics (Figure S1), accounting for > 90% during the northern hemisphere winter months (November – April) and 70% even during the peak emissions from the northern boreal region during June and July (Sindelarova et al., 2014). Despite annually averaged surface ozone mixing ratios being roughly a factor of 2 higher in the northern mid-high latitudes, monoterpene SCI production is still dominated by the tropics. Annually averaged surface monoterpene SCI concentrations across the northern boreal regions are < 2 \( \times 10^3 \text{ cm}^{-3} \); during the summer months (JJA) this value rises to 2 – 5 \( \times 10^3 \text{ cm}^{-3} \).

More than 97% of the total monoterpene derived SCI are SCI-B (Table 6). This is because typical water vapour concentrations in the tropics are > 5.0 \( \times 10^{17} \text{ cm}^{-3} \). This gives SCI-A removal rates (i.e. \( k_3[\text{H}_2\text{O}] \)) of 2 \( \times 10^7 - 1.5 \times 10^5 \text{ s}^{-1} \), whereas removal rates of SCI-B to unimolecular reactions have been determined here to be 1 – 3 orders of magnitude slower, on
the order of 100 - 250 s$^{-1}$. Since the loss of SCI-B is independent of temperature in the model, the highest SCI-B concentrations would be expected to be located in the regions of highest SCI-B production. Recent experimental studies (Smith et al., 2016) have demonstrated a strong temperature dependence for the unimolecular decomposition rate of (CH$_3$)$_2$COO between 283 and 323 K (269 – 916 s$^{-1}$). Therefore, it may be that in reality there would be some geographical variation in the rate of unimolecular loss.

The monoterpene SCI-A + H$_2$O reactions are expected to lead to high yields of both large (e.g. Ma et al., 2008; Ma and Marston, 2008) and small (measured in high yield in the experiments presented here) organic acids.

Figure 8 shows the seasonal removal of SO$_2$ by reaction with monoterpene derived SCI, as a percentage of total gas-phase SO$_2$ oxidation in the surface layer. Monoterpene SCI are most important (relative to OH) for SO$_2$ oxidation over tropical forests, where they account for up to 60% of the local gas-phase SO$_2$ removal during DJF and MAM in some regions. The reasons for this are two-fold: firstly, the highest modelled monoterpene SCI concentrations are found in these regions (Figure 7); but additionally, OH concentrations in the model are low over these areas (Figure S2). Historically there has been discrepancies between modelled and observed OH concentrations over tropical forests, with models appearing to under-predict [OH] by up to a factor of ten (e.g. Lelieveld et al., 2008). It was proposed that this was due to missing sources of OH recycling during isoprene oxidation. During recent years there have been advances in our understanding of isoprene chemistry. GEOS-Chem v-09, used here, includes an isoprene OH recycling scheme largely based on Paulot et al. (2009a, 2009b), with updates from Peeters et al. (2009), Peeters and Müller (2010), and Crounse et al. (2011; 2012), and evaluated in Mao et al. (2013). However, more recent experimental and theoretical work is not yet included.

Annually, monoterpene SCI oxidation accounts for 1.2% of the gas-phase SO$_2$ oxidation in the terrestrial tropics. This accounts for the removal of 2.2 Gg of SO$_2$. Across the northern boreal forests, monoterpene SCI contribute 0.2% to gas-phase SO$_2$ removal annually, removing 0.8 Gg of SO$_2$. Globally, throughout the whole atmosphere, monoterpene SCI account for only 0.5% of gas-phase SO$_2$ removal, removing 8.1 Gg of SO$_2$ annually.

It is noted that MEGAN does not contain oceanic monoterpene emissions, which may increase the global importance of SCI for gas-phase SO$_2$ removal. Luo and Yu (2010) determined annual global oceanic α-pinene emissions to be 29.5 TgC using a top-down approach, with only 0.013 (Luo and Yu, 2010) – 0.26 (Hackenberg et al., 2017) TgC estimated using a range of bottom-
up approaches; clearly there are large uncertainties in oceanic monoterpene emissions. At the upper end of this range they could potentially provide a similar contribution to SCI production and subsequent SO$_2$ oxidation as monoterpenes emitted from the terrestrial biosphere. SCI production more generally could be further amplified by sources such as marine-derived alkyl iodine photolysis.

Blitz et al. (2017) recently calculated a revised SO$_2$ + OH reaction rate ($k_1$ (1 bar N$_2$) (298 K) = $5.8 \times 10^{13}$ cm$^3$ s$^{-1}$), based on experimental work and a master equation analysis, which is ~ 40% lower than the rate given in the most recent JPL data evaluation (Burkholder et al., 2015) ($(k_1$ (1 bar N$_2$) (298 K) = $9.5 \times 10^{13}$ cm$^3$ s$^{-1}$), which is used in the GEOS-Chem model simulation. Figure S3 shows the increased influence of monoterpene derived SCI on gas-phase SO$_2$ oxidation if the alternative SO$_2$ + OH rate is used. This increased the impact of monoterpene SCI to up to 67% of gas-phase SO$_2$ removal in regions of the tropical forests during DJF and MAM, with the contribution of monoterpene SCI to global gas-phase SO$_2$ oxidation increasing to 0.7%.

While certain monoterpenes appear to be more important than others with regard to the production of SCI which will oxidise SO$_2$, these results are sensitive to the kinetics used and the assumptions made for the monoterpenes not studied experimentally here. Hence we do not attempt to draw any conclusions about the relative importance of each monoterpene from the modelling. Clearly the most important monoterpenes will be those with high yields of SCI-B, particularly if those SCI-B have a structure that hinders unimolecular decomposition (such as certain β-pinene derived SCI).

8 Conclusions

We report results from an integrated experimental (simulation chamber), theoretical (quantum chemical) and modelling (global chemistry-transport simulation) study of the impacts of monoterpene ozonolysis reactions on stabilised Criegee intermediate (SCI) formation and SO$_2$ oxidation. The ozonolysis of the monoterpenes α-pinene, β-pinene and limonene have been shown to produce a structurally diverse range of chemically distinct SCIs, with some showing limited sensitivity to / reaction with water vapour under near-atmospheric humidity levels. A multi-component system is required to explain the experimentally observed SO$_2$ removal kinetics. A two-body model system based on the assumption of a fraction of the SCI produced being reactive towards water (SCI-A; potentially contributing to the significant formation of a
range of organic acids in the atmosphere), and a fraction being relatively unreactive towards water (SCI-B), analogous to the structural dependencies observed for the simpler CH$_3$CHOH.

Moreover such an approach is required to accurately predict SCI concentrations, which will be underestimated if a simple average of the properties of the two different SCI classes is used. The atmospheric fate of SCI-B produced from the monoterpenes studied here will be controlled by their removal by unimolecular decomposition. In this work, we have experimentally determined the monoterpene SCI-B decomposition rate to be between 100 and 250 s$^{-1}$. This has significant implications for the role of monoterpene derived SCI as oxidants in the atmosphere.

The fate of SCI-A will be reaction with water or the water dimer, likely leading to the production of a range of organic acids.

A theory-based analysis of the kinetics of the SCI formed from α-pinene, β-pinene ozonolysis has also been performed, which complements the experimental work. The identification of the likely SCI-A and SCI-B populations and the derived kinetics agree with experimental observations within the respective uncertainties.

A modelling study using the GEOS-Chem global 3-D chemical transport model supplemented with the chemical kinetics elucidated in this work suggests that the global monoterpene derived SCI burden will be dominated (> 97%) by SCI-B. The highest annually averaged SCI concentrations are found in the tropics, with seasonally averaged monoterpene SCI concentrations up to $1.4 \times 10^4$ cm$^{-3}$ owing to large monoterpene emissions. Across the boreal forest, average SCI concentrations reach between $3 - 5 \times 10^3$ cm$^{-3}$ during the northern hemisphere summer. Oxidation of SO$_2$ by monoterpene SCI is shown to also be most important in the tropics. While oxidation by SCI contributes < 1% to gas-phase SO$_2$ oxidation globally, over tropical forests this can rise to up to 60% at certain times of the year. Monoterpene SCI driven SO$_2$ oxidation will increase the production of sulfate aerosol – affecting atmospheric radiation transfer, and hence climate; and reduce the atmospheric lifetime and hence transport of SO$_2$. These effects will be substantial in areas where monoterpene emissions are significant, in particular over the Amazon, Central Africa and SE Asian rainforests.

Data Availability
Experimental data will be made available in the Eurochamp database (www.eurochamp.org) from the H2020 EUROCHAMP2020 project, GA nº730997.

Acknowledgements

The assistance of the EUPHORE staff is gratefully acknowledged. Salim Alam, Marie Camredon and Stephanie La are thanked for helpful discussions. This work was funded by EU FP7 EUROCHAMP 2 Transnational Access activity (E2-2012-05-28-0077) and the UK NERC Projects (NE/K005448/1, Reactions of Stabilised Criegee Intermediates in the Atmosphere: Implications for Tropospheric Composition & Climate) and (NE/M013448/1, Mechanisms for Atmospheric chemistry: GeneratioN, Interpretation and FidelitY - MAGNIFY). Fundación CEAM is partly supported by Generalitat Valenciana, and the project DESESTRES (Prometeo Program - Generalitat Valenciana). EUPHORE instrumentation is partly funded by the Spanish Ministry of Science and Innovation, through INNPLANTA project: PCT-440000-2010-003. LV is indebted to the Max Planck Graduate Center with the Johannes Gutenberg-Universität Mainz (MPGC).
References


Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., St. Clair, J. M., Crounse, J. D., Spencer, Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A.,


leading to oxygenated polar compounds and SOA formation: Gas and particulate phase chemical characterization, Atmos. Environ., 75, 196-205, 2013.


Table 1. Monoterpene SCI yields derived in this work and reported in the literature.

<table>
<thead>
<tr>
<th>$\phi_{\text{SCI}}$</th>
<th>Reference</th>
<th>Notes</th>
<th>Methodology</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19 ($\pm$ 0.01)</td>
<td>This work</td>
<td></td>
<td>SO$_2$ loss</td>
</tr>
<tr>
<td>0.15 ($\pm$ 0.07)</td>
<td>Sipiit et al. (2014)</td>
<td></td>
<td>Formation of H$_2$SO$_4$</td>
</tr>
<tr>
<td>0.22</td>
<td>Taipale et al. (2014)</td>
<td>(personal comm. Berndt)</td>
<td></td>
</tr>
<tr>
<td>0.125 ($\pm$ 0.04)</td>
<td>Hatakeyama et al. (1984)</td>
<td></td>
<td>Formation of H$_2$SO$_4$</td>
</tr>
<tr>
<td>0.20</td>
<td>MCMv3.3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Source</td>
<td>Yield</td>
<td>Note</td>
</tr>
<tr>
<td>-----------</td>
<td>--------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>β-pinene</td>
<td>This work</td>
<td>0.60 (± 0.03)</td>
<td>SO2 loss</td>
</tr>
<tr>
<td></td>
<td>Ahrens et al. (2014)</td>
<td>0.46</td>
<td>FTIR detection</td>
</tr>
<tr>
<td></td>
<td>MCMv3.3.1a</td>
<td>0.25</td>
<td>Change in nopinone yields f([H2O])</td>
</tr>
<tr>
<td></td>
<td>Nguyen et al. (2009)</td>
<td>0.42</td>
<td>Change in nopinone yields f([H2O])</td>
</tr>
<tr>
<td></td>
<td>Winterhalter et al. (2000)</td>
<td>0.51</td>
<td>Change in nopinone yields f([H2O])</td>
</tr>
<tr>
<td></td>
<td>Kotzias et al. (1990)</td>
<td>0.44</td>
<td>Formation of H2SO4</td>
</tr>
<tr>
<td></td>
<td>Hatakeyama et al. (1984)</td>
<td>0.25</td>
<td>Formation of H2SO4</td>
</tr>
<tr>
<td></td>
<td>Zhang and Zhang (2005)</td>
<td>0.30</td>
<td>Formation of H2SO4</td>
</tr>
<tr>
<td></td>
<td>Ma and Marston (2008)</td>
<td>&gt; 0.27</td>
<td>Formation of H2SO4</td>
</tr>
<tr>
<td></td>
<td>Hasson et al. (2001)</td>
<td>0.27</td>
<td>Change in nopinone yields f([H2O])</td>
</tr>
</tbody>
</table>

| Limonene  | This work | 0.23 (± 0.01) | SO2 loss |
|          | Sipilä et al. (2014) | 0.27 (± 0.12) | Formation of H2SO4 |
|          | Leungsakul et al. (2005) | 0.34 | Measurement of stable particle and gas-phase products |
|          | MCMv3.3.1a | 0.135 | |

1 Uncertainty ranges (± 2σ, parentheses) indicate combined precision and systematic measurement error components for this work, and are given as stated for literature studies. All referenced experimental studies produced SCI from MT + O3 and were conducted between 700 and 760 Torr. a http://mcm.leeds.ac.uk/MCM/ 
2 Jenkin et al., 2015.
3 a assuming 100 % stabilisation
4 a assuming 40 % stabilisation
5 a assuming 100 % stabilisation
6 a assuming 40 % stabilisation
Table 2. Monoterpane derived SCI relative and absolute⁶ rate constants derived in this work.

<table>
<thead>
<tr>
<th>SCI</th>
<th>$10^7 \frac{k_3}{k_2}$</th>
<th>$10^{-15} \frac{k_3}{k_2}$</th>
<th>$10^{-12} \frac{k_d}{k_2}$</th>
<th>$k_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm³ s⁻¹)</td>
<td>(cm³)</td>
<td>(s⁻¹)</td>
<td></td>
</tr>
<tr>
<td>α-pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>&gt; 140 (± 34)</td>
<td>&gt; 310 (± 75)⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-B</td>
<td>&lt; 8.2 (± 1.5)</td>
<td>&lt; 240 (± 44)⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>&gt; 10 (± 2.7)</td>
<td>&gt; 4 (± 1)⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-B</td>
<td>&lt; 6.0 (± 1.3)</td>
<td>&lt; 170 (± 38)⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limonene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>&lt; 3.5 (± 0.2)</td>
<td>&lt; 7.7 (± 0.6)⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-B</td>
<td>&gt; 4.5 (± 0.1)</td>
<td>&gt; 130 (± 3)⁶</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uncertainty ranges (± 2σ, parentheses) indicate combined precision and systematic measurement error components. ⁶ Scaled to an absolute value using $k_d$(anti-CH₃CHO) = 2.2 × 10⁻¹⁰ cm³ s⁻¹ (Sheps et al., 2014); ⁷ Scaled to an absolute value using $k_d$(anti-CH₃CHO) = 4 × 10⁻¹¹ cm³ s⁻¹ (Ahrens et al., 2014); ⁸ Scaled using $k_d$(syn-CH₃CHO) = 2.9 × 10⁻¹⁵ cm³ s⁻¹ (Sheps et al., 2014).
Table 3. Unimolecular reactions for the CI derived from α-pinene, β-pinene, and d-limonene, as derived by Vereecken et al. (2017). Barrier heights (kcal mol$^{-1}$) listed estimate post-CCSD(T) energies.

<table>
<thead>
<tr>
<th>Carbonyl oxide</th>
<th>Reaction</th>
<th>$E_b$</th>
<th>$k(298K)$ / s$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>α-pinene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-1a</td>
<td>1,4-H-migration</td>
<td>15.8</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>SOZ-formation</td>
<td>15.6</td>
<td>5×10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>1,3-ring closure</td>
<td>21.6</td>
<td>1×10$^{-3}$</td>
</tr>
<tr>
<td>CI-1b</td>
<td>1,3-ring closure</td>
<td>14.8</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>1,3-H-migration</td>
<td>29.0</td>
<td>1×10$^{-6}$</td>
</tr>
<tr>
<td>CI-2a</td>
<td>1,4-H-migration</td>
<td>16.3</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>1,3-ring closure</td>
<td>20.8</td>
<td>6×10$^{-3}$</td>
</tr>
<tr>
<td>CI-2b</td>
<td>1,4-H-migration</td>
<td>17.0</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>SOZ-formation</td>
<td>13.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Ring closure</td>
<td>19.9</td>
<td>3×10$^{-2}$</td>
</tr>
<tr>
<td><strong>β-pinene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-3</td>
<td>1,4-H-migration</td>
<td>15.7</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td>1,3-ring closure</td>
<td>21.1</td>
<td>2×10$^{-3}$</td>
</tr>
<tr>
<td>CI-4</td>
<td>1,3-ring closure</td>
<td>17.2</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Ring opening</td>
<td>23.6</td>
<td>(Slow, Nguyen et al. 2009a)</td>
</tr>
<tr>
<td></td>
<td>1,4-H-migration</td>
<td>24.9</td>
<td>(Slow, Nguyen et al. 2009a)</td>
</tr>
<tr>
<td>CH$_2$OO</td>
<td>1,3-ring closure</td>
<td>19.0</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>1,3-H-migration</td>
<td>30.7</td>
<td>1×10$^{-7}$</td>
</tr>
<tr>
<td><strong>Limonene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-5a</td>
<td>1,4-H-migration</td>
<td>SAR</td>
<td>200$^a$</td>
</tr>
<tr>
<td>CI-5b</td>
<td>1,3-ring closure</td>
<td>SAR</td>
<td>75$^a$</td>
</tr>
<tr>
<td>CI-6a</td>
<td>1,4-H-migration</td>
<td>SAR</td>
<td>430$^a$</td>
</tr>
<tr>
<td>CI-6b</td>
<td>1,4-H-migration</td>
<td>SAR</td>
<td>700$^a$</td>
</tr>
<tr>
<td>CI-7a</td>
<td>1,4-H-migration</td>
<td>SAR</td>
<td>15</td>
</tr>
<tr>
<td>CI-7b</td>
<td>1,4-H-migration</td>
<td>SAR</td>
<td>600</td>
</tr>
</tbody>
</table>

$^a$ Formation of secondary ozonides (SOZ) is not included, and could be the dominant unimolecular loss.
Table 4. Rate coefficients (cm³ molecule⁻¹ s⁻¹) for the reaction of CI with H₂O and (H₂O)₂ as predicted by Vereecken et al. (2017). Values are based on explicit CCSD(T)/aug-cc-pVTZ/M06-2X/aug-cc-pVTZ calculations and multi-conformer TST, including empirical corrections to reference experimental data, except for limonene-derived CI where the values are predicted using a structure-activity relationship. The rate coefficients for CH₂OO, CH₃CHOO, and (CH₃)₂COO are within a factor of 4 of evaluated literature data (Vereecken et al., 2017).

<table>
<thead>
<tr>
<th>Carbonyl oxide</th>
<th>k(298K) H₂O</th>
<th>k(298K) (H₂O)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂OO</td>
<td>8.7×10⁻¹⁶</td>
<td>1.4×10⁻¹²</td>
</tr>
<tr>
<td>syn-CH₃CHOO</td>
<td>6.7×10⁻¹⁹</td>
<td>2.1×10⁻¹⁵</td>
</tr>
<tr>
<td>anti-CH₃CHOO</td>
<td>2.3×10⁻¹⁴</td>
<td>2.7×10⁻¹¹</td>
</tr>
<tr>
<td>(CH₃)₂COO</td>
<td>7.5×10⁻¹⁸</td>
<td>1.8×10⁻¹⁴</td>
</tr>
<tr>
<td>α-pinene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-1a</td>
<td>1.3×10⁻¹⁸</td>
<td>2.9×10⁻¹⁵</td>
</tr>
<tr>
<td>CI-1b</td>
<td>1.5×10⁻¹⁴</td>
<td>1.7×10⁻¹¹</td>
</tr>
<tr>
<td>CI-2a</td>
<td>1.0×10⁻¹⁸</td>
<td>2.5×10⁻¹⁵</td>
</tr>
<tr>
<td>CI-2b</td>
<td>2.4×10⁻¹⁹</td>
<td>7.0×10⁻¹⁶</td>
</tr>
<tr>
<td>β-pinene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-3</td>
<td>1.7×10⁻¹⁸</td>
<td>4.3×10⁻¹⁵</td>
</tr>
<tr>
<td>CI-4</td>
<td>4.2×10⁻¹⁶</td>
<td>6.4×10⁻¹³</td>
</tr>
<tr>
<td>Limonene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-5a</td>
<td>1.5×10⁻¹⁸</td>
<td>4.3×10⁻¹⁵</td>
</tr>
<tr>
<td>CI-5b</td>
<td>1.5×10⁻¹⁴</td>
<td>1.7×10⁻¹¹</td>
</tr>
<tr>
<td>CI-6a</td>
<td>9.1×10⁻¹⁸</td>
<td>2.1×10⁻¹⁴</td>
</tr>
<tr>
<td>CI-6b</td>
<td>1.5×10⁻¹⁷</td>
<td>3.2×10⁻¹⁴</td>
</tr>
<tr>
<td>CI-7a</td>
<td>9.7×10⁻¹⁸</td>
<td>1.9×10⁻¹⁴</td>
</tr>
<tr>
<td>CI-7b</td>
<td>4.3×10⁻¹⁸</td>
<td>1.1×10⁻¹⁴</td>
</tr>
</tbody>
</table>
Table 5. Kinetic parameters used in the global modeling study.

<table>
<thead>
<tr>
<th></th>
<th>$\phi_{SCI}$</th>
<th>$10^{10} k_1$</th>
<th>$10^{11} k_2$</th>
<th>$k_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^3$ s$^{-1}$)</td>
<td>(cm$^3$ s$^{-1}$)</td>
<td>(s$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>0.08</td>
<td>310</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.11</td>
<td>-</td>
<td>2.9</td>
<td>240</td>
</tr>
<tr>
<td>$\beta$-pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>0.25</td>
<td>4</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.35</td>
<td>-</td>
<td>2.9</td>
<td>170</td>
</tr>
<tr>
<td>Limonene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>0.05</td>
<td>7.7</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.18</td>
<td>-</td>
<td>2.9</td>
<td>130</td>
</tr>
<tr>
<td>Myrcene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.30</td>
<td>-</td>
<td>13$^b$</td>
<td>400$^c$</td>
</tr>
<tr>
<td>Ocimene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.30</td>
<td>-</td>
<td>13$^b$</td>
<td>400$^c$</td>
</tr>
<tr>
<td>Sabinene$^d$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>0.25</td>
<td>4</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.35</td>
<td>-</td>
<td>2.9</td>
<td>170</td>
</tr>
<tr>
<td>3-carene$^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCI-A</td>
<td>0.08</td>
<td>310</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>SCI-B</td>
<td>0.11</td>
<td>-</td>
<td>2.9</td>
<td>240</td>
</tr>
</tbody>
</table>

$^a$ $k_d$(SCI-B+SO$_2$) from (SO$_2$+anti-CH$_3$CHOO) – Sheps et al. (2014); $k_d$(SCI-B+SO$_2$) from (SO$_2$+syn-CH$_3$CHO) – Sheps et al. (2014) unless otherwise stated.

$^b$ Temp dependent $k_d$(SCI-B) taken from IUPAC recommendation (2017).

$^c$ Kinetics based on $\beta$-pinene.

$^d$ Kinetics based on $\alpha$-pinene.

$^e$ Kinetics based on $\beta$-pinene.
Table 6. Monoterpene contribution to [SCI] and SO$_2$ oxidation in the surface layer of the model simulation.

<table>
<thead>
<tr>
<th>Monoterpene</th>
<th>Annual emissions (Tg C)</th>
<th>% contribution to [SCI-A]</th>
<th>% contribution to [SCI-B]</th>
<th>% contribution to SO$_2$ oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene</td>
<td>35.4</td>
<td>0.5</td>
<td>11</td>
<td>0.5</td>
</tr>
<tr>
<td>β-pinene</td>
<td>16.9</td>
<td>74</td>
<td>24</td>
<td>55</td>
</tr>
<tr>
<td>limonene</td>
<td>9.2</td>
<td>3.5</td>
<td>18</td>
<td>3.8</td>
</tr>
<tr>
<td>myrcene</td>
<td>3.1</td>
<td>0.0</td>
<td>2.7</td>
<td>0.0</td>
</tr>
<tr>
<td>trans-β-ocimene</td>
<td>14.1</td>
<td>0.0</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>sabinene</td>
<td>7.9</td>
<td>22</td>
<td>13</td>
<td>3.8</td>
</tr>
<tr>
<td>3-carene</td>
<td>6.4</td>
<td>0.0</td>
<td>2.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

$^a$ From MEGAN v2.1 (Guenther et al., 2012)
Scheme 1. Simplified generic mechanism for the reaction of Criegee Intermediates (CIs) formed from alkene ozonolysis.
Scheme 2. Mechanism of formation of the two Criegee Intermediates (CI) from α-pinene ozonolysis.
Scheme 3. Mechanism of formation of the three Criegee Intermediates (CIs) from β-pinene ozonolysis.
Scheme 4. Mechanism of formation of the four Criegee Intermediates (CIs) from limonene ozonolysis.
Figure 1. $\Delta$SO$_2$ vs. $\Delta$O$_3$ during excess SO$_2$ experiments ([H$_2$O] $< 5 \times 10^{15}$ cm$^{-3}$). The gradient determines the minimum SCI yield ($\phi_{\text{min}}$).
Figure 2. Cumulative consumption of SO$_2$ as a function of cumulative consumption of O$_3$, $\Delta$SO$_2$ versus $\Delta$O$_3$, for the ozonolysis of $\alpha$-pinene, $\beta$-pinene and limonene in the presence of SO$_2$ at a range of water vapour concentrations, from $1 \times 10^{15}$ cm$^{-3}$ to $1.9 \times 10^{17}$ cm$^{-3}$. Symbols are experimental data, corrected for chamber dilution. Lines are smoothed fits to the experimental data.
Figure 3. Application of a 2 SCI model fit (Equation E4) and a single SCI model fit (Equation E1) to the measured values (open squares) of \( f/[SO_2] \) for \( \alpha \)-pinene. From the fit we derive relative rate constants for reaction of the \( \alpha \)-pinene derived SCI, SCI-A and SCI-B with H\(_2\)O \( (k_3/k_2) \) and decomposition \(( (k_2 + k_1)/k_2) \) assuming that \( \gamma^A = 0.40 \) and \( \gamma^B = 0.60 \).
Figure 4. Application of a 2 SCI model fit (Equation E4) and a single SCI model fit (Equation E1) to the measured values (open squares) of $f/[SO_2]$ for $\beta$-pinene. From the fit we derive relative rate constants for reaction of the $\beta$-pinene derived SCI, SCI-A and SCI-B with $H_2O$ ($k_3/k_2$) and decomposition ($((k_f+L)/k_2$) assuming that $\gamma^A = 0.41$ and $\gamma^B = 0.59$. 

$\beta$-pinene

- 2 SCI model
- 1 SCI model

$H_2O$
Figure 5. Application of a 2 SCI model fit (Equation E4) and a single SCI model fit (Equation E1) to the measured values (open squares) of $f/[\text{SO}_2]$ for limonene. From the fit we derive relative rate constants for reaction of the limonene derived SCI, SCI-A and SCI-B with H$_2$O ($k_3/k_2$) and decomposition ($(k_3+L_k)/k_2$) assuming that $\gamma_A = 0.22$ and $\gamma_B = 0.78$. 
Figure 6. Variation of $k_3/k_2 (k(SCI-A+H_2O))/(k(SCI-A+SO_2))$ and $k_d (k(SCI-B\ \text{unimol.}))/k(SCI-B+SO_2)$ as a function of the ratio $k_5/k_2 (k(SCI+acid))/k(SCI+SO_2)$, derived from least squares fit of Equation E4 to measurements shown in Figures 3-5 for α-pinene, β-pinene and limonene respectively.
Figure 7. Annual mean monoterpane SCI-A and SCI-B concentrations (cm$^{-3}$) in the surface layer of the GEOS-Chem simulation.
Figure 8. Seasonal SO$_2$ oxidation by monoterpene SCI as percentage of total gas-phase SO$_2$ oxidation in the surface layer.
Discussion and Atmospheric Implications

Monoterpene ozonolysis produces a diverse range of SCIs, with contrasting fates in the atmosphere, dominated by unimolecular reaction or reaction with water vapour, but which may still affect atmospheric SO\(_2\) processing. Monoterpene-derived SCI have the potential to make a significant contribution to gas-phase SO\(_2\) oxidation in specific local (i.e. forested) environments, of up to 50% at certain times of year - amplifying sulfate aerosol formation, reducing the atmospheric lifetime and hence geographic distribution of SO\(_2\), however the results presented here show that their impact upon annual SO\(_2\) oxidation globally is modest.

The results presented here demonstrate that it is important that monoterpene ozonolysis reactions are considered to produce at least two different SCI species if their chemistry is to be adequately represented in global models. This is because even a ‘moderate’ reaction rate with water would be a dominant sink of an SCI with the averaged properties of SCI-A and SCI-B. SCI concentrations are expected to vary greatly depending on the local environment and time of year, e.g. monoterpene abundance may be considerably higher (and with a different reactive mix of alkenes giving a range of structurally diverse SCI) in a forested environment, compared to a rural background. Furthermore, biogenic isoprene and monoterpene emissions are strongly temperature dependent, hence are predicted to change significantly in the future as a response to a changing climate and other environmental conditions (Peñuelas and Staudt, 2010).

This study shows that the ozonolysis of monoterpenes may contribute to significant SCI concentrations in forested areas. Another group of compounds produced by forests that may also have the potential to be a significant source of SCI are sesquiterpenes (C\(_{15}\)H\(_{24}\)). Although generally present at low mixing ratios, this is due to their short atmospheric lifetimes caused by their rapid reaction rates with ozone. The flux through the alkene-ozone reaction for fast reacting monoterpenes and sesquiterpenes is often higher than for monoterpenes with high mixing ratios but low removal rates, e.g. \(\alpha\)-pinene and \(\beta\)-pinene. Ozonolysis of sesquiterpenes has been shown to have very high SCI yields (Beck et al., 2011; Yao et al., 2014) and these SCI have been shown to react with SCI scavengers (e.g. SO\(_2\), H\(_2\)O etc.) in a similar way to smaller SCI (Yao et al., 2014). It has been predicted that SCI from sesquiterpenes may have a high degree of secondary ozonide formation (Chuong et al., 2004) but experimental work has shown very different results for structurally different sesquiterpenes studied (Beck et al., 2011; Yao et al., 2014) hence this is highly uncertain, as is the fate of the SOZ once formed. Therefore, these have the potential to be another significant source of SCI.