Isoprene SCI reviewer comments

We would like to thank both Reviewers for their positive and insightful comments. Specific points are addressed below:

Anonymous Referee #1

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The authors have used the EUPHORE chamber to measure the loss of SO2 during isoprene ozonolysis as a function of relative humidity and dimethyl sulfide (DMS) concentration. This enabled the determination of quantities such as the yield of stabilized Criegee intermediate (SCI), the relative rate coefficients for the reaction of SCI with H2O vs. with SO2, and the relative rate coefficients for the reaction of SCI with DMS vs. with SO2. The authors found a SCI yield of 0.56 ± 0.03, in good agreement with a recent experimental estimate by Sipilä (Atmos. Chem. Phys. 2014, 14, 12143) based on H2SO4 formation and an older theoretical estimate by Zhang (Chem. Phys. Lett. 2002, 358, 171). The derived relative rate coefficients allow the authors to conclude that reaction with water is the main sink for isoprene-derived, and that SCI may be a significant DMS oxidant at dawn and dusk, when both [OH] and [NO3] are low. Overall, I judge the paper to be of high quality. The experimental work and data analysis have been done carefully, and the authors have been transparent about their methodology. The relevant literature has been thoroughly cited and discussed fairly. Moreover, the subject matter treated by the manuscript is clearly important in that it provides evidence that the stabilized Criegee intermediate derived from isoprene ozonolysis will likely not be a significant oxidant of SO2.

One suggestion: Since the authors cite the Hasson (2001) isoprene-SCI yield of 0.27 (in Table 1), they should try to account for the discrepancy between the present result and this earlier result.

> *Hasson et al. (2001) derived their isoprene total SCI yields by measuring the sum of the difference between (i) the H_2O_2 production under dry and high RH conditions and (ii) the difference between hydroxyl-methyl hydroperoxide (HMHP) production under dry and high RH conditions. The H_2O_2 is assumed to be formed from decomposition of a hydroxy-alkyl hydroperoxide formed from the reaction of the non-CH_2OO SCI (i.e. CRB-SCI) with H_2O, the HMHP is assumed to be formed in the reaction of CH_2OO with H_2O. The determined difference in yields for H_2O_2 is 0.11 and for HMHP is 0.15, hence the total yield of 0.26 (wrongly given as 0.27 in Table 1 – this has been corrected to 0.26). However, Hasson et al. do not measure the formic acid yield (to which HMHP decomposes). This could lead to an underestimation of the CH_2OO yield due to HMHP decomposition, which would lead to an underestimation in the HMHP and hence overall SCI yield. Indeed Hasson et al. note that their HMHP yield from isoprene ozonolysis is roughly half of that determined by Neeb et al. (1997) suggesting that they are missing a significant part of the CH_2OO yield. The approach followed also cannot account for SCI that decompose via the hydroperoxide mechanism, since these would not be expected to form H_2O_2. While recent work has shown that such decomposition is likely very small for*

> *CH_2OO (Newland et al., 2015; Chhantyal-Pun et al., 2015), it is likely to be important for some of the CRB-SCI (though our work determines a fairly small overall contribution). Additionally, it is also possible that some of the hydroxyl-alkyl hydroperoxides formed by CRB-SCI + H_2O are stabilised and hence would not be measured by Hasson et al..*
>
> *The following sentences have been added to Section 3.1:*
>
> > "Hasson et al. (2001) calculated a total SCI yield of 0.26 by measuring the sum of the difference between the H_2O_2 production under dry and high RH conditions (to give the non-CH_2OO SCI yield) and the difference between hydroxyl-methyl hydroperoxide (HMHP) production under dry and high RH conditions (to give φ_{CH2OO}). One reason for the significantly lower value for the total SCI calculated by Hasson et al. compared to this work is the low value of φ_{CH2OO} determined, compared to e.g. Neeb et al. (1997) who determined φ_{CH2OO} of twice that determined by Hasson et al., using a similar methodology."

I have no technical corrections to note.

Anonymous Referee #2

Received and published: 4 May 2015

General: This is an interesting contribution on a chamber-based study of Criegee radicals derived from isoprene (ISO) and their reactivity towards SO2, water and DMS.

As the reaction of ISO with ozone is known to be slow, it might be expected that the ISO-CIs will not play a very important role in gas phase chemistry.

> *While the isoprene-ozone reaction rate constant is considerably slower than other potentially important ozonolysis reactions in the atmosphere, such as with monoterpenes, the flux through the reaction, i.e. $k[C_5H_8][O_3]$ is similar, if not larger than, that for many other species because of the higher isoprene mixing ratios found in much of the lower atmosphere.*

These systems under study are very complex when the role of the Criegee radical is to be investigated starting from ozonolysis experiments. It cannot be excluded that products formed after ozonolysis will also establish sinks for the Criegee intermediates and that the sinks for the CIs can really be ascribed to the processes the study of which was intended.

The final suggestion that the reaction of ISO-SCIs with DMS could be important should be viewed with care.

Overall, the manuscript clearly warrants publication.

Details / Specific comments:

1) Experiments have been conducted with fairly high initial reactant mixing ratios (isoprene: 400 ppbv, ozone: 500 ppbv, cyclohexane for OH scavenging: 75 ppmv) and 25% isoprene conversion, i.e. oxidation product generation from ozonolysis and OH reaction in the order of a few 1012 molecules cm-3. Only small information is given regarding the SCI reaction with the oxidation products (carbonyls, acids) in competition with the reactions with SO2 and H2O / DMS depending on reaction time (progress of isoprene conversion). Data analysis considers a fixed, free parameter "L" for additional SCI loss steps. The authors should provide more information how the consecutive reactions of products with SCI could influence their findings especially for low H2O / DMS concentrations. Maybe, a modelling study could be helpful.

Based on reported reaction rate constants of species involved with / formed in the ozonolysis system, the only reaction partners likely to compete significantly with SO_2*,* H_2O *or unimolecular decomposition for reaction with SCI under the experimental conditions applied are organic acids (e.g. HCOOH and CH3COOH); these are formed in the experiments at concentrations reaching up to* 2.5×10^{12} cm^{-3} *(as measured by FTIR).*

We have performed model runs using a box model employing a chemical scheme taken from the MCM, with additional updated SCI chemistry in which a rate constant of 1.1×10^{-10} cm^3 s^{-1} *is used for SCI + HCOOH, as determined by Welz et al. (2014) for* CH_2OO *+ HCOOH, and a yield of 0.5 for HCOOH from ISOPOO+*H_2O*, which gives good agreement with the acid yields measured by FTIR. The reduction in* SO_2 *loss between the model runs without the HCOOH+SCI reaction and those with the reaction varied between 7 % and 17 % (highest at high RH – because of greater HCOOH formation).*

We have extended our analysis to explicitly account for the effect of organic acids by including an explicit acid term in Equation E3 (to give Equation E5) (rather then being included in 'L') and using the acid concentrations measured by FTIR, albeit at a cost of increased complexity in the analysis overall. A value of 3.0 is taken for $k(acid+SCI)/k_2$ *as determined recently by Welz et al. (Science, 2012,* ***335,*** *204-207; Angew. Chem., 2014,* ***53****, 4547-4550) and Sipila et al. (Atmos. Chem. Phys.,* 2014, **14**, 20143-20153*). Use of this approach reduces the previously derived* k_3/k_2 *value by 43% to* 3.1×10^{-5} *and the derived* k_8/k_2 *value by 22% to 3.2 as a consequence of the direct accounting for the loss of SCI through reaction with ozonolysis system products.*

The text of Section 3.2 has been altered to reflect the explicit inclusion of the acid term on the effect of the presence of acids on the determined rate constants.

> "…
> Model runs were performed in which a rate constant of 1.1×10^{-10} cm^3 s^{-1} was used for reaction between SCI and formic and acetic acids (HCOOH, CH_3COOH), as given by Welz et al. (2014) for CH_2OO + HCOOH, together with an acid yield of 0.5 from the reactions of isoprene derived SCI species with water, which gives a good agreement with the experimentally determined acid yields measured by FTIR. The reduction in SO_2 loss between the model runs with the SCI + acid reaction included, and those without the reaction, varied between 7 % and 17 %.

Equation E3 can be extended to explicitly account for the presence of acids by inclusion of a further term (Equation E5). This requires a value for k_9/k_2, the ratio of the rate constants for SCI reactions with acids and with SO_2. Here, we employ a value of 3.0, derived from the mean of the recently reported rates of reaction of CH_2OO with HCOOH and CH_3COOH (Welz et al., 2014), and the rate constant for CH2OO + SO_2 reported by Welz *et al.* (2012) – although in reality this term represents potential reaction of all SCI present with multiple acid species. The acid concentrations are taken from FTIR measurements during the experiments.

$$\mathrm{SCI} + \mathrm{acid} \xrightarrow{k_9} \mathrm{Products} \qquad \text{(R9)}$$

$$[\mathrm{SO_2}](\frac{1}{f}-1)-\frac{k_9}{k_2}[Acid]=\frac{k_3}{k_2}[\mathrm{H_2O}]+\frac{k_d+L}{k_2} \qquad \text{(E5)}$$

…"

The acid term is also included in the two SCI species analysis in Section 3.3 and in the DMS analysis in Section 4. Though the inclusion of the acid term affects the derived rate constants, there is no material change to the overall conclusions of the paper.

2) SCI + H2O: Ozone and SO2 measurements, applied in data analysis, have been done with the help of corresponding monitors. What was the reason for the limited RH range of 0.5 – 27%? Atmospheric conditions exceed this range clearly. A wider range would give more experimental information to allow distinguishing between the H2O monomer and dimer reaction.

The RH range was limited by the experimental system (water interference in the FTIR spectra, and condensation upon the FTIR field mirrors, which are within the chamber and are not purged, hence susceptible to misting). We agree a greater humidity range would give much better separation of water monomer and dimer effects, but unfortunately was not possible with the EUPHORE FTIR system. The sensitivity to water monomer vs dimer impacts is discussed at length (for CH_2OO) in Newland et al., Phys. Chem. Chem. Phys., 2015, **17**, 4076-4088 (referenced in the manuscript); *theory predicts that the dimer reaction will be very slow for the (non-CH_2OO) isoprene SCI (Vereecken and Francisco, Chem. Soc. Rev., 2012, 41, 6259-6293).*

3) Kinetic approach: Did the authors use an initial rate approach and the smoothed fitting procedure served as a tool to generate delta-SO2/delta-O3 at t = 0? Please give a more precise explanation! (It is also important in connection with point 1).) What kind of fitting function was used?

Yes. A model fit was applied, to the data, as stated in the manuscript; we have clarified that this process is described in detail in Newland et al., (2015) (Phys. Chem. Chem. Phys., 2015, **17**, 4076-4088). *The fit to the measurements is generated from model output using the box model described above (point 1). It is indeed important with respect to point 1 that the model fits are used to give delta-SO2/delta-O3 at t = 0, in order to minimise the potential effects of product formation potentially contributing to SCI loss. See discussion above re. impacts of* *reactions with acids also. We have added a statement clarifying this to the manuscript:*

> *“This fit was derived using a box model run in FACSIMILE (Curtis and Sweetenham, 1987) with a chemical scheme taken from the MCM, with additional updated SCI chemistry constrained by the experimental measurements.”*

4) SCI + DMS: The finding of a rate coefficient close to collision limit could be very important for atmospheric chemistry. This rate coefficient was derived from an indirect way of determination using four runs only. The data show a large scattering, cf. Figure 6. The authors should discuss possible errors of k8 in detail.

An important finding from this study shows that the reaction of SCI + DMS does indeed occur - and at a rapid rate - and hence could be important for atmospheric chemistry. Owing to its potential importance and, as this is the first reported rate constant for this reaction, further studies are warranted, especially with respect to understanding the oxidation mechanism and measurement of its products. We have added a further discussion of the experimental uncertainties (Section 4.2).

> *“As noted above, this analysis assumes that the multiple SCI species in reality present may be analysed as a single species (or exhibit the same reactivity). While the data indicate that this approximation satisfactorily describes the observed behaviour under the conditions applied, other work (e.g. Taatjes et al., 2013) has shown that reactivity of different SCIs, and different conformers of the same SCI, can differ, affecting the retrieval of kinetics in multi-SCI ozonolysis systems; Newland et al. (2015) have illustrated this effect in the case of syn- and anti-CH_3CHOO. Similarly, the response of the SCI population to reaction with acids is approximated by a single reaction with those species observed (HCOOH, CH_3OOH). A further approximation is that the mean isoprene-SCI + SO_2 reaction rate may be represented by that measured for CH_2OO with SO_2 (Welz et al., 2012). These approximations introduce systematic uncertainty into the derived rate constants, but given the lack of fundamental data for individual SCI isomers, it is not possible to evaluate this. The data obtained are well within the capability of the experimental approaches: DMS levels were inferred from the (known) volumetric addition to the chamber and are thought unlikely to be significantly in error. O_3 and C_5H_8 were monitored using well established techniques at levels well above detection limits. The observed changes in SO_2 removal upon addition of DMS (Figure 5) was substantial, and well in excess of the sensitivity limit, and uncertainty, of the SO_2 monitor. It is important to note that no constraints regarding the products of the proposed DMS + SCI reaction were obtained; OH reaction with DMS is complex, proceeding through both abstraction and addition/complex formation channels, the latter rendered partially irreversible under atmospheric conditions through subsequent reaction with O_2 (Sander et al., 2011). The observed behaviour (Figure 5) is not consistent with reversible complex formation dominating the SCI-DMS system under the conditions used; however it is possible that decomposition of such a complex to reform DMS, or its further reaction (e.g. with SO_2, analogous to the secondary ozonide mechanism proposed by Hatakeyama et al., 1986) would be consistent with the observed data, and also imply that the reaction may not lead to net DMS removal. Time-resolved laboratory measurements and product studies are needed to provide a test of this possibility.”*

The limitations of the analytical approach are discussed extensively in the original manuscript in general, and as directly related to the DMS measurements in the additional section (above). We have propagated the experimental uncertainties to the reported values for all kinetic data (or their ratios); moreover, irrespective of the analysis, visual inspection of the data (Figure 5) demonstrates a rapid reaction between DMS and the chemical species responsible for SO_2 removal (i.e. the SCI).

Atmospheric Isoprene Ozonolysis: Impacts of Stabilized Criegee Intermediate Reactions with SO_2, H_2O and Dimethyl sulfide

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Mike Newland 31/7/2015 11:23
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Abstract

Isoprene is the dominant global biogenic volatile organic compound (VOC) emission. Reactions of isoprene with ozone are known to form stabilised Criegee intermediates (SCIs), which have recently been shown to be potentially important oxidants for SO_2 and NO_2 in the atmosphere; however the significance of this chemistry for SO_2 processing (affecting sulfate aerosol) and NO_2 processing (affecting NO_x levels) depends critically upon the fate of the SCI with respect to reaction with water and decomposition. Here, we have investigated the removal of SO_2 in the presence of isoprene and ozone, as a function of humidity, under atmospheric boundary layer conditions. The SO_2 removal displays a clear dependence on relative humidity, confirming a significant reaction for isoprene derived SCI with H_2O. Under excess SO_2 conditions, the total isoprene ozonolysis SCI yield was calculated to be 0.56 (±0.03). The observed SO_2 removal kinetics are consistent with a relative rate constant, *k*(SCI + H_2O) / *k*(SCI + SO_2), of 3.1 (± 0.5) × 10^{-5} for isoprene derived SCI. The relative rate constant for *k*(SCI decomposition) / *k*(SCI+SO_2) is 3.0 (± 3.2) × 10^{11} cm^{-3}. Uncertainties are ±2σ and represent combined systematic and precision components. These kinetic parameters are based on the simplification that a single SCI species is formed in isoprene ozonolysis, an approximation which describes the results well across the full range of experimental conditions. Our data indicate that isoprene-derived SCIs are unlikely to make a substantial contribution to gas-phase SO_2 oxidation in the troposphere. We also present results from an analogous set of experiments, which show a clear dependence of SO_2 removal in the isoprene-ozone system as a function of dimethyl sulfide concentration. We propose that this behaviour arises from a rapid reaction between isoprene-derived SCI and DMS; the observed SO_2 removal kinetics are consistent with a relative rate constant, *k*(SCI + DMS) / *k*(SCI + SO_2), of 3.5 (± 1.8). This result suggests that SCIs may contribute to the oxidation of DMS in the atmosphere and that this process could therefore influence new particle formation in regions impacted by emissions of unsaturated hydrocarbons and DMS.

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1 Introduction

Atmospheric chemical processes exert a major influence on atmospheric composition. Identified gas-phase oxidants include the OH radical, ozone, NO_3 and under certain circumstances other species such as halogen atoms. Reactions with these oxidants can lead to (for example) chemical removal of primary air pollutants; formation of secondary pollutants (e.g. ozone, harmful to human and environmental health, and a greenhouse gas); and the transformation of gas-phase species to the condensed phase (e.g., SO_2 oxidation leading to the formation of sulfate aerosol, and the formation of functionalised organic compounds leading to secondary aerosol formation, which can influence radiation transfer and climate).

Stabilised Criegee intermediates (SCI), or carbonyl oxides, are formed in the atmosphere predominantly from the reaction of ozone with unsaturated hydrocarbons, though other processes may be important in certain conditions, e.g. alkyl iodide photolysis (Gravestock et al., 2010), dissociation of the DMSO peroxy radical (Asatryan and Bozzelli, 2008), and reactions of peroxy radicals with OH (Fittschen et al., 2014). SCI have been shown in laboratory experiments and by theoretical calculations to oxidise SO_2 and NO_2 (*e.g.* Cox and Penkett, 1971; Welz et al., 2012; Taatjes et al., 2013; Ouyang et al., 2013; Stone et al., 2014) as well as a number of other trace gases found in the atmosphere. Recent field measurements in a boreal forest (Mauldin et al., 2012) and at a coastal site (Berresheim et al., 2014) have both identified an apparently missing process oxidising SO_2 to H_2SO_4 (in addition to reaction with OH) and have implied SCI as a possible oxidant, acting alongside OH. Assessment of the importance of SCIs for tropospheric processing requires a quantitative understanding of their formation yields and atmospheric fate – in particular, the relative importance of bimolecular reactions (e.g. with SO_2), unimolecular decomposition, and reaction with water vapour. Here we describe an experimental investigation into the formation and reactions of the SCIs derived from isoprene (the most abundant biogenic VOC), formed through the ozonolysis process, which dominates atmospheric SCI production, and studied under boundary layer conditions, to assess their potential contribution to tropospheric oxidation.

1.1 Stabilised Criegee Intermediate Kinetics

Ozonolysis derived CIs are formed with a broad internal energy distribution, yielding both chemically activated and stabilised CIs. SCIs can have sufficiently long lifetimes to undergo bimolecular reactions with H_2O and SO_2, amongst other species. Chemically activated CIs may undergo collisional stabilisation to an SCI (Scheme 1), or unimolecular decomposition or isomerisation.

To date the majority of studies have focused on the smallest SCI, CH_2OO, because of the importance of understanding simple SCI systems (this species is formed in the ozonolysis of all terminal alkenes) and the ability to synthesize CH_2OO from alkyl iodide photolysis, with sufficient yield to probe its kinetics. However, the unique structure of CH_2OO (which prohibits isomerisation to a hydroperoxide intermediate) likely gives it a different reactivity and degradation mechanism to other SCI (Johnson and Marston, 2008).

Recent experimental work (Berndt et al., 2014; Newland et al., 2015; Chao et al., 2015; Lewis et al., 2015) has determined the predominant atmospheric fate for CH_2OO to be reaction with water vapour. Some of these experiments (Berndt et al., 2014; Chao et al., 2015; Lewis et al., 2015) have demonstrated a quadratic dependence of CH_2OO loss on $[H_2O]$, suggesting a dominant role for the water dimer, $(H_2O)_2$, in CH_2OO loss at typical atmospheric boundary layer H_2O concentrations. For larger SCI, both experimental (Taatjes et al., 2013; Sheps et al., 2014; Newland et al., 2015) and theoretical (Kuwata et al., 2010; Anglada et al., 2011) studies have shown that their kinetics, in particular reaction with water, are highly structure dependent. *syn*-SCI (*i.e.* those where an alkyl-substituent group is on the same side as the terminal oxygen of the carbonyl oxide moiety) react very slowly with H_2O, whereas, *anti*-SCI (*i.e.* with the terminal oxygen of the carbonyl oxide moiety on the same side as a hydrogen group) react relatively fast with H_2O. This difference has been predicted theoretically (Kuwata et al., 2010; Anglada et al., 2011) and was subsequently confirmed in recent experiments (Taatjes et al., 2013; Sheps et al., 2014) for the two CH_3CHOO conformers. Additionally, it has been predicted theoretically (Vereecken et al., 2012) that the relative reaction rate constants for the water dimer vs water monomer, $k(SCI+(H_2O)_2)/k(SCI+H_2O)$ of larger SCI (except *syn*-CH_3CHOO) will be over 70 times smaller than that for CH_2OO, suggesting that reaction with the water dimer is unlikely to be the dominant fate for these SCI under atmospheric conditions.

An additional, potentially important, fate of SCI under atmospheric conditions is unimolecular decomposition (denoted k_d in (R4)). This is likely to be a significant atmospheric sink for *syn*-SCI because of their slow reaction with water vapour. Previous studies have identified the hydroperoxide rearrangement as dominant for SCIs with a *syn* configuration, determining their overall unimolecular decomposition rate (Niki et al., 1987; Rickard et al., 1999; Martinez and Herron, 1987; Johnson and Marston, 2008). This route has been shown to be a substantial non-photolytic source of atmospheric oxidants (Niki et al., 1987; Alam et al., 2013). CIs formed in the *anti*-configuration are thought to primarily undergo rearrangement and possibly decomposition *via* a dioxirane intermediate (“the acid/ester channel”), producing a range of daughter products and contributing to the observed overall HO_x radical yield (Johnson and Marston, 2008; Alam et al., 2013).

For CH_2OO, rearrangement via a ‘hot’ acid species represents the lowest accessible decomposition channel with the theoretically predicted rate constant being rather low, 0.3 s^{-1} (Olzmann et al., 1997). Recent experimental work supports this slow decomposition rate for CH_2OO (Newland et al., 2015; Chhantyal-Pun et al., 2015). However, Newland *et al.* (2015) have suggested the decomposition of larger *syn*-SCI to be considerably faster, albeit with substantial uncertainty, with reported rate constants for *syn*-CH_3CHOO of 288 (± 275) s^{-1} and for $(CH_3)_2COO$ of 151 (± 35) s^{-1}. Novelli *et al.* (2014), estimated decomposition of *syn*-CH_3CHOO to be 20 (3-30) s^{-1} from direct observation of OH formation, while Fenske *et al.* (2000), estimated decomposition of CH_3CHOO produced from ozonolysis of *trans*-but-2-ene to be 76 s^{-1} (accurate to within a factor of three).

$$\text{Alkene} + O_3 \xrightarrow{k_1} \phi\text{SCI} + (1-\phi)\text{CI} + \text{RCHO} \qquad \text{(R1)}$$

$$\text{SCI} + SO_2 \xrightarrow{k_2} SO_3 + \text{RCHO} \qquad \text{(R2)}$$

$$\text{SCI} + H_2O \xrightarrow{k_3} \text{Products} \qquad \text{(R3)}$$

$$\text{SCI} \xrightarrow{k_d} \text{Products} \qquad \text{(R4)}$$

$$\text{SCI} + (H_2O)_2 \xrightarrow{k_5} \text{Products} \qquad \text{(R5)}$$

1.2 Isoprene Ozonolysis

Global emissions of biogenic VOCs have been estimated to be an order of magnitude greater, by mass, than anthropogenic VOC emissions (Guenther et al., 1995). The most abundant non-methane biogenic hydrocarbon in the natural atmosphere is isoprene (2-methyl-1,3-butadiene, C_5H_8), with global emissions estimated to be 594 (± 34) Tg yr^{-1} (Sindelarova et al., 2014). While the vast majority of these emissions are from terrestrial sources, there are also biogenic emissions in coastal and remote marine environments, associated with seaweed and phytoplankton blooms (Moore et al., 1994). Isoprene mixing ratios (as well as those of some monoterpenes) have been reported to reach hundreds of pptv (parts per trillion by volume) over active phytoplankton blooms in the marine boundary layer (Sinha et al., 2007; Yassaa et al., 2008), with the potential to impact local air quality (Williams et al., 2010).

Removal of isoprene from the troposphere is dominated by reaction with the OH radical during the day and reaction with the nitrate radical during the night (Calvert et al., 2000). The ozonolysis of isoprene is also a non-photolytic source of HO_x radicals (Atkinson et al., 1992; Paulson et al., 1997; Malkin et al., 2010), with measured yields of OH between 0.25 (Paulson et al., 1997) and 0.27 (Atkinson et al., 1992) (with a current recommended yield of 0.25 (Atkinson et al., 2006)). Isoprene ozonolysis also leads to the formation of a range of multi-functional oxygenated compounds, some of which can form secondary organic aerosol (Noziere et al., 2015).

Isoprene ozonolysis yields five different initial carbonyl oxides (Scheme 2). The three basic species formed are formaldehyde oxide (CH_2OO), methyl-vinyl carbonyl oxide (MVKOO) and methacrolein oxide (MACROO) (Calvert et al., 2000; Atkinson et al., 2006). MVKOO and MACROO both have *syn* and *anti* conformers and each of these can have either *cis* or *trans* configuration (Zhang et al., 2002; Kuwata et al., 2005) with easy inter-conversion between the *cis* and *trans* conformers (Aplincourt and Anglada, 2003). The kinetics and products of isoprene ozonolysis have been investigated theoretically by Zhang *et al*. (2002). They predicted the following SCI yields: CH_2OO, 0.31; *syn*-MVKOO, 0.14; *anti*-MVKOO, 0.07; *syn*-MACROO, 0.01; *anti*-MACROO 0.04. This gives a total SCI yield of 0.57. They predicted that 95% of the chemically activated CH_2OO formed will be stabilized, considerably higher than the experimentally determined stabilization of excited CH_2OO formed during ethene ozonolysis (35% - 54%) (Newland et al., 2015). This is because the majority of the energy formed during isoprene ozonolysis is thought to partition into the larger, co-generated, primary carbonyl species (Kuwata et al., 2005) (*i.e.* methyl-vinyl ketone (MVK) or methacrolein (MACR)). The predicted stabilization of the other SCI ranges from 20% to 54% at atmospheric pressure. It is relevant to note that the total SCI yield from isoprene ozonolysis used in the Master Chemical Mechanism, MCMv3.2 (Jenkin et al., 1997, Saunders et al., 2003), is considerably lower at 0.22, as a consequence of the MCM protocol, which applies a weighted mean of total SCI yields measured for propene, 1-octene and 2-methyl propene (Jenkin et al, 1997). However, the relative yield of CH_2OO (0.50) compared to the total SCI yield in the MCM is very similar to that calculated by Zhang *et al.* (2002) (0.54).

1.3 Dimethyl Sulfide (DMS)

The largest natural source of sulfur to the atmosphere is the biogenically produced compound dimethyl sulfide, DMS (CH_3SCH_3), which has estimated global emissions of 19.4 (±4.4) Tg yr^{-1} (Faloona, 2009). DMS is a breakdown product of the plankton waste product dimethylsulfoniopropionate (DMSP). Jardine et al. (2015) have also recently shown that vegetation and soils can be important terrestrial sources of DMS to the atmosphere in the Amazon Basin, during both the day and at night, and throughout the wet and dry seasons, with measurements of up to 160 pptv within the canopy and near the surface. The oxidation of DMS is a large natural source of SO_2, and subsequently sulfate aerosol, to the atmosphere and therefore is an important source of new particle formation. This process has been implicated

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in an important feedback leading to a regulation of the climate in the pre-industrial atmosphere (Charlson et al., 1987). The two most important oxidants of DMS in the atmosphere are thought to be the OH and NO_3 radicals (Barnes et al., 2006) (Reactions R6 and R7). Because of its photochemical source, OH is thought to be the more important oxidant during the day in tropical regions, while NO_3 becomes more important at night, at high latitudes, and in more polluted air masses (Stark et al., 2007). Certain halogenated compounds, *e.g.* Cl (Wingenter et al., 2005) and BrO (Wingenter et al., 2005; Read et al., 2008), have also been suggested as possible oxidants for DMS in the marine environment.

$$\mathrm{DMS + OH \rightarrow CH_3SCH_2 + H_2O} \qquad \text{(R6a)}$$

$$\mathrm{\rightarrow CH_3S(OH)CH_3} \qquad \text{(R6b)}$$

$$\mathrm{DMS + NO_3 \rightarrow CH_3SCH_2 + HNO_3} \qquad \text{(R7)}$$

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 (2015).

Experiments comprised time-resolved measurement of the removal of SO_2 in the presence of the isoprene-ozone system, as a function of humidity or DMS concentration. SO_2 and O_3 abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. Experiments were performed in the dark (*i.e.* with the chamber housing closed; $j(NO_2) \leq 10^{-6}\ s^{-1}$), 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 (three 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 air, comprised addition of SF_6 and cyclohexane, followed by water vapour (or DMS), O_3 (*ca*. 500 ppbv) and SO_2 (*ca*. 50 ppbv). A gap of five minutes was left prior to addition of isoprene, to allow complete mixing. The reaction was then initiated by addition of the isoprene (*ca.* 400 ppbv), and reagent concentrations followed for 30 -60 minutes; typically *ca*. 25% of the isoprene was consumed after this time. Nine isoprene + O_3 experiments, as a function of [H_2O], were performed over separate days. Each individual run was performed at a constant humidity, with humidity varied to cover the range of [H_2O] = 0.4–21 × 10^{16} molecules cm^{-3}, corresponding to an RH range of 0.5 – 27 % (at 298 K). Five isoprene + O_3 experiments as a function of DMS were also performed. Measured increases in [SO_2] agreed with measured volumetric additions across the SO_2, humidity and DMS ranges used in the experiments.

2.2 Analysis

As in our previous study (Newland et al., 2015), from the chemistry presented in Reactions R1 – R5 SCI will be produced in the chamber from the reaction of the alkene with ozone at a given yield, ϕ. A range of different SCI are produced from the ozonolysis of isoprene (see Scheme 2: 9 first-generation SCI present), each with their own distinct chemical behaviour (*i.e.* yields, reaction rates). It is not feasible (from these experiments) to obtain data for each SCI independently, consequently for analytical purposes we adopt two alternative analyses to treat the SCI population in a simplified (lumped) manner:

In the first of these, we make the approximation that all SCI may be considered as a single species (defined from now on as ISOP-SCI). Alternatively, the SCI population is grouped into two species, the first of which is CH_2OO (for which the kinetics are known) and the second (hereafter termed CRB-SCI) represents all isomers of the other SCI species produced, *i.e.* Σ(MVKOO + MACROO). The implications of these assumptions are discussed further below, but 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.

Following formation in the ozonolysis reaction, the SCI can react with SO_2, with H_2O, with DMS (if present), with other species, or undergo unimolecular decomposition, under the experimental conditions applied. The fraction of the SCI produced that reacts with SO_2 (f) is determined by the SO_2 loss rate ($k_2[SO_2]$) compared to the sum of the total loss processes of the SCI (Equation E1) :

$$f = \frac{k_2[\mathrm{SO_2}]}{k_2[\mathrm{SO_2}] + k_3[\mathrm{H_2O}] + k_d + L} \qquad \text{(E1)}$$

Here, L accounts for the sum of any other chemical loss processes for SCI in the chamber, after correction for dilution, and neglecting other (non-alkene) chemical sinks for O_3, such as reaction with HO_2 (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.

2.2.1 SCI yield calculation

The value for the total SCI yield of ISOP-SCI, $\phi_{\mathrm{ISOP\text{-}SCI}}$, 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 (>95%). From Equation E2, regressing dSO_2 against dO_3 (corrected for chamber dilution), assuming f to be unity (*i.e.* all the SCI produced reacts with SO_2), determines the value of ϕ_{min}, a lower limit to the SCI yield. Figure 1 shows the experimental data, from which ϕ_{min} was derived.

$$\frac{d[\mathrm{SO_2}]}{d[\mathrm{O_3}]} = \varphi.f \qquad \text{(E2)}$$

The lower limit criterion applies as in reality f will be less than one, at experimentally accessible SO_2 levels, as a small fraction of the SCI will still react with trace H_2O present, or undergo decomposition. The actual yield, $\phi_{\mathrm{ISOP\text{-}SCI}}$, 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 $[H_2O]$, to determine k_3/k_2 and k_d/k_2 (see Section 2.2.2), through an iterative process to determine the single unique value of $\varphi_{\mathrm{ISOP\text{-}SCI}}$ which fits both datasets.

2.2.2 *k*(SCI+H_2O)/*k*(SCI+SO_2) and k_d/*k*(SCI+SO_2)

By rearranging Equation E1, the following equation (E3) can be derived. Therefore, in order to determine the relative rate constants k_3/k_2 and $(k_d+L)/k_2$, a series of experiments were performed in which the SO_2 loss was monitored as a function of $[H_2O]$ (see Section 2.1).

$$[SO_2](\frac{1}{f}-1)=\frac{k_3}{k_2}[H_2O]+\frac{k_d+L}{k_2} \qquad \text{(E3)}$$

From Equation E2, regression of the loss of ozone (dO_3) against the loss of SO_2 (dSO_2) for an experiment at a given RH determines the product $f.\phi$ 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, ΔSO_2 and ΔO_3, (as shown in Figure 2) to determine dSO_2/dO_3 (and hence $f.\phi$) at the start of each experiment, for use in Equation E3. This fit was derived using a box model run in FACSIMILE (Curtis and Sweetenham, 1987) with a chemical scheme taken from MCM,v3.2 (http://mcm.leeds.ac.uk/MCM), with additional updated SCI chemistry constrained by the experimental measurements. The start of each experiment (*i.e.* when $[SO_2] \sim 50$ ppbv) was used as this corresponds to the greatest rate of production of the SCI, and hence largest experimental signals (*i.e.* 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). The value $[SO_2]((1/f) - 1)$ can then be regressed against $[H_2O]$ for each experiment to give a plot with a gradient of k_3/k_2 and an intercept of $(k_d + L)/k_2$ (Equation E3). Our data 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, which may be placed on an absolute basis through use of an (external) reference value ($k_2(CH_2OO + SO_2)$ in this case).

2.2.3 *k*(SCI+DMS)/*k*(SCI+SO_2)

A similar methodology was applied to that detailed in Section 2.2.2 to determine the relative reaction rate of ISOP-SCI with DMS *k*(SCI+DMS)/*k*(SCI+SO_2), k_8/k_2. Here, the SO_2 loss was determined as a function of [DMS] rather than $[H_2O]$. $[H_2O]$ was $< 1 \times 10^{16}$ molecules cm^{-3} for all experiments.

$$\mathrm{SCI + DMS} \xrightarrow{k_8} \mathrm{Products} \qquad \text{(R8)}$$

Equation E3 is modified to give Equation E4 by the addition of the DMS term. The gradient of a plot regressing $[SO_2]((1/f) - 1)$ against [DMS] is then k_8/k_2 and the intercept is $k_3/k_2[H_2O] + (k_d + L)/k_2$. Using this intercept, these experiments can also be used to validate the k_3/k_2 and $(k_d + L)/k_2$ values derived from the experiments described in Section 2.2.

$$[SO_2](\frac{1}{f} - 1) = \frac{k_8}{k_2}[DMS] + \frac{k_3}{k_2}[H_2O] + \frac{k_d + L}{k_2} \qquad \text{(E4)}$$

3 Isoprene + Ozone as a function of $[H_2O]$

3.1 SCI Yield

Figure 1 shows the derived ϕ_{min} for isoprene, 0.55, determined from fitting Equation E2 to the experimental data. ϕ_{min} was then corrected (< 3%) as described in Section 2.2.1 using the k_3/k_2 and k_d/k_2 values determined from the measurements shown in Figure 3 using Equation E5. The corrected yield, $\phi_{ISOP\text{-}SCI}$, is 0.56 (± 0.03). Uncertainties are ± 2σ, and represent the combined systematic (estimated measurement uncertainty) and precision components.

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Literature yields for SCI production from isoprene ozonolysis are given in Table 1. The value derived for the yield in this work agrees very well with the value of 0.58 (± 0.26) from a recent experimental study (Sipilä et al., 2014) which used a similar single-SCI analysis approach.

Earlier experimental studies have reported lower values (by up to a factor of 2) for the total isoprene SCI yield. Rickard *et al.* (1999) derive a total yield of 0.28 from the increase in primary carbonyl yield (MVK and MACR) in the presence of a suitable SCI scavenger (excess SO_2). However, owing to the fact that they could not measure a formaldehyde yield, in their analysis it was assumed that 40 % of the chemically activated CH_2OO formed was stabilised (derived from the measured CH_2OO SCI yield for ethene ozonolysis), corresponding to their determination of a CH_2OO SCI yield of 0.18 for isoprene ozonolysis. If it is assumed that 95% of the CH_2OO formed was actually stabilised, as calculated by Zhang *et al.* (2002), then this yield increases to 0.43, giving a total yield, $\phi_{ISOP\text{-}SCI}$, of 0.53, in

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excellent agreement with the current work. Hasson et al. (2001) calculated a total SCI yield of 0.26 by measuring the sum of the difference between (i) the H_2O_2 production under dry and high RH conditions (to give the non-CH_2OO SCI yield) and (ii) the difference between hydroxyl-methyl hydroperoxide (HMHP) production under dry and high RH conditions (to give ϕ_{CH2OO}). One potential reason for the significantly lower total SCI calculated by Hasson et al. compared to this work is the low value of ϕ_{CH2OO} determined, potentially due to HMHP losses. Neeb et al. (1997) determined a value for ϕ_{CH2OO} approximately twice that determined by Hasson et al., using a similar methodology. This discrepancy may be owing to the fact that Hasson et al. do not account for the formation of formic acid, which is a degradation product of HMHP. From theoretical calculations, Zhang *et al.* (2002) predicted a yield of 0.31 for CH_2OO, the most basic SCI, 0.14 for *syn*-MVKOO, 0.07 for *anti*-MVKOO, 0.04 for *anti*-MACROO and 0.01 for *syn*-MACROO. This gives a sum of SCI yields of 0.57, again in very good agreement with the overall value derived here. The MCM (Jenkin et al., 1997; Saunders et al., 2003) applies a $\phi_{ISOP\text{-}SCI}$ of 0.22, based on the limited experimental data available at the time of its original release (Jenkin et al., 1997). Although this total value is slightly lower than the experimental measurements reported prior to the release of MCMv3.2 (i.e. Rickard et al. (1999) and Hasson et al. (2001)), the protocol uses a similar relative yield for stabilised-CH_2OO (0.50) compared to the total SCI yield as reported by Zhang et al. (2002). A probable reason for the low SCI yields in the MCM is the assumption of low stabilisation of the chemically activated CI formed.

The CH_2OO yield (ϕ_{CH2OO}) from isoprene ozonolysis derived in this work can be calculated by multiplying the total SCI yield (0.56) by the fraction of the total SCI yield predicted to be CH_2OO by Zhang *et al.* (2002) (0.54). This gives a yield of stabilised CH_2OO from this work of 0.30. This is in very good agreement with Neeb *et al*. (1997) who derived a yield of stabilised CH_2OO from isoprene ozonolysis of 0.30 by measuring hydroxymethyl hydroperoxide formation (HMHP, the product of $CH_2OO + H_2O$).

3.2 Analysis 1: Single SCI (ISOP-SCI) treatment

Figure 2 shows the cumulative consumption of SO_2 relative to that of O_3, ΔSO_2 versus ΔO_3 (after correction for dilution), for each isoprene ozonolysis experiment as a function of [H_2O]. A fit to each experiment, which has the sole purpose of extrapolating the experimental data to evaluate dSO_2/dO_3 at t = 0 (start of each experimental run) for use in Equations E1 - E3, is

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also shown. This fit is derived using a box model run in FACSIMILE (Curtis and Sweetenham, 1987) as described in Section 2.2.2. The overall change in SO_2, ΔSO_2, is seen to decrease substantially with increasing humidity over a relatively narrow range of $[H_2O]$ (0.4 – 21 × 10^{16} cm^{-3}). This trend is similar to that seen for smaller, structurally less complex alkene ozonolysis systems (Newland et al., 2015), and is as would be expected from the understood chemistry (R1 – R5), as there is competition between SO_2, H_2O, and decomposition for reaction with the SCI formed.

Other potential fates for SCIs under the experimental conditions presented here include reaction with other reactants / co-products: ozone (Kjaergaard et al., 2013; Vereecken et al., 2014; Wei et al., 2014), other SCI (Su et al., 2014; Vereecken et al., 2014), carbonyl products (Taatjes et al., 2012), acids (Welz et al., 2014), or the parent alkene itself (Vereecken et al., 2014). Sensitivity analyses were performed using a box model run in FACSIMILE (Curtis and Sweetenham, 1987) with a chemical scheme taken from the MCM, with additional updated SCI chemistry. Based on reported reaction rates of ozonolysis products with SCIs, these analyses indicate that the only reaction partners likely to compete significantly with SO_2, H_2O or unimolecular decomposition under the experimental conditions applied here are organic acids (i.e. HCOOH and CH_3COOH); these formed during the experiments, at concentrations reaching up to 2.5 × 10^{12} cm^{-3}. All other potential co-reactants listed above were calculated to account for < 10 % (for the worst case run) of the total SCI loss under the experimental conditions applied.

Model runs were performed in which a rate constant of 1.1 × 10^{-10} cm^3 s^{-1} was used for reaction between SCI and formic and acetic acids (HCOOH, CH_3COOH), as given by Welz et al. (2014) for CH_2OO + HCOOH, together with an acid yield of 0.5 from the reactions of isoprene derived SCI species with water, which gave a good agreement with the experimentally determined acid yields measured by FTIR. The reduction in SO_2 loss between the model runs with the SCI + acid reaction included, and those without the reaction, varied between 7 % and 17 %.

Equation E3 can be extended to explicitly account for the presence of acids by inclusion of a further term (Equation E5). This requires a value for k_9/k_2, the ratio of the rate constants for SCI reactions with acids and with SO_2. Here, we employ a value of 3.0, derived from the mean of the recently reported rates of reaction of CH_2OO with HCOOH and CH_3COOH (Welz et al., 2014), and the rate constant for CH_2OO + SO_2 reported by Welz et al. (2012) –

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although in reality this term represents potential reaction of all SCI present with multiple acid species. The acid concentrations are taken from FTIR measurements during the experiments.

$$\mathrm{SCI + acid} \xrightarrow{k_9} \mathrm{Products} \qquad \text{(R9)}$$

$$[\mathrm{SO_2}](\frac{1}{f}-1)-\frac{k_9}{k_2}[Acid]=\frac{k_3}{k_2}[\mathrm{H_2O}]+\frac{k_d+L}{k_2} \qquad \text{(E5)}$$

Figure 3 shows a fit of Equation E5 to the data shown in Figure 2, giving a gradient of k_3/k_2, and an intercept of the (relative) rate of SCI decomposition (k_d + L)/k_2. The results are well described by the linear relationship (E5) across the full range of experimental conditions. This suggests that the analytical approach described – of treating the SCI produced from isoprene ozonolyis as a single system – provides a good quantitative description of the ISO-SCI/O_3/H_2O/SO_2 system under atmospheric boundary layer conditions, and hence provides a good approximation for use in atmospheric modelling studies. Reaction with the water dimer is not considered in this analysis (see discussion below). From Figure 3 it is apparent that the observations can be described well by a linear dependence on [H_2O] across the full range of experimental conditions applied. However, the humidity levels accessible in these experiments were limited (constrained by the operational range of the FTIR retrievals), and [H_2O] can range up to ~1 × 10^{18} cm^{-3} in the atmosphere; the derived relationship may work less well at these high RH as the role of the water dimer becomes more important; this is considered further in Section 3.3 (below) in which the SCI mix formed during isoprene ozonolysis is separated into CH_2OO and the other SCI formed.

From Figure 3, the derived relative rate constant for reaction of ISOP-SCI with water vs. SO_2, k_3/k_2, is 3.1 (± 0.5) × 10^{-5} (Table 2). Newland et al. (2015) recently reported a k_3/k_2 relative rate constant for CH_2OO of 3.3 (± 1.1) × 10^{-5} using the same experimental approach as used in this study. The value derived for ISOP-SCI here is the same, within uncertainty, as that derived for CH_2OO, suggesting that the other SCI formed during isoprene ozonolysis have a mean k_3/k_2 similar to that of CH_2OO.

No absolute values of k_2 (SCI+SO_2) have been measured for ISOP-SCI. However Welz et al. (2012) obtained an absolute value of k_2 (298 K) for CH_2OO (3.9 × 10^{-11} cm^3 s^{-1}), using direct methods at reduced pressure (a few Torr). If this value is used as an approximation for the k_2 value of ISOP-SCI (at atmospheric pressure and ambient temperature), then a k_3 (ISOP-SCI

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H_2O) value of 1.2 (± 0.2) × 10^{-15} cm^3 s^{-1} is determined (assuming the reaction between ISOP-SCI and water vapour is dominated by reaction with the water monomer, rather than the dimer, as discussed above).

From Equation E5, the intercept in Figure 3 gives the term (k_d + L)/k_2. (k_d + L) will be dominated by k_d under the experimental conditions applied and analysis extrapolation to the start of each experimental run; however, the possibility of other chemical loss processes (see below) dictates that the derived value for k_d is technically an upper limit. From Figure 3, k_d/k_2 is determined to be 3.0 (± 3.2) × 10^{11} cm^{-3} (Table 2). Using the k_2 value determined by Welz et al. (2012) to put k_d/k_2 on an absolute scale (as above for k_3) yields a k_d of ≤ 12 (± 12) s^{-1}. Newland et al. (2015) recently determined k_d for CH_2OO to be ≤ 4.7 s^{-1}. This suggests that either k_d for the non-CH_2OO SCI within the ISOP-SCI family is relatively low, *i.e.* a few tens s^{-1}, and/or that CH_2OO dominates the ISOP-SCI population. The limited precision obtained for these k_d values reflects the uncertainty in the intercept of the regression analysis shown in Figure 3.

Sipilä et al. (2014) recently reported a value of k_{loss}/k_2 for isoprene ozonolysis derived SCI, treated using a single-SCI approach, which is analogous to the value ($k_3[H_2O]$ + k_d)/k_2 reported in this section. They derive a value of 2.5 (± 0.1) × 10^{12} cm^{-3} at $[H_2O]$ = 5.8 × 10^{16} cm^{-3}. From the k_3 and k_d values derived in the single SCI analysis in this work (Table 2) we calculate a value of 2.1 (± 0.6) × 10^{12} cm^{-3} at the same $[H_2O]$, in good agreement.

The results presented here suggest that while SCI and conformer specific identification is important to determine the product yields, it does not appear to be important when solely considering the combined effects of isoprene ozonolysis products on the oxidation of SO_2 under the experimental conditions applied.

3.3 Analysis 2: Two-SCI species (CH_2OO + CRB-SCI) treatment

In the preceding section, the combined effects of the five SCI initially produced during isoprene ozonolysis were treated as a single pseudo-SCI, ISOP-SCI. In this section an alternative approach is presented, in which the SCI family is split into two components. These are: CH_2OO, for which the reaction rates with water and the water dimer have been quantified in recent experimental studies, and the sum of the MVKOO and MACROO SCI, denoted CRB-SCI.

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To date, the effects of the water dimer, $(H_2O)_2$ have only been determined experimentally for CH_2OO (Berndt et al., 2014; Chao et al., 2015; Lewis et al., 2015; Newland et al., 2015). Theoretical calculations (Vereecken et al., 2012) predicted the significant effect of the water dimer compared to the monomer for CH_2OO, but also that the ratio of the SCI + $(H_2O)_2$: SCI + H_2O rate constants, k_5/k_3, of the larger, more substituted SCI, *anti*-CH_3CHOO and $(CH_3)_2COO$, are 2 - 3 orders of magnitude smaller than for CH_2OO (Vereecken et al., 2012). This would make the dimer reaction negligible at atmospherically accessible $[H_2O]$ (*i.e.* $< 1 \times 10^{18}$ cm^{-3}) for SCI larger than CH_2OO. The results presented in Section 3.2 show that, under the single-SCI treatment of the isoprene ozonolysis SCI chemistry, a water monomer only approach is able to describe the experimental data. Hence the effect of the water dimer reaction on CRB-SCI is not considered in this analysis (the water dimer reaction is included for CH_2OO).

$$[SO_2](\frac{1}{f}-1)-\frac{k_9}{k_2}[Acid]=\gamma^A\left(\frac{k_3^A[H_2O]+k_5^A[(H_2O)_2]+(k_d^A+L^A)}{k_2^A}\right)+\gamma^C\left(\frac{k_3^C[H_2O]+(k_d^C+L^C)}{k_2^A}\right) \quad (E6)$$

where ^{A} denotes CH_2OO and ^{C} denotes CRB-SCI.

Figure 4 shows three fits, obtained using Equation E6 and corresponding to different treatments for the reaction of CH_2OO with H_2O and with $(H_2O)_2$, to the measured data presented in Figure 3. For all three scenarios, the relative contribution of the two SCI components to the total SCI yield (γ) was assumed to be $\gamma^A = 0.54$ and $\gamma^C = 0.46$, after Zhang *et al*. (2002). k_3^A/k_2^A is assumed to be 3.3×10^{-5} after Newland *et al.* (2015).

The solid red line in Figure 4 is a linear fit to the data to determine k_3^C and k_d^C. The CH_2OO + $(H_2O)_2$ rate constant, k_5^A, was assumed to be zero to reduce the number of free parameters. This assumption is reasonable considering the apparent linear dependence of the presented measurements on $[H_2O]$ across the full range of conditions applied. The linear fit determines a value of k_3^C/k_2^A = 2.9 (±0.7) × 10^{-5} and a value of $(k_d^C+L^C)/k_2^A$(CRB-SCI) = 6.6 (±7.0) × 10^{11} cm^{-3} (Table 2). Again, as for the single species analysis, the decomposition term is poorly constrained.

The dashed blue line fits Equation E6 using the parameters derived above for CRB-SCI and the water dimer relative reaction rate for CH_2OO determined in Newland *et al.* (2015), k_5/k_2 = 0.014 (± 0.018). This still gives a good fit to the data in Figure 4. The dotted green line is a similar fit but uses the recently directly determined CH_2OO + $(H_2O)_2$ rate, k_5^A, of 6.5 (± 0.8)

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× 10^{-12} cm^3 s^{-1} by Chao *et al.* (2015). It is seen that this fit considerably overestimates the observations at higher [H_2O]. However, owing to the quadratic relationship of [$(H_2O)_2$] to [H_2O] a small difference in the rate constant can have a large effect, especially at higher [H_2O]. Possible explanations for this discrepancy are: (i) that the kinetics observed for CH_2OO as formed from CH_2I_2 photolysis are not representative of the behaviour of the CH_2OO moiety as formed through alkene ozonolysis (although the conditions are such that a thermalized population would be expected in both cases); (ii) that the fraction of the total isoprene SCI yield that is CH_2OO is lower than that predicted by Zhang *et al*. (2002), hence the effect of the $(H_2O)_2$ reaction overall is reduced – however, the predicted yield is in good agreement with those determined experimentally, albeit using indirect methods, so it seems unlikely that the actual CH_2OO yield is considerably lower; (iii) multiple effects are affecting the curvature of the results shown in Figure 4. Analogous plots for CH_3CHOO shown in Newland *et al.* (2015) displayed a shallowing gradient with increasing [H_2O] (*i.e.* the opposite curvature to that caused by the $(H_2O)_2$ reaction). The probable explanation for the curvature observed for CH_3CHOO is the presence of a mix of *syn* and *anti* conformers (Scheme 2) in the system and the competing effects of the different kinetics of these two distinct forms of CH_3CHOO. A similar effect may arise for the isoprene derived CRB-SCI which include multiple *syn* and *anti* conformers (see Scheme 2). The competition of this effect with that expected from the water dimer reaction may effectively lead to one masking the other under the experimental conditions applied.

Rate data for the reactions of isoprene derived SCI obtained using both analytical approaches described are given in Table 2.

3.4 Atmospheric Implications

Treatment of the SCI produced from isoprene ozonolysis as a single SCI system appears to describe the observations well over the full range of experimental conditions accessible in this work (Section 3.2). The derived values for k_3(ISOP-SCI) reported here, obtained by fitting Equation E5 to the measurements, placed on an absolute basis using the measured k_2(CH_2OO + SO_2) of 3.9 × 10^{-11} cm^3 s^{-1} (Welz et al., 2012)), corresponds to a loss rate for ISOP-SCI from reaction with H_2O in the atmosphere of 340 s^{-1} (assuming [H_2O] = 2.8 × 10^{17} molecules cm^{-3}, equivalent to an RH of 65 % at 288 K). Comparing this to the derived k_d value, 12 (±12) s^{-1}, it is seen that reaction with H_2O is predicted to be the main sink for isoprene derived SCI

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in the atmosphere, with other sinks, such as decomposition and other bimolecular reactions, being negligible. Hence k_d is neglected in the following analysis.

An estimate of a mean steady state ISOP-SCI concentration in the background atmospheric boundary layer can be calculated using Equation E7.

$$[ISOP-SCI]_{ss} = \frac{[\text{Isoprene}][\text{O}_3]k_1\phi}{k_3[\text{H}_2\text{O}]} \qquad \text{(E7)}$$

Using the data given below, a steady state SCI concentration of 4.1×10^2 molecules cm^{-3} is calculated for an isoprene ozonolysis source. This assumes an ozone mixing ratio of 40 ppbv, an isoprene mixing ratio of 1 ppbv, an SCI yield ϕ of 0.56, and a reaction rate constant k_1 (isoprene – ozone) of 1.0×10^{-17} cm^3 s^{-1} (288 K) (Atkinson et al., 2006); k_2 (ISOP-SCI + SO_2) of 3.9×10^{-11} cm^3 s^{-1}, k_3 (ISOP-SCI + H_2O) of 1.2×10^{-15} cm^3 s^{-1} with [H_2O] of 2.8×10^{17} cm^{-3} (RH ~ 65 % at 288 K). A typical diurnal loss rate of SO_2 to OH (k_{OH}[OH]) is 9×10^{-7} s^{-1} (Welz et al., 2012), while the SO_2 loss rate arising from reaction with ISOP-SCI, using the values above, would be 1.6×10^{-8} s^{-1}. This suggests, for the conditions given above, the diurnally averaged loss of SO_2 to SCI to be a very small fraction (1 – 2 %) of that due to OH. This analysis neglects additional chemical sinks for SCI, which would reduce SCI abundance, and the possibility of other alkene ozonolysis products leading to SO_2 oxidation which may increase the impact of alkene ozonolysis upon gas-phase SO_2 processing (Mauldin et al., 2012; Curci et al., 1995; Prousek, 2009). However, the analysis also neglects additional sources of SCI, *e.g.* photolysis of alkyl iodides (Gravestock et al., 2010; Stone et al., 2013), dissociation of the dimethyl sulfoxide (DMSO) peroxy radical (Asatryan and Bozzelli, 2008; Taatjes et al., 2008), and reactions of peroxy radicals with OH (Fittschen et al., 2014), which are currently poorly constrained and may even dominate SCI production over an ozonolysis source in some environments.

SCI concentrations are expected to vary greatly depending on the local environment, *e.g.* alkene 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, isoprene emissions exhibit a diurnal cycle in forested environments owing to a strong temperature dependence, hence are predicted to change significantly in the future as a response to a changing climate and other environmental conditions (Peñuelas and Staudt, 2010).

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4 Isoprene + Ozone as a function of DMS

4.1 Results

A series of experiments analogous to those reported in Section 3 were performed as a function of dimethyl sulfide concentration, [DMS], rather than [H_2O]. Figure 5 shows that SO_2 loss in the presence of isoprene and ozone is increasingly inhibited by the presence of greater amounts of DMS. Under the experimental conditions applied, it is assumed that the SCI produced in isoprene ozonolysis are reacting with DMS in competition with SO_2 (Reaction R8).

Equation E4 is analogous to Equation E3 but for varying [DMS] rather than [H_2O]. However, as for the isoprene + O_3 as a function of water experiments described in Section 3, there is potential for the acid products of the isoprene ozonolysis reaction to provide an additional sink for SCI in the chamber. Using the same methodology as described in Section 3.2, an explicit acid term was included in Equation E4 to give Equation E8.

$$[\mathrm{SO_2}]\left(\frac{1}{f}-1\right)-\frac{k_9}{k_2}[Acid]=\frac{k_8}{k_2}[\mathrm{DMS}]+\frac{k_3}{k_2}[\mathrm{H_2O}]+\frac{k_d+L}{k_2} \qquad \text{(E8)}$$

Figure 6 shows a fit of Equation E8 to the experimental data. This yields a gradient of k_8/k_2 and an intercept of $(k_3[H_2O] + k_d + L)/k_2$. The derived relative rate constant of $k(SCI+DMS)/k(SCI+SO_2)$, k_8/k_2, using this method is 3.5 (± 1.8). Using the absolute value of $k_2(CH_2OO + SO_2)$ derived by Welz et al. (as described previously) determines a value of k_8 = 1.4 (± 0.7) × 10^{-10} cm^3 s^{-1} (Table 2).

The intercept of the linear fit in Figure 6 is 1.0 (± 1.7) × 10^{12} cm^{-3}. This represents $(k_3[H_2O] + k_d + L)/k_2$ and hence can also be compared with the kinetic parameters derived in Section 3 from the isoprene + O_3 as a function of H_2O experiments. From Figure 3, $(k_d + L)/k_2$ = 3.0 (± 3.2) × 10^{11} cm^{-3} and $k_3 [H_2O] / k_2$ = 2.5 (± 0.4) × 10^{11} cm^{-3} (with [H_2O] = 8 × 10^{15} cm^{-3}, the mean of the values for the five DMS experiments (6.7 – 8.8 × 10^{15} cm^{-3})), giving a combined value of 5.5 (± 3.2) × 10^{11} cm^{-3}. These two values therefore agree within the precision of the data.

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4.2 Experimental Uncertainties

As noted above, this analysis assumes that the multiple SCI species in reality present in the ozonolysis system may be analysed as a single species (or exhibit the same reactivity). While the data indicate that this approximation satisfactorily describes the observed behaviour under the conditions applied, other work (*e.g.* Taatjes et al., 2013) has shown that reactivity of different SCIs, and different conformers of the same SCI, can differ, affecting the retrieval of kinetics in multi-SCI ozonolysis systems; Newland et al. (2015) have illustrated this effect in the case of *syn*- and *anti*-CH_3CHOO. Similarly, the response of the SCI population to reaction with organic acids is approximated by a single reaction with those species observed (i.e. HCOOH, CH_3COOH). A further assumption made is that the mean isoprene-SCI + SO_2 reaction rate may be represented by that directly measured for CH_2OO with SO_2 (Welz et al., 2012). These approximations introduce systematic uncertainty into the derived rate constants, but given the lack of fundamental data for individual SCI isomers, it is not possible to evaluate this. The data obtained are well within the capability of the experimental approaches: DMS levels were inferred from the known volumetric addition to the chamber and are thought unlikely to be significantly in error. O_3 and isoprene were monitored using well-established techniques at levels well above their detection limits. The observed changes in SO_2 removal upon addition of DMS (as shown in Figure 5) were substantial, well in excess of the sensitivity limit and uncertainty of the SO_2 monitor. However, it is important to note that no constraints regarding the products of the proposed DMS + SCI reaction were obtained; OH reaction with DMS is complex, proceeding through both abstraction and addition/complex formation channels, the latter rendered partially irreversible under atmospheric conditions through subsequent reaction with O_2 (Sander et al., 2011). The observed behaviour (Figure 5) is not consistent with reversible complex formation dominating the SCI-DMS system under the conditions used; however it is possible that decomposition of such a complex to reform DMS, or its further reaction (*e.g.* with SO_2, analogous to the secondary ozonide mechanism proposed by Hatakeyama et al., 1986) would be consistent with the observed data, and also imply that the reaction may not lead to net DMS removal. Time-resolved laboratory measurements and product studies are needed to provide a test of this mechanistic possibility.

4.3 Discussion and Atmospheric Implications

To the authors' knowledge, this is the first work to show the relatively fast (in relation to other recently determined SCI bimolecular reactions, e.g. SCI + SO_2 and NO_2, and the well established OH + DMS reaction) rate of reaction of SCI with DMS, although the products have yet to be identified. While this work presents only SCI derived from isoprene ozonolysis, it seems likely that the fast reaction rate will apply to all SCI (though the precise rate will be structure dependent).

DMS is mainly produced as a by-product of phytoplankton respiration and so the highest concentrations are found in marine coastal environments or above active phytoplankton blooms. Furthermore, Jardine et al. (2015) have recently shown that DMS mixing ratios within and above a primary Amazonian rainforest ecosystem can reach levels of up to 160 pptv, in canopy and above the surface, for periods of up to 8 hours during the evening and into the night, with levels peaking at 80 pptv above canopy.

SCI can also be expected to be present in the marine environment. As already discussed, mixing ratios of isoprene (Sinha et al., 2007; Yassaa et al., 2008) and monoterpenes (Yassaa et al., 2008) have been reported to reach in the region of hundreds of pptv over active phytoplankton blooms in the marine boundary layer. Additionally, the emission of small alkenes from coastal waters has been observed (Lewis et al., 1999). Furthermore, the photolysis of alkyl iodides (prevalent in the coastal environment (Jones et al., 2010)) may be a significant source of SCI (Stone et al., 2013). Berresheim et al. (2014) have suggested that small SCI derived from alkyl iodide photolysis may be responsible for observed H_2SO_4 production, in excess of that expected from measured SO_2 and OH concentrations, at the coastal atmospheric observatory Mace Head, Ireland. Jones et al. (2014) proposed SCI produced from alkyl iodide photolysis as a possible source of surprisingly high formic acid concentrations observed in the marine environment in the European Arctic. Other non-ozonolysis sources of SCI include dissociation of the dimethyl sulfoxide (DMSO) peroxy radical (Asatryan and Bozzelli, 2008; Taatjes et al., 2008) (which could be an important source in the marine environment, where DMSO is an oxidation product of OH + DMS), and potentially from reactions of peroxy radicals with OH in remote atmospheres (Fittschen et al., 2014).

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From the analysis in Section 3.4 a concentration of ISOP-SCI of 4.1 × 10^2 molecules cm^{-3} was calculated, assuming an isoprene concentration of 1 ppbv. In a remote marine

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environment isoprene concentrations are probably an order of magnitude lower than this and consequently [ISOP-SCI] would be calculated to be on the order of 4 × 10^1 molecules cm^{-3}. However, some regions will be impacted by both high isoprene and DMS concentrations, for example tropical islands, such as Borneo, which can have high isoprene concentrations and are strongly influenced by marine air masses (MacKenzie et al., 2011), as well as significant terrestrial sources from vegetation and soils in the Amazon, especially into the evening and at night (Jardine et al., 2015), when ozonolysis chemistry is at its most effective relative to photochemical OH chemistry. High sulfate composition of organic aerosols collected from the Borneo rain forests likely arises from the chemical processing of oceanic emissions of DMS and SO_2 (Hamilton et al., 2013). The sulphate content of aerosols was observed to increase further over oil palm plantations in Borneo, where isoprene concentrations may reach levels on the order of tens of ppbv (MacKenzie et al., 2011), indicating scope for alkene ozonolysis – DMS chemical interactions to become significant. If a diurnally averaged [OH] is taken as 5 × 10^5 molecules cm^{-3} then the loss rate of DMS to OH is ~ 3.5 × 10^{-6} s^{-1} while the loss to ISOP-SCI, at a concentration of 1 × 10^2 cm^{-3}, is ~ 2 × 10^{-8} s^{-1}, *i.e.* about 0.4 % of the loss to OH. However in an environment with particularly high isoprene mixing ratios, such as over the oil palm plantations in Borneo this could rise to a few percent.

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SCI derived from isoprene ozonolysis are unlikely to compete with OH during the day-time or NO_3 during the night, as an oxidant of DMS. However, alternative SCI sources have been suggested which may lead to significantly higher SCI concentrations in marine environments those predicted from ozonolysis alone. Further investigation is required to clarify the reasons for the observed discrepancies in SO_2 and DMS oxidation and the possibility that these may be, at least in part, explained by the presence of SCI, dependent on the products of SCI-DMS interactions. SCI are most likely of a similar importance to other minor reaction channels for DMS processing such as reaction with atomic chlorine or BrO, reported to have a reaction rate constant of ~3.4 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298K (Atkinson et al., 2004) and marine boundary layer concentrations on the order of 10^3 - 10^4 molecules cm^{-3} (von Glasow and Crutzen, 2007). SCI may be most important for DMS oxidation during the evening period and early morning periods, when OH and NO_3 production are both relatively low.

5 Conclusions

Isoprene ozonolysis leads to gas-phase SO_2 removal, which decreases significantly with increasing water vapour. This trend is consistent with production of stabilised Criegee intermediates (SCIs) from the ozonolysis reaction, and the subsequent reaction of these species with SO_2 or H_2O. Competition between H_2O and SO_2 for reaction with the SCI leads to this observed relationship, in which SCI abundance is sensitive to water vapour concentration, even at the dry end of the range found in the troposphere (ca. 1 – 20 % RH). The kinetics of this system can be described well by treatment of the SCI population as a single pseudo-SCI species under the experimental conditions applied, allowing for relatively easy integration into atmospheric chemical models. The results indicate that SCI derived from isoprene ozonolysis are unlikely to make a substantial contribution to atmospheric SO_2 oxidation and hence sulphate aerosol formation in the troposphere.

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Furthermore we show, for the first time, that SO_2 loss in the presence of isoprene and ozone significantly decreases with the addition of dimethyl sufide (DMS). The data suggest a fast reaction of isoprene derived SCI with DMS. However, the exact mechanistic nature of the reaction, including the likely oxidation products, need to be elucidated. This result has implications for the oxidation of DMS in the atmosphere. Although it seems unlikely that SCI produced from isoprene ozonolysis alone are important for DMS oxidation, it is possible that (the sum of) SCI species produced from other alkene-ozone reactions, or from other (photo)chemical sources (which may be prevalent in the marine boundary layer), could be a significant source of DMS oxidant under certain atmospheric conditions, and hence influence new particle formation above environments influenced by emissions of unsaturated hydrocarbons and DMS.

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

$\phi_{ISOP-SCI}$	**Reference**	**Methodology**
0.56 (± 0.03)	This work	SO_2 loss
0.58 (± 0.26)	Sipilä *et al.* (2014)	Formation of H_2SO_4
0.30 (ϕ_{CH2OO})[a]	Neeb *et al.* (1997)	HMHP[b] yield
0.26	Hasson *et al.* (2001)	Sum of difference between HMHP and H_2O_2 yields at high / low [H_2O]
0.28	Rickard *et al.* (1999)	Assumes stabilisation of 40% of CH_2OO produced + difference between MVK and MACR production at high / low [SO_2]
0.53	Rickard *et al.* (1999)	Assuming 95% of CH_2OO is stabilised (after Zhang *et al.* [23]) + difference between MVK and MACR production at high / low [SO_2]
0.57	Zhang *et al.* (2002)	Theoretical
0.22	MCMv3.2[c]	Based on a weighted average of the yields for propene, 1-octene and 2-methyl propene.

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 $C_5H_8 + O_3$ and were conducted between 700 and 760 Torr. [a] Yield of stabilised CH_2OO only, [b] Hydroxymethyl hydroperoxide (a first order product of $CH_2OO + H_2O$). c http://mcm.leeds.ac.uk/MCM/ (Jenkin et al., 1997).

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Table 2. Isoprene derived SCI relative and absolute rate constants derived in this work [a]

SCI	$10^5\ k_3/k_2$	$10^{15}\ k_3$ ($cm^3\ s^{-1}$)	$10^{-11}\ k_d/k_2$ (cm^{-3})	k_d (s^{-1})	k_8/k_2	$10^{10}\ k_8$ ($cm^3\ s^{-1}$)
CH_2OO[b]	3.3 (±1.1)	1.3 (±0.4)	-2.3[c] (±3.5)	-8.8[c] (±13)		
ISOP-SCI	3.1 (±0.5)	1.2 (±0.2)	3.0 (±3.2)	12 (±12)	3.5 (±2.2)	1.4 (±0.7)
CRB-SCI	2.9 (±0.7)	1.1 (±2.7)	6.6 (±7.0)	26 (±27)		

Uncertainty ranges (± 2σ, parentheses) indicate combined precision and systematic measurement error components. [a] Scaled to an absolute value using $k_2(CH_2OO) = 3.9 \times 10^{-11}\ cm^3\ s^{-1}$ (Welz et al., 2012). [b] From Newland *et al.* (2015). [c] Values are indistinguishable from zero within the measurement uncertainties.

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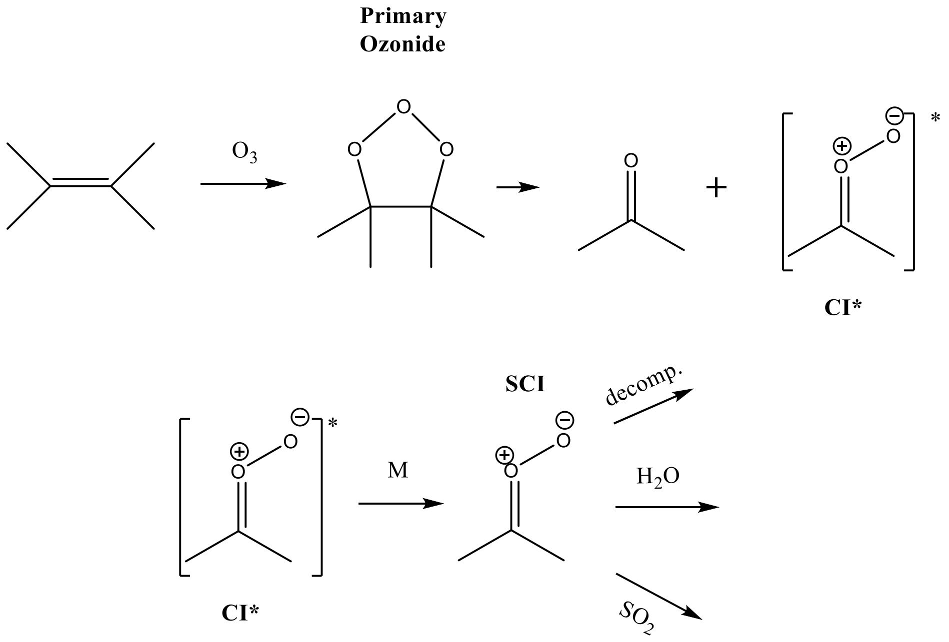
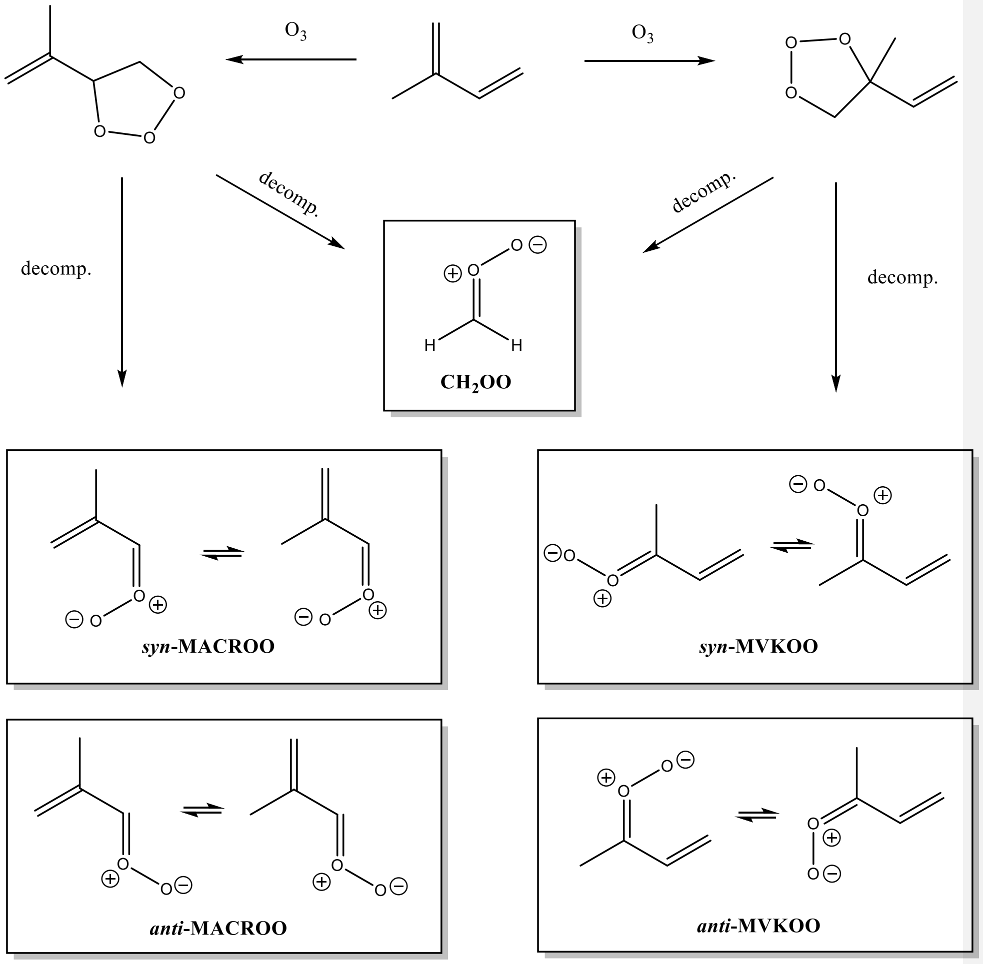


Scheme 1. Simplified generic mechanism for the reaction of Criegee Intermediates (CIs) formed from alkene ozonolysis.



Scheme 2. Mechanism of formation of the nine possible Criegee Intermediates (CIs) from isoprene ozonolysis.

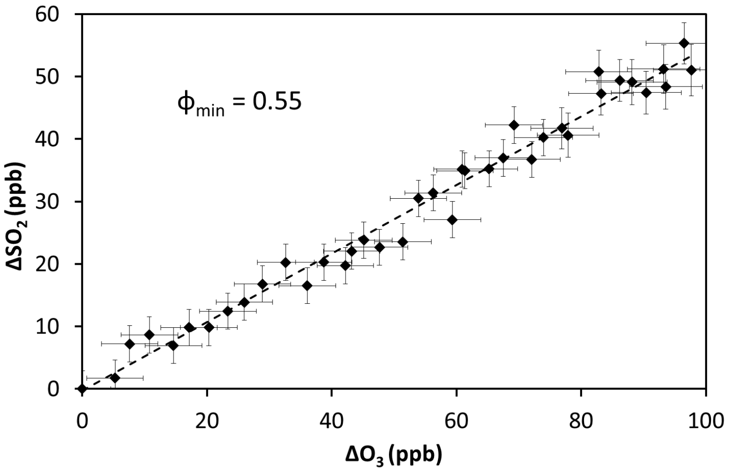


Figure 1. ΔSO_2 .vs. ΔO_3 during the excess SO_2 experiments ($[H_2O] < 5 \times 10^{15}$ cm^{-3}). The gradient determines the minimum SCI yield (ϕ_{min}) from isoprene ozonolysis.

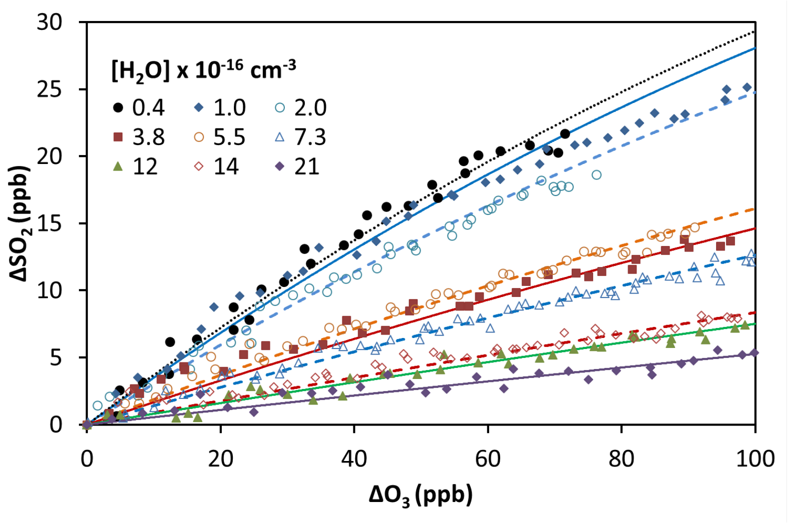


Figure 2. Cumulative consumption of SO_2 and O_3, ΔSO_2 versus ΔO_3, for the ozonolysis of isoprene in the presence of SO_2 at a range of water vapour concentrations, from 4×10^{15} cm^{-3} to 2.1×10^{17} cm^{-3}. Symbols are experimental data corrected for chamber dilution. Lines are smoothed fits to the experimental data.

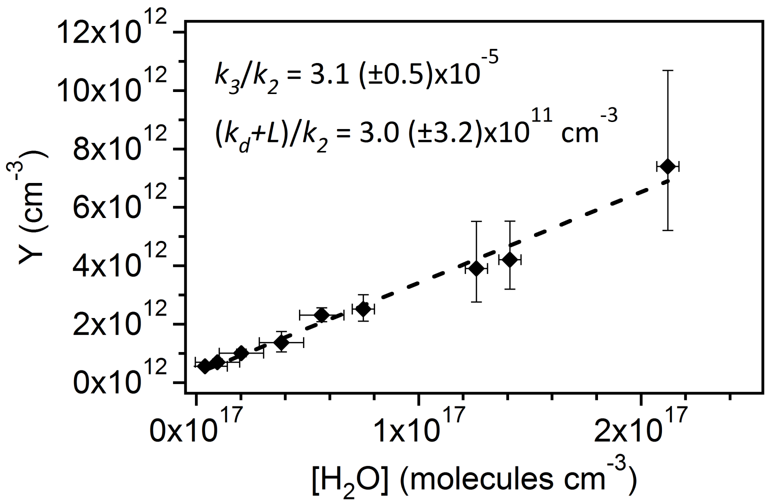


Figure 3. Application of Equation E5 to derive relative rate constants for reaction of the isoprene derived SCI with H_2O (k_3/k_2) and decomposition ($(k_d+L)/k_2$). Y = [SO_2]((1/f)-1) – k_9[acid]/k_2 .

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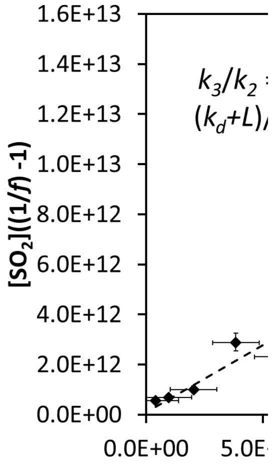

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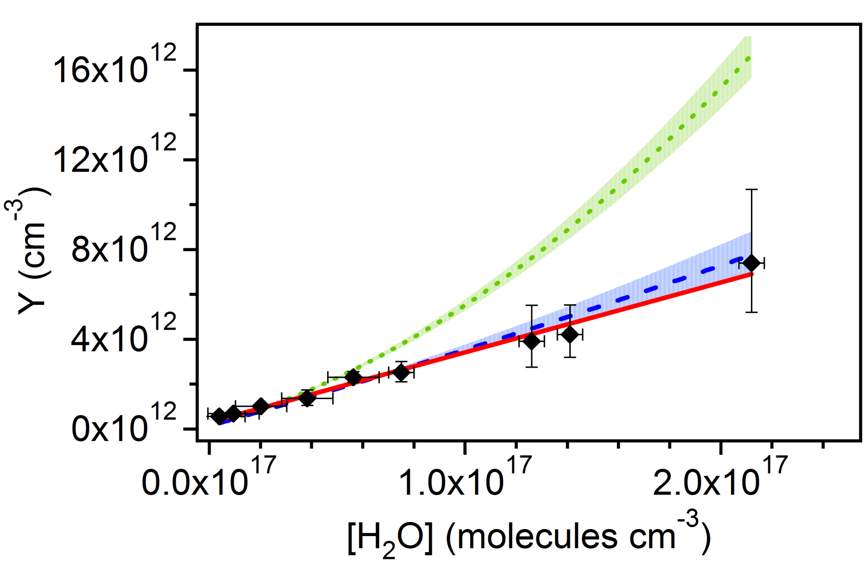

Figure 4. Application of Equation E5 to derive relative rate constants for reaction of the sum of the MVKOO and MACROO SCI (CRB-SCI) with the water monomer, and the decomposition rate. Red line: water monomer only reactions; blue dashed line: water monomer reaction and CH_2OO water dimer reaction rate from Newland et al. (2015); green dotted line: CH_2OO water dimer reaction rate from Chao et al. (2015). Shaded areas indicate reported uncertainties on dimer reaction rates. Y = $[SO_2]((1/f)-1) – k_9[\text{acid}]/k_2$.

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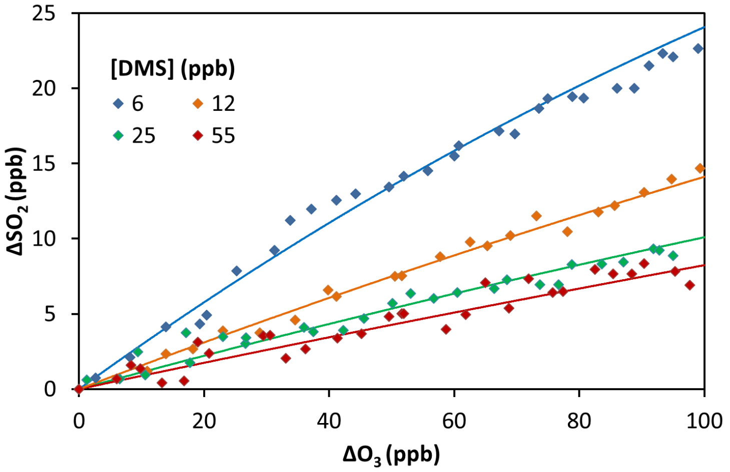

Figure 5. Cumulative consumption of SO_2 and O_3, ΔSO_2 versus ΔO_3, for the ozonolysis of isoprene in the presence of SO_2 at a range of DMS concentrations, from 6 ppbv to 55 ppbv. $[H_2O]$ in all experiments was $< 9 \times 10^{15}$ cm^{-3}. Markers are experimental data, corrected for chamber dilution. Solid lines are smoothed fits to the experimental data.

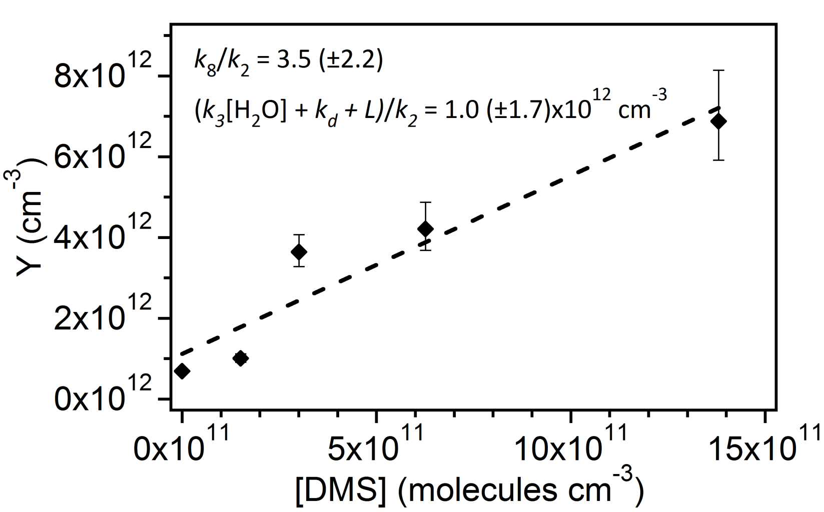

Figure 6. Application of Equation E8 to derive rate constants for reaction of ISOP-SCI with DMS (k_8) relative to that for reaction with SO_2. Y = $[SO_2]((1/f)-1) – k_9[acid]/k_2$.

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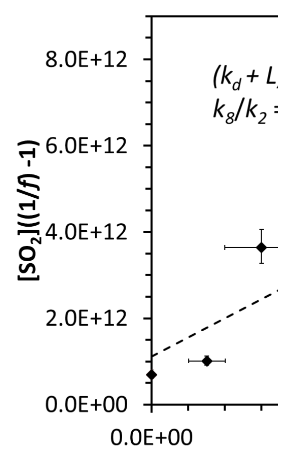

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