

Anonymous Referee #2

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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 SO₂, H₂O 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 $1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ is used for $\text{SCI} + \text{HCOOH}$, as determined by Welz et al. (2014) for $\text{CH}_2\text{OO} + \text{HCOOH}$, and a yield of 0.5 for HCOOH from $\text{ISOPOO} + \text{H}_2\text{O}$, which gives good agreement with the acid yields measured by FTIR. The reduction in SO_2 loss between the model runs without the $\text{HCOOH} + \text{SCI}$ 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 than 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 $k(\text{acid} + \text{SCI})/k_2$ 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.

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Model runs were performed in which a rate constant of $1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ was used for reaction between SCI and formic and acetic acids (HCOOH , CH_3COOH), as given by Welz et al. (2014) for $\text{CH}_2\text{OO} + \text{HCOOH}$, 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 $\text{SCI} + \text{acid}$ 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 $\text{CH}_2\text{OO} + \text{SO}_2$ 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.



$$[\text{SO}_2] \left(\frac{1}{f} - 1 \right) - \frac{k_9}{k_2} [\text{Acid}] = \frac{k_3}{k_2} [\text{H}_2\text{O}] + \frac{k_d + L}{k_2} \quad (\text{E5})$$

...”

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 CH₂OO) 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-CH₂OO) 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 $\Delta\text{SO}_2/\Delta\text{O}_3$ 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 $\Delta\text{SO}_2/\Delta\text{O}_3$ 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 k_8 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-CH₃CHOO. Similarly, the response of the SCI population to reaction with acids is approximated by a single reaction with those species observed (HCOOH, CH₃OOH). A further approximation is that the mean isoprene-SCI + SO₂ reaction rate may be represented by that measured for CH₂OO with SO₂ (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. O₃ and C₃H₈ were monitored using well established techniques at levels well above detection limits. The observed changes in SO₂ removal upon addition of DMS (Figure 5) was substantial, and well in excess of the sensitivity limit, and uncertainty, of the SO₂ 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 O₂ (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 SO₂, 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 SO₂ removal (i.e. the SCI).

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