

## Comment on “Kinetics of dimethyl sulfide (DMS) reactions with isoprene-derived Criegee intermediates studied with direct UV absorption” by Kuo et al., 2020.

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In the work described by Kuo et al. (2020) on the “*Kinetics of dimethyl sulfide (DMS) reactions with isoprene-derived Criegee intermediates studied with direct UV absorption*”, the authors generate SCI from the photolysis of di-iodo precursors, and use a UV absorption technique to demonstrate that the direct reactions of the SCI species CH<sub>2</sub>OO and (one conformer of) MVKOO with DMS are slow, with no observable effect of DMS on the rate of SCI loss under their experimental setup, and hence conclude these reactions to be unimportant in the atmosphere. A set of quantum chemical calculations (now added to the original version of the manuscript) on CH<sub>2</sub>OO + DMS come to similar conclusions.

The authors focus heavily on the differences between their observations and the only previous experimental study pertinent to these reactions, the chamber work of Newland et al. (2015a) looking at isoprene ozonolysis in the presence of DMS. The directly measured rate constants in the present study, for the reactions of CH<sub>2</sub>OO and a subset of the MVKOO stabilised Criegee intermediates, are several orders of magnitude lower than the aggregated relative rate constants determined by Newland et al. (2015a) for all conformers formed in isoprene ozonolysis, using an indirect technique. However, we feel that the main differences between the two complementary studies / techniques are important to interpret the results; and we highlight some considerations here. The earlier Newland et al. (2015a) study looks at the impact of an important atmospheric ozonolysis system as a whole, under representative boundary layer conditions, whereas the present work focuses more on the kinetics of two of the individual component SCI species that are formed in the ozonolysis of isoprene, but synthesised in the laboratory from the photolysis of di-iodo compounds. In this comment we would like to expand on this discussion, looking at how these complementary approaches can be used to give further chemical insight into the relatively complex mechanism of isoprene ozonolysis and its impact on atmospheric chemistry.

The experimental design and the relative rate methodology employed by Newland et al. (2015a) has previously been used to derive SCI yields and kinetic data (i.e.  $k(\text{H}_2\text{O})$ ,  $k(\text{H}_2\text{O})_2$  and  $k_d$  (unimolecular dissociation)) for small SCI species formed in a range of atmospherically important ozonolysis systems (namely CH<sub>2</sub>OO, *syn*-CH<sub>3</sub>CHOO, *anti*-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO). These experiments have provided an observational dataset, derived under atmospherically relevant conditions, that is consistent with the well understood general ozonolysis mechanism as well as kinetic data derived from direct literature measurements where individual SCI species are photolytically synthesised from suitable di-iodo precursors (see discussion and references in Newland et al., (2015b)). However, it is important to point out that the isoprene-ozone

system is significantly more complex than these previously studied ozonolysis systems, with a range of different SCI species formed, with different yields and exhibiting different bimolecular and unimolecular kinetics.

Isoprene ozonolysis forms five different initial carbonyl oxides (Scheme 2; Newland et al., (2015a)). The three basic species formed are formaldehyde oxide (CH<sub>2</sub>OO), methyl vinyl carbonyl oxide (MVKOO) and methacrolein oxide (MACROO). MVKOO and MACROO both have *syn* and *anti* conformers, and each of these can be in either a *cis* or *trans* configuration. Therefore 9 different types and configurations of SCI can be formed in the isoprene ozonolysis system under boundary layer conditions. It is clear from the literature that *syn* and *anti* SCI conformers exhibit significantly different unimolecular and bimolecular kinetics, affecting their atmospheric impacts<sup>1</sup>, as discussed in Newland et al. (2015b), and references within.

As noted in Kuo et al. (2020), owing to their high reactivity, and hence short lifetimes, detection of SCI species in the ambient atmosphere has yet to be successful, and direct laboratory studies of SCI kinetics have been challenging until the pioneering work of Taatjes, Percival and co-workers on using photolabile di-iodo precursors that give specific CI in an almost 100% stabilised form (Welz et al., (2012))<sup>2</sup>, the synthesis of which have been (until very recently) limited to only the smaller, simpler C<sub>1</sub>-C<sub>3</sub> CI species.

Therefore, in order to investigate the atmospheric impacts of isoprene derived SCI with SO<sub>2</sub>, water vapour and DMS, Newland et al. (2015a) employed an indirect relative rate technique in which the dependence of SO<sub>2</sub> removal in the isoprene-ozone system as a function of water vapour and dimethyl sulfide concentration was used to derive aggregated relative rate data where the combined kinetic effects of the SCI formed are treated as a single “pseudo-SCI” species and as a 2 body system (CH<sub>2</sub>OO + CRB-SCI). This experimental approach allows us to assess the atmospheric impact of a range of SCI formed in such an atmospherically important ozonolysis system. It is important to experimentally probe such systems under appropriate boundary layer conditions, which can also be chemically quite complex. The results of such experiments can then be used to drive complementary theoretical investigations as well as direct studies, once the experimental methods are available to synthesise and sensitively detect all of the individual SCI species involved (rather than individual conformers), the results of which can then be compared and contrasted to those from the atmospherically relevant complex system.

5 years on from the original Newland et al. (2015a) study, such methods are now available for MVKOO (Barber et al., 2018, Vansco et al., 2018, Vansco et al., 2019), which have subsequently been employed by Caravan et al. (2020) to look at the kinetics of *syn*-MVKOO with SO<sub>2</sub>, water vapour and formic acid and in the present study looking at a subset isoprene derived SCI reactions with DMS.

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<sup>1</sup> Note that the authors do not give the relative fractions of *syn* and *anti*-MVKOO formed in the photolysis of 1,3-diiodo-2-butene in the presence of oxygen under the conditions of their experimental set up. It would be useful to include the full distribution of conformers present.

<sup>2</sup> Note that the authors state that “*In fact, no direct detection of CIs has been known before Welz et al. reported a novel method to efficiently generate CIs other than through ozonolysis of alkenes*”. This is not in fact the case as Taatjes et al., (2008) directly detected the CH<sub>2</sub>OO Criegee, derived from photolytically-initiated CI oxidation of dimethyl sulfoxide (DMSO), in 2008.

In discussions on the likely causes of the differences seen between the two different studies, the authors state “Newland et al. monitored the consumption of SO<sub>2</sub> over a measurement period of up to 60 min until approximately 25% of isoprene was consumed (Newland et al., 2015). Additional uncharacterized sources and/or sinks of SO<sub>2</sub> and DMS would lead to a bias in the inferred rate coefficients. A more likely cause for the discrepancies is differences in chemical compositions of the studied reaction mixtures and, hence, the different impact of side reactions. While our direct measurements and kinetics are very straightforward, the ozonolysis experiments of Newland et al. might have been more complex than the authors (Newland et al., 2015) had assumed. For example, one may consider the possibility of converting DMS to SO<sub>2</sub> via surface or gas-phase reactions (Chen et al., 2018) under the complicated conditions of isoprene ozonolysis”

The potential complexities of the system are addressed in the discussion section of Newland et al. (2015a) and it may be useful for the present study to reflect aspects of this - as discussed in the uncertainties section of Newland et al. (2015a) – annotated with additional points in bold below: “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 (e.g. Veres et al., 2020) and addition/complex formation channels, the latter rendered partially irreversible under atmospheric conditions through subsequent reaction with O<sub>2</sub> (Sander et al., 2011). The observed behaviour of the experiments is not consistent with “non-reactive” reversible complex formation dominating the SCI-DMS system under the conditions used; however it is possible that “reactive” decomposition of such a complex, with DMS reformation (i.e. net isomerisation of the SCI), or its further “catalytic” reaction (e.g. with SO<sub>2</sub>, 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.” It is unlikely that heterogeneous chemistry is playing a role (as suggested by the Kuo et al.) given the experimental conditions employed (little aerosol formed, very low surface to volume ratio of ~ 1 m<sup>-1</sup> of the chamber limited any dark wall reactions – it may be instructive to compare this to the ratio for the laboratory set-up).

In conclusion, the chamber experiments performed by Newland et al. (2015a), under atmospherically relevant conditions, show a clear dependence of SO<sub>2</sub> removal in the isoprene + ozone system as a function of dimethyl sulfide concentration. Under the carefully designed (but chemically complex) conditions employed, this behaviour was interpreted to arise from a rapid reaction between isoprene-derived SCIs and DMS. However, in the light of the current study by Kuo et al. (2020) looking directly at individual CH<sub>2</sub>OO and MVKOO reactions with DMS, coupled to the theoretical work presented on the CH<sub>2</sub>OO + DMS system, it would appear that this observation may not be the result of a direct reaction with a stabilised Criegee intermediate – at least for those conformers formed in the Kuo et al. experiments. One explanation of this observation is that DMS could be acting to catalyze certain reactions, either chemically (by acting as a transfer intermediate) or energetically (e.g. energy release in complexation or lowering barriers by complexation without being a reaction partner). Some discussion on this is now given in the additional theoretical section of the

supplementary material to Kuo et al., (2020). Clearly there is still more work needed on the detailed atmospheric chemistry of isoprene ozonolysis. Higher level theory quantum chemical calculations and repeat experiments of isoprene ozonolysis in the presence of DMS, including the exploration of conformer-dependent reactivity, would be very timely and may reveal previously unidentified chemical pathways.

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