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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Kinetics of dimethyl sulfide (DMS) reactions with isoprene-derived Criegee intermediates studied with direct UV absorption" *by* Mei-Tsan Kuo et al.

Anonymous Referee #3

Received and published: 30 July 2020

Kuo et al. report direct experimental and theoretical investigations of the reactions of two isoprene-derived Criegee intermediates with dimethyl sulfide (DMS). Using the diiodoalkane/diiodoalkene photolysis method to selectively generate each Criegee intermediate in turn, the authors probe the kinetics by UV absorption and deduce upper limit rate coefficients that are orders of magnitude slower than those obtained in the ozonolysis work of Newland et al. using the relative rate technique. The slow rate coefficient measured in the present work for CH2OO + DMS is substantiated by stationary point calculations coupled with CTST that yield a rate coefficient of 5.5E-19 cm-3 s-1 at 298 K.

The paper is reasonably thorough and raises interesting discussion about ozonolysis vs. direct Criegee intermediate experimental kinetic studies, that have been significantly expanded by the other reviewers. The paper would benefit from some points of clarification (suggested below) and additional theoretical work on the MVK-oxide + DMS reaction to compare with the experimental results and contrast with the calculations on the CH2OO system. Please note that many of the comments in this review reflect the points that have already been raised in the thorough reviews of Rickard. Newland and Bloss, Blitz and the anonymous reviewer.

Main text

Page 2, line 33: The Welz et al. 2012 work is preceded by the Taatjes et al. JACS paper in which DMSO was used to generate the CH2OO Criegee intermediate.

Page 2, line 41: It is already established that ozonolysis experiments are by their very nature complicated – the authors should instead be more specific about the potential concerns they have regarding obtaining rate coefficients of Criegee intermediates from ozonolysis studies.

Page 2, line 51: The very recent Cox et al. paper in ACPD (https://www.atmos-chem-phys-discuss.net/acp-2020-472/) is also a thorough and up-to-date reference for existing studies of Criegee intermediate kinetics.

Page 3, line 90: A reference (or some further explanation) is needed regarding the MVKO precursor absorption at 308 nm.

Page 4, line 110: The authors should be able to determine an approximation of at least the MVK-oxide precursor concentration in their system. The vapor pressure of the precursor can be estimated using the Antoine coefficients. If the precursor was delivered to the reactor via a bubbler at a known flow rate, then the approximate concentration of the precursor can be deduced. In the event that the absorption coefficient of the precursor is deduced at a later date, this information would enable the concentration of

MVK-oxide used in the present work to be obtained.

Page 6, line 159: Under the present experimental conditions, CH3 would most likely undergo reaction with O2 to form CH3OO and so it would be best to compare the reactivity of CH3OO (rather than CH3) with I atom and Criegee intermediates.

Page 7, line 205: As the authors point out, there is currently significant uncertainty in the estimated and modelled steady state concentrations of Criegee intermediates. Because of this, it would be instructive to also frame the competitiveness of Criegee-initiated DMS oxidation vs. OH or NO3-initiated oxidation in terms of what concentration of Criegee intermediates are needed to oxidize a certain fraction (e.g. 5%, 10% or 20%) of atmospheric DMS using the theoretically determined rate coefficient.

Page 8, line 220. It seems peculiar that you have chosen to investigate theoretically only the CH2OO reaction and not the MVK-oxide reaction also. In MVK-oxide, the conjugation of the unsaturated side chain with the carbonyl oxide group has the potential to substantially alter the surface. These calculations are likely significantly more complex than for the CH2OO case because of the need to consider syn and anti conformers, and cis/trans forms of each of these. However, given the interesting structural and conformeric dependence of Criegee intermediate reactivity, it is a regretful omission.

Page 8, line 233: A reference is needed to substantiate the statement regarding high barriers for DMS C-H insertion.

Page 8, line 251: Do you anticipate stabilization of the (CH3)2SCH2OO adduct under tropospheric conditions?

Page 9, line 261: You hypothesize that surface reactions converting DMS to SO2 in the chamber study of Newland could be the source of discrepancy between the present work and the work of Newland et al. I encourage the authors to respond to the comments of Rickard, Newland and Bloss, and Blitz regarding this matter.

Figure 2: Please include a note to address if the error bars are included or not included

on this plot (as noted for Figure 4). Given that the rate coefficients for the self-reaction of CH2OO and the reaction of CH2OO + I (see Blitz review) are now well established, it would be pertinent to deduce which of these is the major source of increased loss rates at higher laser fluence are under your experimental conditions.

Supplementary information

Table S3: Because both the reaction forming MVK-oxide from the precursor + O2 reaction as well as the MVK-oxide + SO2 reaction features an adduct, the authors should label more caerefully the adduct referred to in the ‘adduct yield’ column of the table to avoid confusion.

Figures S1, S2: Provide details about error bars (c.f. comment about Figure 2).

Figure S4: Please discuss the proposed origin of the “spike” at time zero.

S10: These additional investigations are illuminating and interesting.

Additional comments regarding MVK-oxide conformers

I would like to add some discussion to the comments made by other reviewers regarding which conformers of MVK-oxide are produced from the photolytic scheme vs. ozonolysis. While the distribution of these conformers has not yet been deduced, the recent literature on direct MVK-oxide kinetic and spectroscopic studies that indicated that both syn (Caravan et al., PNAS 2020) and anti (Vansco et al., JPCA 2020) confirmers are produced from the 1,3,-diiodobut-2-ene photolysis scheme used in the present work (Barber et al., JACS 2018). Additionally, due to the rapid unimolecular decay of anti compared with syn (Barber et al., JACS 2018 and Vereecken et al., PCCP 2017), it is unlikely that reaction with DMS could compete with unimolecular decay under tropospheric conditions for the anti conformer.

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