

## Kinetics of dimethyl sulfide (DMS) reactions with isoprene-derived Criegee intermediates studied with direct UV absorption

### General comments

Time-resolved experiments have been carried out to generate two Criegee: CH<sub>2</sub>OO, which has been studied many times; and MVKOO, which has only very recently been studied. In the presence of dimethyl sulphide, no additional Criegee removal was evident. Hence, only an upper limit is assigned for the rate coefficients. A theoretical potential energy surface has been calculated for CH<sub>2</sub>OO + (CH<sub>3</sub>)<sub>2</sub>S that has a significant barrier to products (DMSO + CH<sub>2</sub>O) and its rate coefficient is lower than the experimental upper limit. These results are clear-cut and only a few specific comments are raised.

If this were the only study on the titled reaction, the lack of reactivity would probably mean this paper would not be considered for publication in ACP. The reason this result is significant is that a previous study (Newland 2015) suggested the stabilized Criegee formed from O<sub>3</sub>/isoprene (mainly CH<sub>2</sub>OO/MKVO) react rapidly with dimethyl sulphide, with a rate coefficient close to the gas-kinetic frequency. As this other study generated the Criegees via ozonolysis (O<sub>3</sub>/isoprene), it does ask the question how we best understand ozonolysis in the atmosphere. Is stabilized Criegee chemistry the most important component of ozonolysis? More detail would help this paper. The comment from Andrew Rickard expands on this.

### Specific comments

**Line 39** *“Surprisingly, the obtained rate coefficients are up to 10<sup>4</sup> times larger than previous results deduced from ozonolysis 40 experiments, indicating that the ozonolysis experiments could be quite complicated such that reliable kinetic results may be hard to retrieve.”*

This needs a reference. This is interesting in that relative rate experiments appear to be out by orders of magnitude. Is there explanation of these studies with today's knowledge? Is it wrong rate coefficients or is it more to do with the experiment itself?

**Line 103** *“To compensate for this effect, which was caused by the optics and the photolysis laser pulse, we recorded background traces without adding the precursor before and after each set of experiments. The reported data are after background subtraction.”* Can you state the typically size of this signal, i.e. what is I/I<sub>0</sub> in the absence of added chemicals. Is it related to a heating effect?

**Line 134** “e.g., bimolecular reactions with radical byproducts like I atoms, wall loss, etc.” Probably self-reaction is most important. Any evidence for a second-order component?

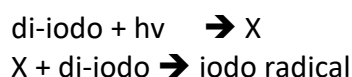
This paper has probably done most to unravel the removal the kinetics in absence of added reagent.

CH2OO Criegee intermediate UV absorption cross-sections and kinetics of CH2OO + CH2OO and CH2OO + I as a function of pressure By: [Mir, ZS](#) (Mir, Zara S.)<sup>11</sup>; [Lewis, TR](#) (Lewis, Thomas R.)<sup>11</sup>; [Onel, L](#) (Onel, Lavinia)<sup>11</sup>; [Blitz, MA](#) (Blitz, Mark A.)<sup>121</sup>; [Seakins, PW](#) (Seakins, Paul W.)<sup>11</sup>; [Stone, D](#) (Stone, Daniel)<sup>11</sup>

**Line 155** “and show the results in Table S4.”, From Table S4, the results given in Figure 2 are fairly obvious. I would expect a similar result even if 248 nm photolysis was used. Significant photolysis of DMS could potentially lead to enhanced reactivity, and an energy dependence would be good practice. However, in the present case, there is no evidence of enhanced Criegee removal so there is not too much to worry about.

**Line 171** “See SI (Sect. S3, page S5) for details.” From the SI, the instant yield of MVKOO decreases with total pressure, which is consistent with population into CH<sub>3</sub>(C<sub>2</sub>H<sub>3</sub>)CIOO, i.e. the SV is linear. However, *kr* appears to be faster at low pressures. *kr* is the rate coefficient for the peroxy radical to react to MVKOO + I. It is not possible for a rate coefficient to increase at lower total pressure. There are too few pressures to say anything for definite, but it does highlight that the *kr* errors are not realistic.

I wonder if there is another explanation for the results in Table S3. If you had an additional species, produced from the photolysis of the di-iodo compound, X, that can react with the di-iodo compound to make the iodo radical.



The pressure dependence could be linked to the fact the MVKOO species has a double bond.

If *kr* is the unimolecular reaction CH<sub>3</sub>(C<sub>2</sub>H<sub>3</sub>)CIOO → MVKOO + I, then changing the temperature should be the easiest way to identify it.

**Line 172** “This difference is consistent with the fact that MVKO is resonance-stabilized due to the extended conjugation of its vinyl group (Barber et al., 2018) and thus the adduct CH<sub>3</sub>(C<sub>2</sub>H<sub>3</sub>)CIOO is relatively less stable due to disruption of the conjugation.”

It will be the properties of CH<sub>3</sub>(C<sub>2</sub>H<sub>3</sub>)CIOO that will most strongly influence its formation and unimolecular dissociation, *kr*.

**Line 194** “Here we choose the boundary of three standard deviations as the upper limits for  $k_{DMS+CI}$ ,  $k_{DMS+CH_2OO} \leq 4.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  and  $k_{DMS+MVKO} \leq 1.6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ ” As you have done calculations, it would be better to state that the expts provide only an upper limit, and it is most likely that the  $k$  are smaller and closer to the theoretical values.

**Line 203** “[ $CI$ ]<sub>ss</sub> is expected to be low, at least a couple of orders of magnitude lower than the steady-state [ $OH$ ]<sub>ss</sub>.” On this basis, reactions need to be two orders of magnitude faster than  $OH$  to compete.  $SO_2$ ,  $H_2O$  vapour and acids fit the bill but not many other reagents.

**Line 216** “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  $SO_2$  via surface or gas-phase reactions (Chen et al., 2018) under the complicated conditions of isoprene ozonolysis.”

Is this a reasonable conclusion? In the introduction, you mentioned that prior to direct time-resolved experiments, Criegee +  $SO_2$  rate coefficients were thought to be slow. Is this another example of “surface” reactions? Is there more going in these ozonolysis experiments that bring about chemical change that if not captured by these direct measurements. Or are these relative rate reactions simply flawed?

Are there any suggested DMS →  $SO_2$  schemes via the gas-phase?

**Line 220** Any reason why MKVOO +  $SO_2$  not calculated?

## TYPOS / UNDERSTANDING

Is it MKVO or MVKOO? I think the later. This occurs several times

Also, MACRO or MACROO?

**Line 74** “ozonlolyis” Typo

**Line 91** “However, DMS absorbs weakly at 248 nm. We therefore performed additional experiments by photolyzing  $CH_2I_2$  at 248 nm to assess the impact of DMS photolysis at 248 nm on the decay of the CIs.” Do you mean 308 nm?

**Line 63** “Newland et al. noted, however, that the presented rate coefficients do not correspond to the rates of single elementary reactions but rather describe the general reactivity of CIs towards DMS or  $H_2O$ ” Can you re-phrase this as I’m not sure the point you making, be more explicit.

**Line 36** Beames et al., 2013 This is a depletion experiment.

