We thank the referees for their careful reading of the manuscript and helpful comments, which are repeated below (in black font). Our replies are given in blue font directly after each comment.

Referee 1:

General comments

Time-resolved experiments have been carried out to generate two Criegee: CH_2OO, which has been study 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 CH2OO + (CH3)2S that has a significant barrier to products (DMSO + CH_2O) 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_3/isoprene (mainly CH_2OO/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_3/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 10^4 times larger than previous results deduced from ozonolysis 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?

AUTHORS' REPLY:

Welz et al. (2012) compared their rate coefficients with previous values applied in contemporary tropospheric models (Johnson and Marston, 2008; Johnson et al., 2001; Hatakeyama and Akimoto, 1994). For ozonolysis experiments, typically only the ratios of reaction rate coefficients, e.g. $k_{\mathrm{DMS}}/k_{\mathrm{SO2}}$ (Newland et al., 2015), are obtained. The researchers have to compare with (at least) one absolute rate coefficient to get the rest rate coefficients. Unfortunately, the selected absolute rate coefficient (at that time) has large uncertainty, which propagates to other reported values. In addition, the reaction mechanism may be rather complicated and even the ratios of the rate coefficients must be treated with care. The above three references will be included in the main text.

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/I0 in the absence of added chemicals. Is it related to a heating effect?

AUTHORS' REPLY:

Typical background traces as well as raw signal traces (without background subtraction) obtained at 248 nm and 308 nm will be shown in Figures S5 and S6, respectively. These backgrounds are originated from the different longpass filters used for coupling the laser beam and probe beam into the reactor. Yes, it is likely that the backgrounds are from a heating effect of the longpass filters.

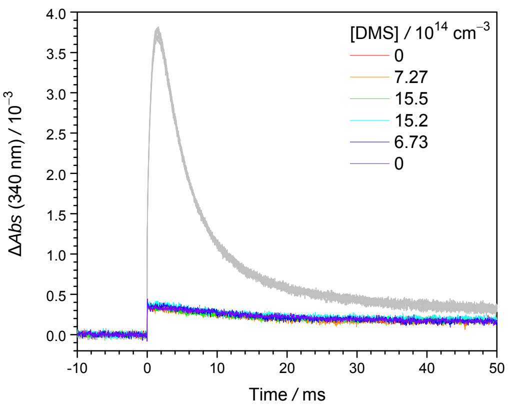


Fig. S5. Background traces under normal DMS concentrations, represented in colour lines, and the raw signal traces (without background subtraction), represented in grey lines, obtained with 248 nm photolysis laser ($I_{248\text{nm}}$ = 2.43 mJ cm^{-2}). See Exp#22 of Table S3 for the experimental conditions.

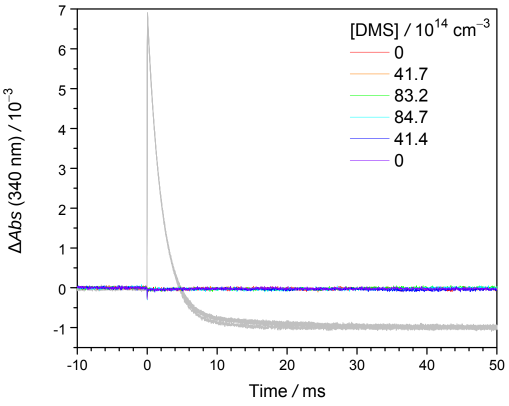


Fig. S6. Background traces under normal DMS concentrations, represented in colour lines, and the raw signal traces (without background subtraction), represented in grey lines, obtained with 308 nm photolysis laser ($I_{308\text{nm}}$ = 2.35 mJ cm^{-2}). See Exp#2 of Table S1 for the experimental condition. Note that the optics (longpass filters) are different from those at 248 nm.

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.)[1] ; Lewis, TR (Lewis, Thomas R.)[1] ; Onel, L (Onel, Lavinia)[1] ; Blitz, MA (Blitz, Mark A.)[1,2] ; Seakins, PW (Seakins, Paul W.)[1] ; Stone, D (Stone, Daniel)[1]

AUTHORS' REPLY:

In the previous works of Smith et al. (Smith et al., 2016) and Li et al. (Li et al., 2020), the contributions of the pseudo-first-order reactions and second-order reactions are both considered and the kinetic model can be represented in the following equation:

$$\frac{-d[\mathrm{CI}]}{dt} = k_1[\mathrm{CI}] + k_2[\mathrm{CI}]^2$$

The above equation can be simplified when extrapolating the rate coefficients to zero concentration of $[\mathrm{CI}]_0$:

$$\frac{-d[\mathrm{CI}]}{dt} \cong (k_1 + \frac{1}{2}k_2[\mathrm{CI}]_0)[\mathrm{CI}] = k_{\mathrm{obs}}[\mathrm{CI}]$$

The difference between the complete and simplified equations only shows up at high $[\mathrm{CI}]_0$. Most important of all, the self-reaction of CIs would not affect the determination of k_{DMS}, since $[\mathrm{CI}]_0$ was kept constant in every experimental set.

Based on the absolute absorption cross section of CH_2OO at 340 nm (σ = 1.23×10^{-17} cm^2) and the pressure-dependent yield of CH_2OO from $CH_2I + O_2$ (0.46 at 300 Torr) (Ting et al., 2014a) the number densities of relevant species can be estimated to be the following (for Exp#1, Table S1).

$[CH_2OO]_0 = 6.7\times10^{11}$ cm^{-3}; $[\mathrm{I}]_0 = 2.1\times10^{12}$ cm^{-3}; $[CH_2IOO]_0 = 7.7\times10^{11}$ cm^{-3}.

The first-order decay rate coefficient of CH_2OO (k_{eff}) can be approximately estimated (Li et al., 2020) as:

$$k_{\mathrm{eff}} = k_{\mathrm{I}}[\mathrm{I}]_0 + k_{\mathrm{self}}[CH_2OO]_0$$

Using $k_{\mathrm{self}} = 8\times10^{-11}$ cm^3 s^{-1} and $k_{\mathrm{I}} = 5.8\times10^{-11}$ cm^3 s^{-1} at 300 Torr (Mir et al., 2020), the estimated k_{eff} is 180 s^{-1}, consistent with the observed value of 232 s^{-1} for k_0. Therefore, the main loss processes of CH_2OO are reaction with iodine atoms (and other radicals) and its self-reaction.

In Figure S7, we can see a nice linear relationship between k_0 and the total produced radicals (proportional to the product of the laser fluence and the precursor concentration), further supporting the above mechanism. We would add the following sentences in the caption of Figure S7.

"The main loss processes of CH_2OO are reactions with radical byproducts like iodine atoms and its self-reaction. The observed values of k_0 (e.g., 232 s^{-1} for Exp#1) are consistent with the values (e.g., 180 s^{-1} at the condition of Exp#1) that are estimated using the reported kinetic data (yield and rate coefficients) (Mir et al., 2020; Ting et al., 2014)."

We will also modify the relevant sentences in the main text to:

"*The subsequent decay in absorption is due to the consumption of CH_2OO either through reaction with DMS or through other processes, e.g., bimolecular reactions with radical byproducts like I atoms, wall loss, etc. In addition, self-reaction of CH_2OO has been found to be rather fast ($k_{self} = 8\times10^{-11} cm^3\ s^{-1}$)(Mir et al., 2020). However, the effect of the self-reaction (Smith et al., 2016;Li et al., 2020) would not affect the determination of k_{DMS} under our experimental conditions.*"

Line 155 "*and show the results in Table S4.*" , From Table S4, the results given in Figure 2 are fairly obvious. I would expected 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.

AUTHORS' REPLY:

In Table S4, we have shown that $[DMS]_{diss}$ is about ten times less than $[CH_2I_2]_{diss}$ under typical experimental conditions when 248 nm photolysis is applied. However, we have observed a strong absorption in the background traces when 248 nm photolysis and high [DMS] are applied (Figure S4). The extra absorption from the dissociated DMS would be problematic when performing the background subtraction. Therefore we constrained the laser fluence and [DMS] to preclude the influence of [DMS] photolysis.

Line 171 "*See SI (Sect. S3, page S5) for details.*" From the SI (Table S3), the instant yield of MVKOO decreases with total pressure, which is consistent with population into $CH_3(C_2H_3)CIOO$, i.e. the SV is linear. However, k_r appears to be faster at low pressures. k_r 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 k_r 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.

di-iodo + hv →X

X + di-iodo →iodo radical

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

If k_r is the unimolecular reaction $CH_3(C_2H_3)CIOO \rightarrow$ 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 $CH_3(C_2H_3)CIOO$ is relatively less stable due to disruption of the conjugation.*"

It will be the properties of $CH_3(C_2H_3)CIOO$ that will most strongly influence its formation and unimolecular dissociation, k_r.

AUTHORS' REPLY (To lines 171-172):

The reviewer is right about the role of $CH_3(C_2H_3)CIOO$ and that changing the temperature should be the easiest way to identify the related process. In fact, we have discussed the issues of the adduct, including the temperature and pressure effects, in our recent paper (Lin et al., 2020). Since MVKO is a resonance-stabilized molecule, adduct would be relatively less stable, compared with CIs without resonance structure, such as CH_2OO or CH_3CHOO. Therefore, the unimolecular decomposition of the adduct is observed in our experimental time scale. The reason why k_r appears to be larger at lower pressure is that the fitted k_r should include the unimolecular decomposition of the adduct and the reaction of the adduct with other radicals (X) such as iodine atoms.

$$k_r = k_{\mathrm{uni}}(\mathrm{adduct}) + k_x[\mathrm{X}]$$

The concentration of the radicals would increase as the precursor concentration increases, leading to a higher k_r. This relation can be observed explicitly through plotting k_r against $I_{248\ \mathrm{nm}}$ × *Abs*(238 nm) (photolysis laser fluence times precursor absorbance). As for the temperature effect, we have also observed a positive temperature dependence of k_r (E_a = 12.7±0.3 kcal mol^{-1}), consistent with the calculation result for the bond dissociation energy of the adduct (14 kcal mol^{-1}) (Lin et al., 2020).

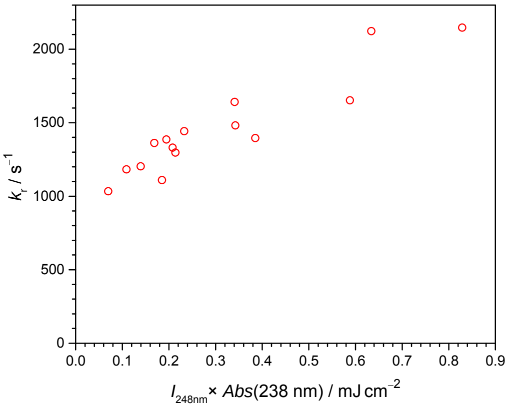


Fig. S?. Plot of k_r against the product of the laser fluence (I_{248nm}) and the absorbance of 1,3-diiodo-2-butene at 238 nm in the photolysis cell (*Abs*(238nm)) for the experiments of MVKO+DMS reaction (Exp#15-29, Tables S3). The x-axis essentially represents the total amounts of radical species generated through the photolysis of the precursor (R1) and the subsequent reactions (R2). Higher radical concentration results in faster decay of the adduct, thus higher k_r.

Please note that the error bars in Tables S1-S3 do NOT include any systematic errors. For k_r, it is correlated with other fitting parameters like $(1-\alpha)$. Since MVKO does not react with DMS (essentially all the traces are almost the same at various [DMS]), it is hard to 'disentangle' the correlation among fitting parameters. In the paper by Lin et al., we used SO_2 to scavenge MVKO and to obtain more robust results (Lin et al., 2020).

We will add a notation regarding the error bar of k_r after Table S3:

"*averaged value ± 1 sigma error of the mean (statistical only, not including systematic* *errors). The actual error bar would be larger since k_r is highly correlated with other fitting parameters like $(1-\alpha)$. Lin et al. has used SO_2 scavenger to obtain more robust results for k_r (Lin et al., 2020).”*

Line 194 “*Here we choose the boundary of three standard deviations as the upper limits for k_{DMS}+CI, k_{DMS}+$CH_2OO \leq 4.2\times10^{15}$ cm^3s^{-1} and k_{DMS}+MVKO $\leq 1.6\times10^{14}$ cm^3s^{-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.

AUTHORS’ REPLY

Indeed, the actual value of $k_{\mathrm{DMS+CI}}$ would be smaller than the upper limits we reported, and the actual value of $k_{\mathrm{DMS+CH2OO}}$ may be closer to the theoretical value ($k_{\mathrm{DMS+CH2OO}} = 5.5\times10^{-19}$ $\mathrm{cm^3\ s^{-1}}$). However, the calculation is not at the best level (while it is still good enough for the discussion in this paper) and there are uncertainties in the calculated values. Thus we decided not to say that the rate coefficients would be closer to the theoretical values.

Line 203 “*[CI]ss is expected to be low, at least a couple of orders of magnitude lower than the steady-state [OH]ss.*” On this basis, reactions need to be two orders of magnitude faster than OH to compete. SO2, H2O vapour and acids fit the bill but not many other reagents.

AUTHORS’ REPLY

We totally agree with your point. Thus we think the reaction of CI+DMS would not be a major path for the oxidization of DMS since the rate coefficient of CI+DMS is quite small.

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 SO2 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?

AUTHORS' REPLY

The reviewer raised a few important and interesting questions, which are awaiting more investigations. As mentioned before, researchers have to postulate the reaction mechanism of the ozonolysis reaction to deduce the rate coefficients. We believe there are more to be studied for the ozonolysis of isoprene. For clarification, we would modify the related text to the following.

"For the determination of the relative rate of the CI + DMS reaction, Newland et al. monitored the consumption of SO_2 over a measurement period of up to 60 min until approximately 25% of isoprene was consumed (Newland et al., 2015). Additional uncharacterized reaction pathways (e.g., reactions with the products) would lead to a bias in the inferred rate coefficients. A part of this high complexity of the isoprene-ozone-DMS-SO_2 system has been discussed by Newland et al. in the section of Experimental Uncertainties (Newland et al., 2015). Our direct measurements and kinetics are very straightforward; the obtained results for individual CIs may provide useful constraints for related ozonolysis systems."

Line 220 Any reason why MKVOO + SO_2 not calculated?

AUTHORS' REPLY

We guess the reviewer meant MVKO+DMS. Now we have the calculation result of MVKO+DMS reaction. Similar to the reaction with H_2O (Vereecken et al., 2017), the direct reaction of *E*- and *Z*-MVKO with DMS is expected to be slower than for CH_2OO, as the organic groups and the conjugation of the carbonyl oxide moiety with the double bond stabilizes the CI. Indeed, for MVKO (all conformers), no adduct seems to exist at the M06-2X/cc-pVDZ level of theory: the needed C−S bond in the adduct appears to be too weak to compensate for the loss of the conjugation in the carbonyl oxide, and the system reverts to the MVKO + DMS complex instead, without a formal C−S bond. As a result, the barrier for the migration of a DMS methyl H-atom to the carbonyl oxide oxygen to form a methylidene adduct is ~10 kcal/mol higher than for the analogous TS in the CH_2OO+DMS system which does feature a weakly bonded intermediate adduct. The direct oxygen transfer from *E*- or *Z*-MVKO to DMS, forming MVK + DMSO, was found to have a similarly high energy barrier as in the CH_2OO+DMS system. No viable reaction channels were found involving the double bond in MVKO. The lack of accessible transition states then prohibits rapid direct reaction between DMS and MVKO.

We also have additional calculation on the cyclisation of MVKO in the presence of DMS. Again, no accessible pathways were found.

TYPOS / UNDERSTANDING

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

Also, MACRO or MACROO?

AUTHORS' REPLY

MVKO is short for methyl-vinyl-ketone-oxide, and is the correct notation (i.e. MVK + 1 oxide O-atom). Likewise, MACRO is an acronym for methacroleine-oxide. We have standardized on these notations, consistent with our previous paper (Lin et al., 2020).

Line 74 "ozonlolysis" Typo

AUTHORS' REPLY

(will be fixed). Thanks for your reminder.

Line 91 "However, DMS absorbs weakly at 248 nm. We therefore performed additional experiments by photolyzing CH2I2 at 248 nm to assess the impact of DMS photolysis at 248 nm on the decay of the CIs."

Do you mean 308 nm?

AUTHORS' REPLY

We want to emphasize that DMS absorbs weakly at 248 nm ($\sigma = 1.28\times10^{-20}$ cm^2) but barely absorbs at 308 nm ($\sigma < 1\times10^{-22}$ cm^2) (Limão-Vieira et al., 2002). At low [DMS], the weak absorption of DMS at 248 nm may not cause a problem, but in this work, [DMS] is quite high and thus the photolysis of DMS at 248 nm should be taken into consideration.

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 H2O*" Can you re-phrase this as I'm not sure the point you making, be more explicit.

AUTHORS' REPLY:

Thank you for pointing out. The sentences will be rephrased to

"*Newland et al., who used ozonolysis of isoprene to generate a mixture of CIs (CH_2OO, MVKO, and MACRO), reported a combined reactivity of these CIs toward DMS and H_2O under conditions similar to the atmospheric boundary layer. Their reported rate coefficients might not correspond to those of single elementary reactions.*"

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

AUTHORS' REPLY:

Thank you for pointing out. The sentence will be rephrased to

"… UV-visible absorption/depletion spectroscopy …"

Anonymous referee 2:

One reason for the difference is the current results and the results reported in Newland 2015 may be the impact of DMS on the MVKO + SO_2 reaction. It is not necessary to perform calculations on this reaction, but some mechanistic discussion would be pertinent.

AUTHORS' REPLY:

The reactions of carbonyl oxides (CI) with SO_2 proceed by a barrierless cycloaddition (Kuwata et al., J. Phys. Chem. A, 119, 10316, 2015) with a very fast capture rate coefficient for complex formation near the collision limit, and a partial redissociation to the free reactants leading to a rate coefficient somewhat below the collision limit. The DMS-complex of a CI reacting with SO_2 can be expected to have a lower rate coefficient than the direct CI+SO_2 reaction, as the DMS shields part of the approach vectors of the SO_2 reactant, and the long-range attractive force is diminished due to a somewhat lower dipole moment of the complex compared to the free CI. However, the reduction of the rate coefficient is not expected to be all that large, and more importantly the CI+DMS complex is not overly strong such that only a small fraction of the CI will be present as a CI+DMS complex. This makes it hard to understand how DMS could affect any CI+SO_2 capture reaction (CH_2OO, MVKO, or CH_3CHOO) to the extent observed in Newland et al. It is for this reason that we have done exploratory calculations on the redissociation of the CI+SO_2 cyclo-adduct, but have found no indication that this would have the required impact on the effective CI+DMS rate of product formation.

Line 224: What is the evidence for the CH_2OO-DMS adduct having "very strong zwitterionic character?"

AUTHORS' REPLY:

At the level of theory used here, the wavefunction for the adduct converges to a closed-shell structure with no biradical character, where the O-atoms have a strongly negative partial charge (up to -0.46 in the Mulliken population analysis), and where the S-atom is positively charged S-atom (+0.28 in the Mulliken population analysis, compared to the Mulliken partial charge of -0.06 in DMS). This suggests that the CH_2OO-DMS adduct, similar to the parent carbonyl oxide, has a zwitterionic character with very strong charge separation between the S and O atoms, rather than a biradical wavefunction.

Supplemental Information S20-S21: The authors should present some calculations on the MVKO. In particular, it would be worthwhile to consider how DMS might affect the cyclization of the anti conformer of MVKO to the dioxole (see J. Am. Chem. Soc. 2018, 140, 10866). Here, I reiterate the comment of Rickard that it would be useful for the authors to estimate the relative amounts of the syn and anti conformers of MVKO.

AUTHORS' REPLY:

The dominant unimolecular reaction of *E*-MVKO is a 1,4-H-shift (VHP-channel), analogous to *Z*-CH_3CHOO, for which we already showed that any catalytic effect is insufficient to allow for fast reactions. We now also calculated the impact of a DMS spectator complexing agent on the cyclization in *Z*-MVKO at the M06-2X/cc-pVDZ level of theory, finding similar results as for the methylated CH_3CHOO, i.e. the barrier height without (12.1 kcal/mol) and with complexing DMS (14.2 kcal/mol from the ground state of the complex) are essentially identical. The complex stability for *Z*-MVKO + DMS (−9.9 kcal/mol) is also similar to that for CH_2OO, *Z*-CH_3CHOO, and *E*-CH_3CHOO. Any catalyzing effect by DMS would then be due to chemical activation by the energy released in the complexation. The net energy barrier for the DMS catalysed *Z*-MVKO unimolecular reaction is ~ +4 kcal/mol, then still implies a slow bimolecular reaction, in agreement with the experimental observations.

Also see Reply to Referee 1 (for Line 220) for the calculation results on the direct reaction of MVKO + DMS.

Regarding the relative amounts of the *syn* and *anti* conformers of MVKO, we would add the following sentences to clarify the MVKO conformation. (after line 80)

"*For MVKO, there are 4 possible conformers. Following the nomenclature of Barber et al., syn/anti-MVKO (E/Z-MVKO) has a methyl/vinyl group at the same side of the terminal oxygen, while cis and trans refer to the orientation between the vinyl C=C and the carbonyl C=O bonds (Barber et al., 2018). It has been reported that syn- and anti-MVKO do not interconvert due to a high barrier between them but the barrier between cis and trans forms is low enough to permit fast interconversion at 298 K (Barber et al., 2018;Vereecken et al., 2017). Caravan et al., have shown that anti-MVKO is unobservable under thermal (298 K) conditions due to short lifetime and/or low yield, and thus, the UV-Vis absorption signal is from an equilibrium mixture of cis and trans forms of syn-MVKO (Caravan et al., 2020;Vereecken et al., 2017). For simplicity we will use MVKO to represent syn-MVKO (E-MVKO).*"

Lines 232-233: "*We did not examine more exotic CI reaction such as insertion in the DMS C–H bonds, as these are known to have comparatively high barriers.*" This statement should have a reference.

AUTHORS' REPLY:

We would add the paper of (Decker et al. ***Phys. Chem. Chem. Phys.***, 2017,**19**, 8541-8551, doi:10.1039/C6CP08602K) into the reference

Supplemental Information S20-S21: The authors should tabulate the relative energies predicted by the M06-2X/cc-pVDZ calculations.

AUTHORS' REPLY:

A table is now included in the supporting information.

Table S_: ZPE-corrected DMS complex energies, E(complex), and barrier heights E_b without and with a DMS complexing agent, at the M06-2X/cc-pVDZ level of theory. Energies are in kcal mol^{-1} and relative to the free reactants.

CI reaction	E_b	E(complex)	E_b(complex)
CH_2OO → cyc-CH_2OO-	22.0	-9.6	14.5
Z-CH_3CHOO → CH_2CHOOH	12.7	-8.6	7.2
Z-CH_3CHOO → cyc-$CH(CH_3)OO$-	25.8	-8.6	18.2
E-CH_3CHOO → cyc-$CH(CH_3)OO$-	18.4	-10.9	9.5
Z-$(CH{=}CH_2)C(CH_3)OO$ → cyc-CH-$CH_2C(CH_3)OO$-	12.1	-9.9	4.4
Z-$(CH{=}CH_2)C(CH_3)OO$ + DMS → MVK + DMSO	8.7		
E-$(CH_3)C(CH{=}CH_2)OO$ + DMS → MVK + DMSO	8.0		
$(CH_3)C(CH{=}CH_2)OO$ + DMS → $S(CH_3)(=CH_2)C(CH_3)(CH{=}CH_2)OOH$	11.2		

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.

AUTHORS' REPLY:

The reviewer is correct. However, the method reported by Taatjes et al.(Taatjes et al., 2008) is less efficient than that by Welz et al. (Welz et al., 2012) Nowadays, most photolytic generation of Criegee intermediates follow the method by Welz et al. The related sentences

"However, due to their high reactivity and, hence, short lifetimes, laboratory studies of the reactions of CIs have been challenging. 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 (Welz et al., 2012)."

would be modified to

"However, due to their high reactivity and, hence, short lifetimes, laboratory studies of the reactions of CIs have been challenging until the work by Welz et al. who reported a novel

method to efficiently generate CIs other than through ozonolysis of alkenes (Welz et al., 2012).”

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.

AUTHORS’ REPLY:

We will clarify the situation by revising the related text to

“Surprisingly, the obtained rate coefficients are up to 10^4 *times larger than previous results deduced from ozonolysis experiments (Johnson and Marston, 2008;Johnson et al., 2001;Hatakeyama and Akimoto, 1994). For ozonolysis experiments, typically only the ratios of reaction rate coefficients are obtained. The researchers have to compare with (at least) one absolute rate coefficient to get the rest rate coefficients. Unfortunately, the selected absolute rate coefficient (at that time) has large uncertainty, which propagates to other reported values. In addition, the reaction mechanism may be rather complicated and even the ratios of the rate coefficients need to be treated with care.”*

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

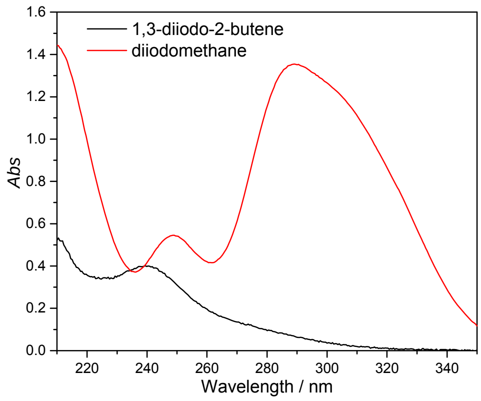
AUTHORS’ REPLY:

Thanks. We will include this new reference. (Cox et al., 2020)

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

AUTHORS’ REPLY:

Below would be the measured absorbance of the diiodomethane (Exp# 12) and 1,3-diiodo-2-butene (Exp# 15) in the absorption cell (they are much diluted in the reactor cell). The absorption of 1,3-diiodo-2-butene at 308 nm is c.a. one-tenth of that at 248 nm. Consequently, we only perform the photolysis of 1,3-diiodo-2-butene at 248 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.

AUTHORS' REPLY:

Currently we don't have the available data for the cross section nor the empirical coefficients of Antoine coefficients for 1,3-diiodo-2-butene; hence we couldn't derive the absolute concentration. We have reported the deduced absorbance (*Abs*) of the precursor in the photolysis cell of different experiments sets in Table S3. The absolute concentration of precursor can be deduced from the *Abs* of precursor and other experimental conditions shown in Table S3., once the absolute cross section of 1,3-diiodo-2-butene is available.

We have modified the text to

"However, because no absolute absorption cross sections for 1,3-diiodo-2-butene have been reported, its absolute concentration cannot be determined. We alternatively report the absorbance (Precursor Abs) of 1,3-diiodo-2-butene in the photolysis reactor (Table S3)."

Page 6, line 159: Under the present experimental conditions, CH_3 would most likely undergo reaction with O_2 to form CH_3OO and so it would be best to compare the reactivity of CH_3OO (rather than CH_3) with I atom and Criegee intermediates.

AUTHORS' REPLY:

Thanks for pointing out. We will revise the sentences to

"The expected products of DMS photolysis are CH_3 + CH_3S (Bain et al., 2018). Under the presence of O_2 (10 Torr), CH_3 would be converted into CH_3OO. These radicals (CH_3, CH_3OO, and CH_3S) are less reactive than I atoms or CIs."

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.

AUTHORS' REPLY:

Possible concentrations of NO_3 and OH in the troposphere are found to be:

[OH] = 1×10^6 cm^{-3} (Li et al., 2018) and [NO_3] = 10 ppt = 2.5×10^8 cm^{-3} (Khan et al., 2015). Together with the reaction rate coefficients ($k_{\mathrm{DMS+OH}}$ = 4.8×10^{-12} cm^3 s^{-1}, $k_{\mathrm{DMS+NO3}}$ = 6.8×10^{-11} cm^3 s^{-1} (Atkinson et al., 2004)), the concentration of CIs would have to be unreasonably high, at the order of 10^{11} cm^{-3}, to be competitive (5% of the effective reaction rate) with the DMS+OH and DMS+NO_3 reactions.

We would add the following sentences

"If the DMS reactions with CIs were to be competitive to those with NO_3 (e.g., 2.5×10^8 cm^{-3}) and OH (e.g., 1×10^6 cm^{-3}) (e.g., 5% of the overall DMS removal), the concentration of CIs would have to be unreasonably high, at the order of 10^{11} cm^{-3}."

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.

AUTHORS' REPLY:

Now we have the calculation result of MVKO+DMS reaction. Please see Reply to Referee 1 (for Line 220) for the calculation results on the direct reaction of MVKO + DMS, and the reply to referee 2 for catalysis reactions by DMS on unimolecular reactions of MVKO.

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

AUTHORS' REPLY:

We would add the paper of Decker et al. (***Phys. Chem. Chem. Phys.***, 2017,**19**, 8541-8551, doi:10.1039/C6CP08602K) in to the reference

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

The bonding is too weak to be stabilized 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.

AUTHORS' REPLY:

We would respond to the comments of Rickard et al. separately in the online discussion system of ACP.

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.

AUTHORS' REPLY:

(i) We would add the following text in the caption:

"For each data point, the error of the single exponential fitting is less than 1% (thus not shown)."

(ii) Based on the absolute absorption cross section of CH_2OO at 340 nm ($\sigma = 1.23\times10^{-17}$ cm^2) and the pressure-dependent yield of CH_2OO from $CH_2I + O_2$ (0.46 at 300 Torr) (Ting et al., 2014a) the number densities of relevant species can be estimated to be the following (for Exp#1, Table S1).

$[CH_2OO]_0 = 6.7\times10^{11}$ cm^{-3}; $[I]_0 = 2.1\times10^{12}$ cm^{-3}; $[CH_2IOO]_0 = 7.7\times10^{11}$ cm^{-3}.

The first-order decay rate coefficient of CH_2OO (k_{eff}) can be approximately estimated (Li et al., 2020) as:

$$k_{eff} = k_I[I]_0 + k_{self}[CH_2OO]_0$$

Using $k_{self} = 8\times10^{-11}$ cm^3 s^{-1} and $k_I = 5.8\times10^{-11}$ cm^3 s^{-1} at 300 Torr (Mir et al., 2020), the estimated k_{eff} is 180 s^{-1}, consistent with the observed value of 232 s^{-1} for k_0. Therefore, the main loss processes of CH_2OO are reaction with iodine atoms (and other radicals) and its self-reaction.

In Figure S7, we can see a nice linear relationship between k_0 and the total produced radicals (proportional to the product of the laser fluence and the precursor concentration), further supporting the above mechanism. We would add the following sentences in the caption of Figure S7.

"The main loss processes of CH_2OO are reactions with radical byproducts like iodine atoms and its self-reaction. The observed values of k_0 (e.g., 232 s^{-1} for Exp#1) are consistent with the values (e.g., 180 s^{-1} at the condition of Exp#1) that are estimated using the reported kinetic data (yield and rate coefficients) (Mir et al., 2020; Ting et al., 2014)."

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.

AUTHORS' REPLY: We will add a footnote after the "adduct yield[a]"

[a] *The yield of* $CH_3(C_2H_3)CIOO$.

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

AUTHORS' REPLY:

We would add the following text into the caption

"For each data point, the error of the single exponential fitting is lees than 1% (thus not shown)."

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

AUTHORS' REPLY:

The photolysis of DMS produces radicals like CH_3 and CH_3S. A few vibronic bands of the A-X transition of the CH_3S radical (Liu et al., 2005) are within our probe window (335-345 nm). Thus it is possible that the "spike" near time zero is due to the absorption of the radical products of DMS photolysis, likely CH_3S or vibrationally excited CH_3S. We would add the following sentence in the figure caption.

"The absorbance change under zero [DMS] comes from the interaction of the optics and the photolysis laser pulse, whereas the "spike" near time zero at high [DMS] may come from the absorption of the radical products of DMS photolysis, likely CH_3S *(Liu et al., 2005) and/or vibrationally excited* CH_3S*."*

S10: These additional investigations are illuminating and interesting.

AUTHORS' REPLY: Thanks.

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., 2020) and anti (Vansco et al., 2020) confirmers are produced from the 1,3,-diiodobut-2-ene photolysis scheme used in the present work (Barber et al., 2018). Additionally, due to the rapid unimolecular decay of anti compared with syn (Barber et al., 2018;Vereecken et al., 2017), it is unlikely that reaction with DMS could compete with unimolecular decay under tropospheric conditions for the anti conformer.

AUTHORS' REPLY:

Same as the reply to Referee 2 (for Supplemental Information S20-S21), we have added some description to after line 80 to clarify the MVKO conformation.

"*For MVKO, there are 4 possible conformers. Following the nomenclature of Barber et al., syn/anti-MVKO (E/Z-MVKO) has a methyl/vinyl group at the same side of the terminal oxygen, while cis and trans refer to the orientation between the vinyl C=C and the carbonyl C=O bonds (Barber et al., 2018). It has been reported that syn- and anti-MVKO do not interconvert due to a high barrier between them but the barrier between cis and trans forms is low enough to permit fast interconversion at 298 K (Barber et al., 2018;Vereecken et al., 2017). Caravan et al., have shown that anti-MVKO is unobservable under thermal (298 K) conditions due to short lifetime and/or low yield, and thus, the UV-Vis absorption signal is from an equilibrium mixture of cis and trans forms of syn-MVKO (Caravan et al., 2020;Vereecken et al., 2017). For simplicity we will use MVKO to represent syn-MVKO (E-MVKO).*"

References:

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species, Atmos. Chem. Phys., 4, 1461-1738, https://doi.org/10.5194/acp-4-1461-2004, 2004.

Bain, M., Hansen, C. S., and Ashfold, M. N. R.: Communication: Multi-mass velocity map imaging study of the ultraviolet photodissociation of dimethyl sulfide using single photon ionization and a PImMS2 sensor, J. Chem. Phys., 149, 081103, 10.1063/1.5048838, 2018.

Barber, V. P., Pandit, S., Green, A. M., Trongsiriwat, N., Walsh, P. J., Klippenstein, S. J., and Lester, M. I.: Four-Carbon Criegee Intermediate from Isoprene Ozonolysis: Methyl Vinyl Ketone Oxide Synthesis, Infrared Spectrum, and OH Production, J. Am. Chem. Soc., 140, 10866-10880, 10.1021/jacs.8b06010, 2018.

Caravan, R. L., Vansco, M. F., Au, K., Khan, M. A. H., Li, Y.-L., Winiberg, F. A. F., Zuraski, K., Lin, Y.-H., Chao, W., Trongsiriwat, N., Walsh, P. J., Osborn, D. L., Percival, C. J., Lin, J. J.-M., Shallcross, D. E., Sheps, L., Klippenstein, S. J., Taatjes, C. A., and Lester, M. I.: Direct kinetic measurements and theoretical predictions of an isoprene-derived Criegee intermediate, Proc. Natl. Acad. Sci., 117, 9733-9740, 10.1073/pnas.1916711117, 2020.

Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII - Criegee intermediates, Atmos. Chem. Phys. Discuss., 2020, 1-41, 10.5194/acp-2020-472, 2020.

Decker, Z. C. J., Au, K., Vereecken, L., and Sheps, L.: Direct experimental probing and theoretical analysis of the reaction between the simplest Criegee intermediate CH_2OO and isoprene, Phys. Chem. Chem. Phys., 19, 8541-8551, 10.1039/C6CP08602K, 2017.

Hatakeyama, S., and Akimoto, H.: Reactions of criegee intermediates in the gas phase, Res. Chem. Intermed., 20, 503-524, 10.1163/156856794X00432, 1994.

Johnson, D., Lewin, A. G., and Marston, G.: The Effect of Criegee-Intermediate Scavengers on the OH Yield from the Reaction of Ozone with 2-methylbut-2-ene, J. Phys. Chem. A, 105, 2933-2935, 10.1021/jp003975e, 2001.

Johnson, D., and Marston, G.: The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere, Chem. Soc. Rev., 37, 699-716, 10.1039/B704260B, 2008.

Khan, M. A. H., Cooke, M. C., Utembe, S. R., Archibald, A. T., Derwent, R. G., Xiao, P., Percival, C. J., Jenkin, M. E., Morris, W. C., and Shallcross, D. E.: Global modeling of the nitrate radical (NO_3) for present and pre-industrial scenarios, Atmospheric Research, 164-165, 347-357, https://doi.org/10.1016/j.atmosres.2015.06.006, 2015.

Kuwata, K. T., Guinn, E. J., Hermes, M. R., Fernandez, J. A., Mathison, J. M., and Huang, K.: A Computational Re-examination of the Criegee Intermediate–Sulfur Dioxide Reaction, J. Phys. Chem. A, 119, 10316-10335, 10.1021/acs.jpca.5b06565, 2015.

Li, M., Karu, E., Brenninkmeijer, C., Fischer, H., Lelieveld, J., and Williams, J.: Tropospheric OH and stratospheric OH and Cl concentrations determined from CH_4, CH_3Cl, and SF_6 measurements, npj Climate and Atmospheric Science, 1, 29, 10.1038/s41612-018-0041-9, 2018.

Li, Y.-L., Kuo, M.-T., and Lin, J. J.-M.: Unimolecular decomposition rates of a methyl-substituted Criegee intermediate *syn*-CH_3CHOO, RSC Advances, 10, 8518-8524, 10.1039/D0RA01406K, 2020.

Limão-Vieira, P., Eden, S., Kendall, P. A., Mason, N. J., and Hoffmann, S. V.: High resolution VUV photo-absorption cross-section for dimethylsulphide, $(CH_3)_2S$, Chemical Physics Letters, 366, 343-349, https://doi.org/10.1016/S0009-2614(02)01651-2, 2002.

Lin, Y.-H., Li, Y.-L., Chao, W., Takahashi, K., and Lin, J. J.-M.: The role of the iodine-atom adduct in the synthesis and kinetics of methyl vinyl ketone oxide—a resonance-stabilized Criegee intermediate, Phys. Chem. Chem. Phys., 22, 13603-13612, 10.1039/D0CP02085K, 2020.

Liu, C.-P., Reid, S. A., and Lee, Y.-P.: Two-color resonant four-wave mixing spectroscopy of highly predissociated levels in the $\tilde{A}A_{12}$ state of CH_3S, J. Chem. Phys., 122, 124313, 10.1063/1.1867333, 2005.

Mir, Z. S., Lewis, T. R., Onel, L., Blitz, M. A., Seakins, P. W., and Stone, D.: CH_2OO Criegee intermediate UV absorption cross-sections and kinetics of $CH_2OO + CH_2OO$ and $CH_2OO + I$ as a function of pressure, Phys. Chem. Chem. Phys., 22, 9448-9459, 10.1039/D0CP00988A, 2020.

Newland, M. J., Rickard, A. R., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: Atmospheric isoprene ozonolysis: impacts of stabilised Criegee intermediate reactions with SO_2, H_2O and dimethyl sulfide, Atmos. Chem. Phys., 15, 9521-9536, 10.5194/acp-15-9521-2015, 2015.

Smith, M. C., Chao, W., Takahashi, K., Boering, K. A., and Lin, J. J. M.: Unimolecular Decomposition Rate of the Criegee Intermediate $(CH_3)_2COO$ Measured Directly with UV Absorption Spectroscopy, J. Phys. Chem. A, 120, 4789-4798, 10.1021/acs.jpca.5b12124, 2016.

Taatjes, C. A., Meloni, G., Selby, T. M., Trevitt, A. J., Osborn, D. L., Percival, C. J., and Shallcross, D. E.: Direct Observation of the Gas-Phase Criegee Intermediate (CH_2OO), J. Am. Chem. Soc., 130, 11883-11885, 10.1021/ja804165q, 2008.

Ting, W. L., Chang, C. H., Lee, Y. F., Matsui, H., Lee, Y. P., and Lin, J. J. M.: Detailed mechanism of the $CH_2I + O_2$ reaction: Yield and self-reaction of the simplest Criegee intermediate CH_2OO, J. Chem. Phys., 141, 104308, 10.1063/1.4894405, 2014a.

Ting, W. L., Chen, Y. H., Chao, W., Smith, M. C., and Lin, J. J. M.: The UV absorption spectrum of the simplest Criegee intermediate CH_2OO, Phys. Chem. Chem. Phys., 16, 10438-10443, 10.1039/c4cp00877d, 2014b.

Vansco, M. F., Caravan, R. L., Zuraski, K., Winiberg, F. A. F., Au, K., Trongsiriwat, N., Walsh, P. J., Osborn, D. L., Percival, C. J., Khan, M. A. H., Shallcross, D. E., Taatjes, C. A., and Lester, M. I.: Experimental Evidence of Dioxole Unimolecular Decay Pathway for Isoprene-Derived Criegee Intermediates, J. Phys. Chem. A, 124, 3542-3554, 10.1021/acs.jpca.0c02138, 2020.

Vereecken, L., Novelli, A., and Taraborrelli, D.: Unimolecular decay strongly limits the atmospheric impact of Criegee intermediates, Phys. Chem. Chem. Phys., 19, 31599-31612, 2017.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2, Science, 335, 204-207, 10.1126/science.1213229, 2012.