



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

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Abstract. Criegee intermediates (CIs) are formed in the ozonolysis of unsaturated hydrocarbons and play a role in atmospheric chemistry as a non-photolytic OH source or a strong oxidant. Using a relative rate method in an ozonolysis experiment, Newland et al. (2015) reported high reactivity of isoprene-derived Criegee intermediates towards dimethyl sulfide (DMS) relative to that towards SO₂ with the ratio of the rate coefficients $k_{\text{DMS+CI}}/k_{\text{SO}_2+\text{CI}} = 3.5 \pm 1.8$. Here we reinvestigated the kinetics of DMS reactions with two major Criegee intermediates formed in isoprene ozonolysis, CH₂OO, and methyl vinyl ketone oxide (MVKO). The individual CI was prepared following the reported photolytic method with suitable (diiodo) precursors in the presence of O₂. The concentration of CH₂OO or MVKO was monitored directly in real time through their intense UV–visible absorption. Our results indicate the reactions of DMS with CH₂OO and MVKO are both very slow; the upper limits of the rate coefficients are 4 orders of magnitude smaller than the rate coefficient reported by Newland et al. (2015). These results suggest that the ozonolysis experiment could be complicated such that interpretation should be careful and these CIs would not oxidize atmospheric DMS at any substantial level.

1 Introduction

As a non-photolytic OH source or a strong oxidant, Criegee intermediates (CIs) influence the chemical processes in the troposphere (Nguyen et al., 2016; Novelli et al., 2014; Johnson and Marston, 2008; Atkinson and Aschmann, 1993; Gutbrod et al., 1997; Zhang et al., 2002) and, ultimately, have an impact on the formation of secondary aerosols and other pollutants (Percival et al., 2013; Wang et al., 2016; Meidan et al., 2019). A detailed understanding of CI chemistry under atmospheric conditions is, thus, necessary to be able to accurately predict and describe the evolution of Earth's atmosphere.

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). They utilized Reactions (R1) and (R2) to prepare CH₂OO and directly measured the rate coefficients of CH₂OO reactions with SO₂ and NO₂ by following the time-resolved decay of CH₂OO.



Surprisingly, the obtained rate coefficients are up to 10⁴ times larger than previous results deduced from ozonolysis experiments (Johnson et al., 2001; Hatakeyama and Aki-

moto, 1994; Johnson and Marston, 2008). For ozonolysis experiments, typically only the ratios of certain 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.

After this pioneering work, the same method has been applied for generation of other CIs, like CH_3CHOO (Taatjes et al., 2013), $(\text{CH}_3)_2\text{COO}$ (Liu et al., 2014a; Chang et al., 2016), methyl vinyl ketone oxide (MVKO) (Barber et al., 2018), methacrolein oxide (MACRO) (Vansco et al., 2019), etc. These CIs have been identified with various detection methods, like photoionization mass spectrometry (Taatjes et al., 2013), infrared action (Liu et al., 2014b) and absorption (Su et al., 2013; Lin et al., 2015) spectroscopy, UV–visible absorption or depletion spectroscopy (Liu et al., 2014a; Beames et al., 2013; Sheps, 2013; Smith et al., 2014; Chang et al., 2016; Ting et al., 2014), microwave spectroscopy (McCarthy et al., 2013; Nakajima et al., 2015), etc. In addition, utilizing the direct detection of CIs, a number of kinetic investigations of CI reactions, e.g. with SO_2 (Huang et al., 2015), water vapor (Chao et al., 2015), alcohols (Chao et al., 2019), thiols (Li et al., 2019), amines (Chhantyal-Pun et al., 2019), carbonyl molecules (Taatjes et al., 2012), and organic (Welz et al., 2014) and inorganic (Foreman et al., 2016) acids, etc., have been reported (Lee, 2015; Osborn and Taatjes, 2015; Lin and Chao, 2017; Khan et al., 2018; Cox et al., 2020).

Recently, Newland et al. (2015) studied the reactivity of CIs with H_2O and, for the first time, with dimethyl sulfide (DMS) in the ozonolysis of isoprene at the EUPHORE simulation chamber facility and found a rapid reaction of CIs with DMS. A mixture of CH_2OO , MVKO, and MACRO was generated through ozonolysis of isoprene with a total CI yield of 0.56 ± 0.03 (Newland et al., 2015). The relative yields of the individual CIs have previously been estimated to be 0.58 or 0.55 for CH_2OO , 0.23 or 0.37 for MVKO, and 0.19 or 0.08 for MACRO by an analysis based on a large laboratory, modeling, and field data set (Nguyen et al., 2016) or an earlier theoretical calculation (Zhang et al., 2002), respectively. To determine reaction rates, Newland et al. (2015) used a relative rate method and followed the removal of SO_2 versus the removal of other reactants. For the reaction $\text{CI} + \text{DMS}$ relative to the reaction $\text{CI} + \text{SO}_2$, they obtained a relative rate coefficient of $k_{\text{DMS}+\text{CI}}/k_{\text{SO}_2+\text{CI}} = 3.5 \pm 1.8$ (Newland et al., 2015). Since the reactions of typical CIs with SO_2 are very fast, with rate coefficients on the order of $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Welz et al., 2012; Lee, 2015; Osborn and Taatjes, 2015; Lin and Chao, 2017; Khan et al., 2018), this result suggests that the reaction of $\text{CI} + \text{DMS}$ is extremely fast, with a rate coefficient of ca. $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value is extremely large, close to those of the fastest reactions of CIs.

Newland et al. (2015), 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 may not correspond to those of single elementary reactions.

DMS is the major sulfur-containing species in the atmosphere with high abundances in the marine boundary layer (Yvon et al., 1996) but also, for example, in the Amazon basin (Jardine et al., 2015) and has been shown to play an important role in the formation of SO_2 and sulfuric acid, which are precursors of sulfide aerosols (Andreae and Crutzen, 1997; Charlson et al., 1987; Faloon, 2009). The results of Newland et al. (2015) therefore suggest that in regions with high concentrations of CIs, the $\text{CI} + \text{DMS}$ reactions will have a comparable impact on the oxidation of DMS, considering the main atmospheric oxidants are OH and NO_3 ($k_{\text{DMS}+\text{OH}} = 4.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $k_{\text{DMS}+\text{NO}_3} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$; Atkinson et al., 2004).

Here we report the first direct kinetic study of DMS reactions with CH_2OO and MVKO, the main CIs formed in the ozonolysis of isoprene. CIs have strong UV–visible absorption (Lin and Chao, 2017). For example, CH_2OO and MVKO absorb strongly (peak cross section $\sigma \geq 1 \times 10^{-17} \text{ cm}^2$) in the wavelength ranges of 285–400 nm (Ting et al., 2014; Lewis et al., 2015) and 315–425 nm (Vansco et al., 2018) (> 20 % of the peak value), respectively. This strong and distinctive absorption has been utilized to probe CIs in a number of kinetic experiments, including their reactions with SO_2 , water vapor, alcohols, thiols, organic and inorganic acids, carbonyl compounds, alkenes, etc. (Khan et al., 2018; Lin and Chao, 2017; Osborn and Taatjes, 2015; Lee, 2015). In this work, both CH_2OO and MVKO were directly probed in real time via their strong UV absorption at 340 nm. For MVKO, there are four possible conformers. Following the nomenclature of Barber et al. (2018), *syn*- or *anti*-MVKO (*E*- or *Z*-MVKO) has a methyl or vinyl group, respectively, at the same side of the terminal oxygen, while *cis* and *trans* refer to the orientation between the vinyl $\text{C}=\text{C}$ and the carbonyl $\text{C}=\text{O}$ bonds. 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. (2020), 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).

Surprisingly, our experimental results do not indicate any significant reactivity of DMS with CH_2OO or MVKO. We therefore propose upper limits of the rate coefficients for these reactions. Implications for atmospheric chemistry are discussed.

2 Method

2.1 Experimental setup

The experimental setup has been described previously (Chao et al., 2019; Chao et al., 2015). To generate CH₂OO and MVKO, we followed the approaches of Welz et al. (2012) and Barber et al. (2018), respectively. The MVKO formation is through the reaction sequence ICH₂–CH=C(I)–CH₃ + *hν* → CH₃(C₂H₃)CI + I, CH₃(C₂H₃)CI + O₂ → MVKO + I, analogue to Reactions (R1) and (R2). We applied a 308 nm photolysis laser (XeCl excimer laser) for generating CH₂OO, while a photolysis laser at 248 nm (KrF excimer laser) was used for generating MVKO because the MVKO precursor absorbs 308 nm photons too weakly. However, a small amount of DMS would absorb 248 nm light and dissociate; the photodissociated DMS may affect the kinetics of the CIs. 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.

Experiments were conducted in a photolysis reactor (inner diameter: 1.9 cm, effective length: 71 cm). The photolysis laser beam was coupled into and out of the reactor by two long-pass filters (248 nm: Eksma Optics, custom-made 275 nm long pass; 308 nm: Semrock LP03-325RE-25) and monitored with an energy meter (Gentec-EO, QE25SP-H-MB-D0). The probe light was from a plasma Xe lamp (Energetiq, EQ-99) (Su and Lin, 2013) and directed through the reactor collinearly with the photolysis beam. It passes through the reactor six times, resulting in an effective absorption path length of ca. 426 cm. After passing through band-pass filters (340 nm, Edmund, no. 65129, 10 nm bandwidth, OD 4), the probe beam and a reference beam which did not pass through the reactor were both focused on a balanced photodiode detector (Thorlabs, PDB450A). Output signals were recorded in real time with a high-resolution oscilloscope (LeCroy, HDO4034, 4096 vertical resolution) and averaged for 120 laser shots (repetition rate ~ 1 Hz). We observed a small time-dependent variation in transmittance even when no precursor was introduced into the reactor. 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.

All reactant gas flows were controlled by calibrated mass-flow controllers (Brooks: 5850E and Bronkhorst: EL-FLOW prestige) and mixed before entering the reactor. Reactant concentrations were determined prior to the mixing of the reactant flows by UV absorption spectroscopy in two separate absorption cells for either DMS (absorption path length 90.4 cm for [DMS] ≤ 1.7 × 10¹⁵ cm⁻³ or 20.1 cm for [DMS] ≤ 8.1 × 10¹⁵ cm⁻³) or the respective diiodo precursors (absorption path length 90.4 cm) using the reported absorption cross sections (Sander et al., 2011; Limão-Vieira et al., 2002). However, because no absorption cross sections

for 1,3-diiodo-2-butene have been reported, its absolute concentration cannot be determined. We, thus, can only report the absorbance (precursor *Abs*) of 1,3-diiodo-2-butene in the photolysis reactor (Table S3). Typical concentration ranges were [CH₂I₂] = (0.23–2.54) × 10¹⁴ cm⁻³, [O₂] = (3.28–3.30) × 10¹⁷ cm⁻³, and [DMS] = (0–8.1) × 10¹⁵ cm⁻³. We assume ideal gas behavior for the concentration calculation. The majority of the experiments were performed at 300 Torr (N₂) and 298 K.

2.2 Theoretical methodology

The potential energy surface (PES) of the CH₂OO + DMS reaction was first explored at the M06-2X/cc-pVDZ level of theory (Dunning, 1989; Zhao and Truhlar, 2008), characterizing the geometries and rovibrational characteristics of the reactants, intermediates, and transition states for a wide range of potential reaction channels. The pathways found were re-optimized with a larger basis set using M06-2X/aug-cc-pV(T+d)Z, where the triple-zeta basis set is enhanced by tight d orbitals to improve the description of the sulfur atom bonds (Bell and Wilson, 2004; Dunning et al., 2001). Finally, CCSD(T)/aug-cc-pVTZ single-point energy calculations were performed to obtain more reliable energies (Dunning, 1989; Purvis and Bartlett, 1982). The *T*₁ diagnostics, all ≤ 0.026 except for CH₂OO (0.042), suggest that the calculations are not affected by strong multi-reference character in intermediates or transition states. The molecular characteristics thus obtained were used in canonical transition state theory (CTST) calculations to derive the temperature-dependent rate coefficient *k*(*T*) (Truhlar et al., 1996). All calculations were performed using the Gaussian-09 software suite (Frisch et al., 2009). The Supplement discusses additional calculations.

3 Results and discussion

3.1 CH₂OO + DMS

Representative time traces of CH₂OO absorption recorded at 340 ± 5 nm ($\sigma = 1.23 \times 10^{-17}$ cm² at 340 nm) (Ting et al., 2014) under various [DMS] values are depicted in Fig. 1. Similar results but recorded with different initial concentrations of CH₂I₂ and/or different photolysis laser fluences are displayed in Figs. S12–S14. At *t* = 0, CH₂OO is generated within 10⁻⁵ s by photolysis of CH₂I₂ at 308 nm (nanosecond pulsed laser) (Reaction R1) and the fast reaction of CH₂I with O₂ (Reaction R2) ($k_{O_2} = 1.4 \times 10^{-12}$ cm³ s⁻¹ (Eskola et al., 2006); [O₂] = 3.3 × 10¹⁷ cm⁻³). The subsequent decay in absorption is due to the consumption of CH₂OO 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 CH₂OO has been found to be rather fast ($k_{\text{self}} = 8 \times 10^{-11}$ cm³ s⁻¹) (Mir et al., 2020). However, the effect of the self-reaction (Smith et al.,

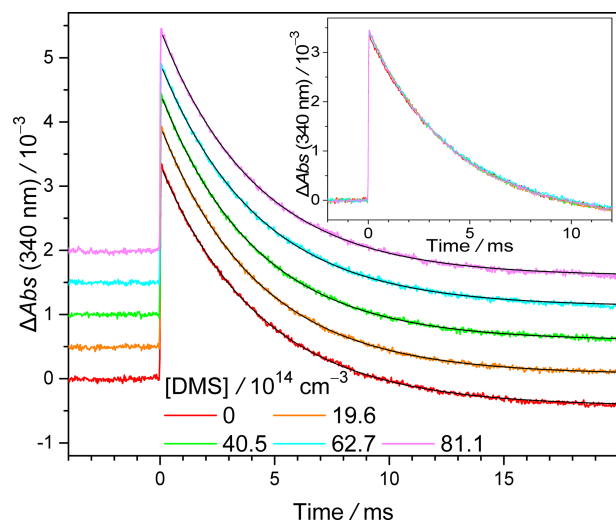


Figure 1. Representative time traces of CH_2OO absorption recorded at 340 ± 5 nm under various $[\text{DMS}]$ values. The traces are shifted upward by various amounts for clearer visualization. Smooth black lines are the exponential fit. The photolysis laser (308 nm) pulse defines $t = 0$. The negative baseline (more obvious at long reaction time) is due to depletion of the precursor, CH_2I_2 , which absorbs weakly at 340 nm ($\sigma = 8.33 \times 10^{-19} \text{ cm}^2$) (Atkinson et al., 2008). This depletion is constant in the probed time window and would not affect the kinetics of CH_2OO . The inset shows the profiles without upshifting to show the overlapping. See Exp#1 of Table S1 for detailed experimental conditions.

2016; Li et al., 2020) would not affect the determination of k_{DMS} under our experimental conditions. We can see that the decay curves of CH_2OO at various $[\text{DMS}]$ values are extremely similar to one another, indicating that the reaction of $\text{CH}_2\text{OO} + \text{DMS}$ is not significant.

The decay of CH_2OO can be well described with an exponential function ($R^2 > 0.995$) (e.g. Fig. 1).

$$[\text{CH}_2\text{OO}](t) = [\text{CH}_2\text{OO}]_0 e^{-k_{\text{obs}} t} \quad (1)$$

The fitting error of k_{obs} is less than 1% mostly. Under the conditions of this study, the consumption of CH_2OO can be described as

$$-\frac{d[\text{CH}_2\text{OO}]}{dt} = k_{\text{obs}} [\text{CH}_2\text{OO}] = (k_0 + k_{\text{DMS}+\text{CH}_2\text{OO}} [\text{DMS}]) [\text{CH}_2\text{OO}], \quad (2)$$

where k_0 represents the sum of the effective rate coefficients for all consumption channels of CH_2OO except its reaction with DMS, which is described as the bimolecular rate coefficient $k_{\text{DMS}+\text{CH}_2\text{OO}}$.

The CH_2OO decay rate coefficients k_{obs} as functions of $[\text{DMS}]$ for different photolysis laser fluences are summarized in Fig. 2. At higher laser fluences, more CH_2OO and radical byproducts are generated, resulting in shorter CH_2OO lifetimes (see Fig. S7: plot of k_0 against $[\text{CH}_2\text{I}_2] \times I_{308 \text{ nm}}$),

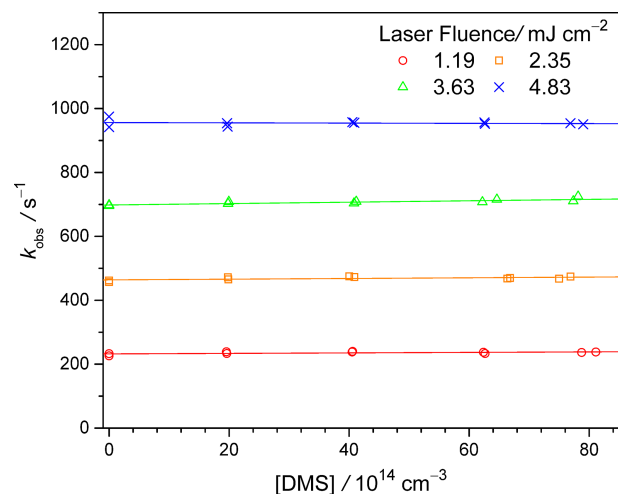


Figure 2. k_{obs} of CH_2OO against $[\text{DMS}]$ determined from experiments (Exp#1–4, Table S1) at different photolysis laser fluences $I_{308 \text{ nm}}$; solid lines are linear fits. For each data point, the error of the single exponential fitting is less than 1% (thus not shown).

similar to previous works (Smith et al., 2016; Li et al., 2020; Zhou et al., 2019). The slopes of the linear fits of Fig. 2 would correspond to $k_{\text{DMS}+\text{CH}_2\text{OO}}$ (see Eq. 2). However, the slope values are quite small, close to our detection limit (Lin et al., 2018). Within experimental uncertainty, $k_{\text{DMS}+\text{CH}_2\text{OO}}$ exhibits no clear correlation to the photolysis laser fluence and other experimental conditions like $[\text{CH}_2\text{I}_2]$ (see Table S1 and Fig. S9). From a total of 11 experimental data sets (Exp#1–11, Table S1), we inferred an average $k_{\text{DMS}+\text{CH}_2\text{OO}} = (1.2 \pm 1.0) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (error bar is 1 standard deviation of the 11 data points).

3.2 Test of the effect of DMS photolysis

Although the absorption cross section of DMS is quite small ($1.28 \times 10^{-20} \text{ cm}^2$ at 248 nm and $< 1 \times 10^{-22} \text{ cm}^2$ at 308 nm) (Limão-Vieira et al., 2002), the photolysis of DMS, especially at 248 nm, should be considered. We have performed a quantitative estimation of radical concentrations originating from the photolysis of DMS under the experimental conditions of this work (Sect. S5 in the Supplement) and show the results in Table S4.

In order to reduce the influence of DMS photolysis for the MVKO experiments, which require 248 nm photolysis (see Sect. 3.3), we constrain $[\text{DMS}] \leq 1.7 \times 10^{15} \text{ cm}^{-3}$ and the laser fluence $I_{248 \text{ nm}} \leq 3.72 \text{ mJ cm}^{-2}$. Then the amount of dissociated $[\text{DMS}]$ would be $\leq 1 \times 10^{11} \text{ cm}^{-3}$, smaller than the dissociated $[\text{CH}_2\text{I}_2] \cong 1.2 \times 10^{12} \text{ cm}^{-3}$ by an order of magnitude or more.

The expected products of DMS photolysis are $\text{CH}_3 + \text{CH}_3\text{S}$ (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. Thus, the small amount of dissociated [DMS] would only have a minor effect. And indeed, the results of $\text{CH}_2\text{OO} + \text{DMS}$ reaction obtained with 248 nm photolysis (Figs. S2, S15, Table S2) are very similar to those with 308 nm photolysis (Figs. 2, S1, S12–S14, Table S1), indicating the effect of DMS photolysis is very minor. The values of $k_{\text{DMS}+\text{CH}_2\text{OO}}$ obtained with 248 nm photolysis (Table S2) range from 1.6×10^{-15} to $3.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, which are only slightly higher than the results obtained with 308 nm photolysis (see Fig. S9). This indicates that the effect of the DMS photolysis would be on the order of $(1\text{--}3) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for $k_{\text{DMS}+\text{CH}_2\text{OO}}$.

3.3 MVKO + DMS

Typical absorbance–time profiles of MVKO under various [DMS] values ($\leq 1.3 \times 10^{15} \text{ cm}^{-3}$) are presented in Fig. 3. When generating MVKO via the reaction of $\text{CH}_3(\text{C}_2\text{H}_3)\text{CI} + \text{O}_2$ at a high pressure like 300 Torr, the MVKO signal profiles rise more slowly than those of CH_2OO , with the maximum of the MVKO signal being at about 1.5 ms. Lin et al. (2020) have conducted detailed kinetic and quantum chemical studies on this phenomenon and concluded that the slow rise of the MVKO signal is due to the thermal decomposition of an adduct, $\text{CH}_3(\text{C}_2\text{H}_3)\text{CIOO} \rightarrow \text{CH}_3(\text{C}_2\text{H}_3)\text{COO} + \text{I}$. See Supplement (Sect. S3) for details. 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 $\text{CH}_3(\text{C}_2\text{H}_3)\text{CIOO}$ is relatively less stable due to disruption of the conjugation. Nevertheless, no significant changes in the absorbance–time profiles of MVKO with varying [DMS] values can be noted (Fig. 3 inset), indicating the reaction of $\text{MVKO} + \text{DMS}$ is insignificant. In Fig. 3, we can see that the lifetime of MVKO is on the order of 10 ms (i.e. a decay rate coefficient of ca. 100 s^{-1}) and the variation in the MVKO signal is insignificant upon adding [DMS]. This indicates that the reaction with DMS only changes, at the most, the MVKO lifetime by a small fraction (< 0.1) (a larger change would cause obvious deviation from the experimental observations of Fig. 3). Thus, $k_{\text{DMS}+\text{MVKO}}$ can be estimated to be on the order of $(100 \text{ s}^{-1})(0.1)/(1.3 \times 10^{15} \text{ cm}^{-3}) \cong 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. A similar conclusion can be drawn from additional profiles recorded with different precursor concentrations and photolysis laser fluences and at different pressures (Figs. S16–S18).

To obtain more quantitative values of $k_{\text{DMS}+\text{MVKO}}$, we performed kinetic analysis and the details are given in the Supplement (Sect. S3); selected results of k_{obs} as functions of [DMS] are presented in Fig. 4. Similar to the $\text{CH}_2\text{OO} + \text{DMS}$ case, the rate coefficients for the reaction $\text{MVKO} + \text{DMS}$ show no clear dependence on laser fluence or precursor concentration. From a total of 15 experiment sets (Exp#15–29, Table S3), we obtain an average rate coefficient $k_{\text{DMS}+\text{MVKO}} = (6.2 \pm 3.3) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (error bar is 1 standard deviation of the 15 data points). As mentioned

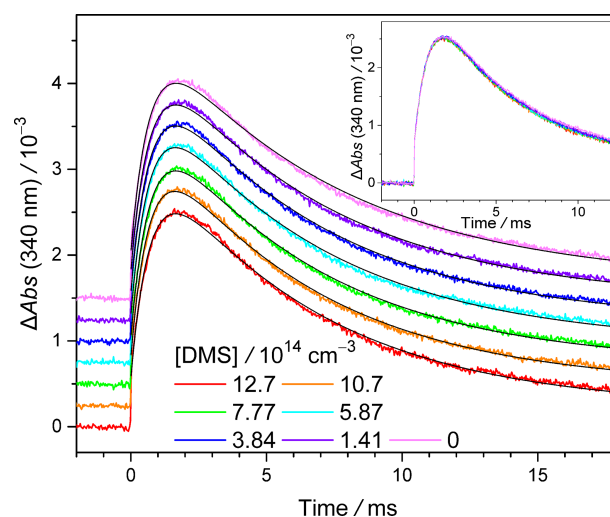


Figure 3. Representative MVKO absorbance–time profiles recorded at 340 nm under various [DMS] values (298 K, 300 Torr, see Exp#16 of Table S3). The profiles are upshifted by various amounts to avoid overlapping. The color lines are experimental data and the smooth black lines are the model fit. The inset shows the profiles without upshifting to show the overlapping.

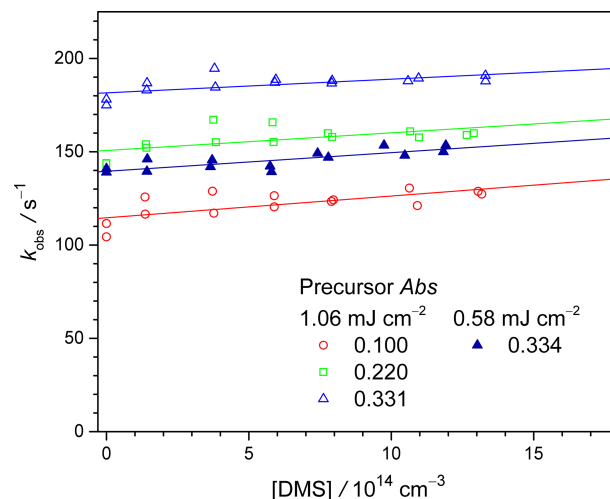


Figure 4. Plot of the observed decay rate coefficient of MVKO k_{obs} against [DMS] at various laser fluences and precursor absorbances (Exp#15–18). For each data point, the fitting error bar is less than 1% (thus, not shown).

above, the MVKO precursor absorbs light weakly at 308 nm and requires 248 nm photolysis, such that small amounts of DMS would also be photodissociated. However, the above $\text{CH}_2\text{OO} + \text{DMS}$ results indicate that the effect of DMS photolysis in our experiments is minor (on the order of $(1\text{--}3) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for $k_{\text{DMS}+\text{CH}_2\text{OO}}$), but may still lead to overestimation of $k_{\text{DMS}+\text{MVKO}}$. In this regard, the true value of $k_{\text{DMS}+\text{MVKO}}$ may be smaller than the above number.

3.4 Upper limiting rate coefficients and implications for atmospheric modeling

The experimental values of $k_{\text{DMS}+\text{CI}}$ (Tables S1 and S3) are quite small, and their standard deviations are comparable to their average values, indicating that the measured $k_{\text{DMS}+\text{CI}}$ values are close to our detection limit. Here we choose the boundary of 3 standard deviations as the upper limits for $k_{\text{DMS}+\text{CI}}$, $k_{\text{DMS}+\text{CH}_2\text{OO}} \leq 4.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, and $k_{\text{DMS}+\text{MVKO}} \leq 1.6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ (Table 1). From Table 1, we can see that for the reactions of both CIs studied, the upper limits of the rate coefficients for their reactions with DMS, k_{DMS} , are much smaller than the literature values of their reactions with SO_2 , k_{SO_2} . The resulting ratios $k_{\text{DMS}}/k_{\text{SO}_2}$ are about 4 orders of magnitude smaller than that reported by Newland et al. (2015).

The steady-state concentrations of CIs, $[\text{CI}]_{\text{ss}}$, in the troposphere have not been well established yet (Kim et al., 2015; Khan et al., 2018; Vereecken et al., 2017; Bonn et al., 2014; Boy et al., 2013). Novelli et al. (2017) have estimated an average CI concentration of $5 \times 10^4 \text{ molecules cm}^{-3}$ (with an order of magnitude uncertainty) for two environments they have investigated. Due to fast thermal decomposition (Li et al., 2020; Smith et al., 2016; Vereecken et al., 2017; Stephenson and Lester, 2020) and/or fast reaction with water vapor (Chao et al., 2015; Lee, 2015; Osborn and Taatjes, 2015; Lin and Chao, 2017; Khan et al., 2018), $[\text{CI}]_{\text{ss}}$ is expected to be low, at least a couple of orders of magnitude lower than the steady-state concentration of OH radicals $[\text{OH}]_{\text{ss}}$. The small k_{DMS} values obtained in this work imply that these reactions would not compete with the conventional DMS oxidation pathways like the reactions with OH or NO_3 , of which both the reactant concentrations and rate coefficients are significantly larger. If the DMS reactions with CIs were to be competitive (e.g. 5 % of the overall DMS removal) to those with NO_3 (e.g. $[\text{NO}_3] \cong 2.5 \times 10^8 \text{ cm}^{-3}$) and OH (e.g. $[\text{OH}] \cong 1 \times 10^6 \text{ cm}^{-3}$), the concentration of CIs would have to be unreasonably high, on the order of 10^{11} cm^{-3} .

Newland et al. (2015) performed their experiments on a mixture of three CIs (CH_2OO , MVKO, MACRO) as resulting from the ozonolysis of isoprene. The presence of these three CIs, however, cannot explain the difference of 4 orders of magnitude to our results. Due to the lower yield of MACRO compared to the high yield for $\text{CH}_2\text{OO} + \text{MVKO}$ (Nguyen et al., 2016; Zhang et al., 2002), it would require an unreasonably large $k_{\text{DMS}+\text{MACRO}}$ to explain the conclusion of Newland et al. (2015). In addition, the electronic structures of MACRO and MVKO are similar. Thus, similar reactivities are expected.

For the determination of the relative rate of the CI + DMS reaction, Newland et al. (2015) monitored the consumption of SO_2 over a measurement period of up to 60 min until approximately 25 % of isoprene was consumed. 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. (2015) in the section Experimental uncertainties. Our direct measurements and kinetics are very straightforward; the obtained results for individual CIs may provide useful constraints for related ozonolysis systems.

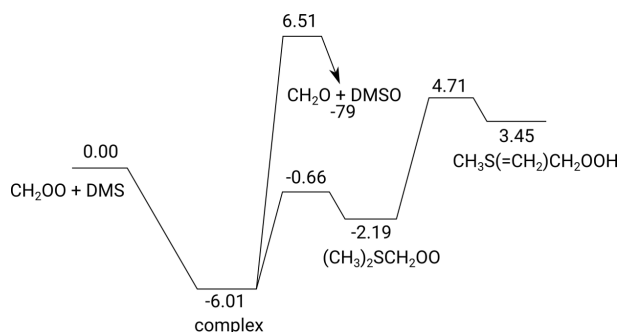
3.5 Theoretical predictions for the reaction of $\text{CH}_2\text{OO} + \text{DMS}$

The potential energy surface for $\text{CH}_2\text{OO} + \text{DMS}$ is shown in Fig. 5. The reaction proceeds through a pre-reaction complex at $-6.0 \text{ kcal mol}^{-1}$ below the free reactants, from which a weakly bonded adduct, $(\text{CH}_3)_2\text{SCH}_2\text{OO}$ at an energy of $-2.2 \text{ kcal mol}^{-1}$, can be formed through a submerged transition state (TS). At our level of theory, the wave function of this adduct converges to a closed-shell species with very strong zwitterionic character. A potential cycloadduct with a four-membered $-\text{SCH}_2\text{OO}-$ ring was found to be unstable. Two accessible product-forming transition states were discovered. The first channel starts from the pre-reaction complex and leads to $\text{DMSO} + \text{CH}_2\text{O}$ by direct transfer of the terminal O atom of CH_2OO . A high barrier was found, $6.5 \text{ kcal mol}^{-1}$ above the free reactants, leading to a slow reaction despite the predicted strong exothermicity of 79 kcal mol^{-1} for this channel. The second channel involves the migration of a DMS methyl H atom to the outer oxygen of the $(\text{CH}_3)_2\text{SCH}_2\text{OO}$ adduct with a barrier of $4.7 \text{ kcal mol}^{-1}$ above the free reactants, endothermically forming $\text{CH}_3\text{S}(=\text{CH}_2)\text{CH}_2\text{OOH}$ (i.e. the methyldene hydroperoxy equivalent of DMSO) with an energy $3.5 \text{ kcal mol}^{-1}$ above the free reactants. No further low-lying reaction channels for this product were found, including formation of $\text{C}\cdot\text{H}_2\text{OOH} + \text{CH}_3\text{SC}\cdot\text{H}_2$ which has an energy barrier of $\geq 20 \text{ kcal mol}^{-1}$ at the M06-2X/cc-pVDZ level of theory. 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 (Decker et al., 2017). As described in the Supplement, reaction with O_2 appears not competitive, as expected given that all intermediates are closed-shell (zwitterionic) species. For the reactions of DMS with substituted CI (*syn*- CH_3CHOO and *anti*- CH_3CHOO ; see Supplement), we found similar complex stability but the adducts are energetically even less favorable, hampering their formation. For MVKO, the adduct was found to be unstable, and formation of DMSO or H migration of the DMS methyl hydrogen atoms has similar energy barriers as with CH_2OO . The most likely fate of the intermediates in the reaction of CI + DMS is thus reformation of the free reactants, with rapid equilibration between free reactants, pre-reaction complex, and adduct (where applicable). For $\text{CH}_2\text{OO} + \text{DMS}$, complex and adduct interconvert at rates $> 10^7 \text{ s}^{-1}$ at room temperature ($> 4 \times 10^6 \text{ s}^{-1}$ at 200 K). The lifetime of the complex or adduct with respect to redissociation to the free reactants is estimated to be of the

Table 1. Summary of the experimental bimolecular reaction rate coefficients of CI + SO₂ and CI + DMS.

CI	$k_{\text{DMS}}/$ $\text{cm}^3 \text{s}^{-1}$	$k_{\text{SO}_2}/$ $\text{cm}^3 \text{s}^{-1}$	$k_{\text{DMS}}/k_{\text{SO}_2}$	Reference
CH ₂ OO	$< 4.2 \times 10^{-15}$	3.7×10^{-11} ^a	$< 1.1 \times 10^{-4}$	This work
MVKO	$< 1.6 \times 10^{-14}$	4.1×10^{-11} ^b	$< 3.9 \times 10^{-4}$	This work
CI _s	–	–	3.5 ± 1.8	Newland et al. (2015)

^a The average value of $(3.4 \pm 0.4) \times 10^{-11}$ (Stone et al., 2014), $(3.5 \pm 0.3) \times 10^{-11}$ (Liu et al., 2014c), $(3.8 \pm 0.04) \times 10^{-11}$ (Chhantyal-Pun et al., 2015), $(3.9 \pm 0.7) \times 10^{-11}$ (Welz et al., 2012), and $(4.1 \pm 0.3) \times 10^{-11}$ (Sheps, 2013). ^b Caravan et al. (2020).

**Figure 5.** The potential energy surface of CH₂OO + DMS (kcal mol⁻¹), based on ZPE-corrected (ZPE signifies zero-point energy) CCSD(T)//M06-2X relative energies.

order of microseconds or less at room temperature, assuming a barrierless complexation channel.

The Supplement also describes a set of calculations at a lower level of theory on the catalytic effect of DMS on a set of unimolecular and bimolecular loss processes of CI reactants. We conclude that DMS does not catalyze unimolecular decay of any of the CIs examined and that DMS does not enhance redissociation of the CI + SO₂ cycloadduct. No information is available on the impact of DMS on the forward reaction rates of CI bimolecular reactions. In the absence of catalytic effects, the observed elementary reaction of CI with DMS must occur through the pathways depicted in Fig. 5. The total rate coefficient for product formation, i.e. DMSO or CH₃S(=CH₂)CH₂OOH, is predicted at

$$k(298 \text{ K}) = 5.5 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1};$$

$$k(200 - 450 \text{ K}) = 1.34 \times 10^{-44} T^{10.28} \exp(129 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1}.$$

Both channels contribute roughly equally at 298 K, with the higher TS being more loose and the lower TS being more rigid. The CH₃S(=CH₂)CH₂OOH product is intrinsically not very stable and reverses to the (CH₃)₂SCH₂OO adduct with a rate coefficient $\geq 10^{12} \text{ s}^{-1}$, over a very low reverse barrier of 1.3 kcal mol⁻¹. It seems unlikely that this product can undergo any bimolecular reactions prior to redissociation; reaction with O₂ was already found to be very slow. We should then consider that the only stable product effec-

tively formed is DMSO + CH₂O, with the following rate coefficient:

$$k_{\text{eff}}(298 \text{ K}) = 3.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1};$$

$$k_{\text{eff}}(200 - 450 \text{ K}) = 1.34 \times 10^{-26} T^{4.40}$$

$$\exp(-2415 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1}.$$

These theoretical rate predictions are in full agreement with the experimental observations on the elementary reactions of CI with DMS. As documented in the Supplement, similarly slow rate coefficients were predicted for substituted CIs, including MVKO formed in the ozonolysis of isoprene.

4 Summary

In this work, we present the first direct kinetic study of the reactions of DMS with CH₂OO and MVKO, which are the major CIs formed in the ozonolysis of isoprene. We generated the individual CIs by photolysis of the corresponding diiodo precursors in the presence of O₂ and monitored their decay via their strong UV absorption at 340 nm in real time. Our results do not indicate any notable reactivity of DMS with the two CIs studied. We therefore inferred the rate coefficients $k_{\text{DMS}+\text{CH}_2\text{OO}} \leq 4.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and $k_{\text{DMS}+\text{MVKO}} \leq 1.6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. For the reaction of CH₂OO + DMS, quantum chemistry calculation did not find any low-energy reaction pathways, either by direct reaction or by catalysis of unimolecular reactions, and the calculation predicted an even smaller rate coefficient of $k_{\text{DMS}+\text{CH}_2\text{OO}} = 3.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ at 298 K. Similarly low rate coefficients are predicted for substituted CIs such as CH₃CHOO and MVKO. Our results indicate that even in regions with high abundance of CIs and high concentrations of DMS, the isoprene-derived CIs will not notably contribute to the oxidation of DMS.

Data availability. More experimental and calculation data can be found in the Supplement.

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-20-12983-2020-supplement>.

Author contributions. JJML conceived the experiment. MTK set up the experiment. MTK and IW performed the measurements. MTK analyzed the experimental data. LV performed the theoretical calculations. MTK, IW, CF, LV, and JJML discussed the results and wrote the paper.

Competing interests. The authors declare that they have no conflict of interest.

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