Surprisingly Long Lifetime of Methacrolein Oxide, an Isoprene Derived Criegee Intermediate, Under Humid Conditions

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Abstract

Ozonolysis of isoprene, the most abundant alkene in the atmosphere, produces three distinct Criegee intermediates (CIs): CH_2OO , methyl vinyl ketone oxide (MVKO) and methacrolein oxide (MACRO). Here we investigated the UV-visible spectroscopy and reaction kinetics of thermalized MACRO. An extremely fast reaction of *anti*-MACRO with SO_2 has been found with a rate coefficient of $(1.5 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 298 K (150–500 Torr), which is ca. 4 times the value for *syn*-MVKO. However, the reaction of *anti*-MACRO with H_2O has been observed to be quite slow with a rate coefficient of $(8 \pm 6) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 298 K (300 to 500 Torr), which is smaller than literature values by 1 or 2 orders of magnitude. Our results indicate that *anti*-MACRO has an atmospheric lifetime much longer than previously thought, resulting in a much higher steady-state concentration. Owing to larger reaction rate coefficient, the impact of *anti*-MACRO on the oxidation of atmospheric SO_2 would be substantial, even larger than that of *syn*-MVKO.

Introduction

Isoprene is the most abundant unsaturated hydrocarbon in the atmosphere.¹ Ozonolysis of isoprene produces three kinds of carbonyl oxides (also called Criegee Intermediates, CIs): CH_2OO , methyl vinyl ketone oxide (MVKO: $\text{CH}_3\text{C}(\text{C}_2\text{H}_3)\text{OO}$) and methacrolein oxide (MACRO: $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CHOO}$).^{2–4} CIs are very reactive species. In 2012, their reactions with SO_2 are found to be faster than previously thought by orders of magnitude.⁵ The oxidation of SO_2 ($\text{SO}_2 \rightarrow \text{SO}_3$) has gained wide attention because it is an important process in the formation of secondary aerosols ($\text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$).^{6–15} Field and chamber studies, pioneered by Mauldin et al., indicate that there is a non-OH oxidant contributing to the oxidation of atmospheric SO_2 and this new oxidant may be Criegee intermediates.^{9–15}

On the other hand, laboratory studies on individual CI reactions have revealed that the atmospheric fate of a CI would strongly depend on its structure.^{16–17} For CH_2OO and *anti*- CH_3CHOO , which have a H-atom at the *syn* position, the main decay pathway is their reactions with water vapor (H_2O monomer and dimer).^{17–22} These reactions are extremely fast, resulting in very low steady-state concentrations of such CIs, which are too low to oxidize atmospheric SO_2 at any substantial level.¹⁶ For *syn*- CH_3CHOO and $(\text{CH}_3)_2\text{COO}$, which have an alkyl group at the *syn* position, their unimolecular reactions via intramolecular 1,4-H-atom transfer are the major decay process.^{23–30} These unimolecular processes are not slow and essentially limit the steady-state concentrations of such CIs.^{16,31}

Different from alkyl substituted CIs, MVKO and MACRO have a $\text{C} = \text{C}$ double bond, which forms extended conjugation with the carbonyl oxide functional group (resonance stabilized). The pioneering works of Lester and coworkers have demonstrated a photolytic synthesis method that allows direct detection of MVKO and MACRO.^{32–33} Via this new synthesis scheme, recent studies have shown that the resonance-stabilization would affect the reactivity and thus the atmospheric fate of MVKO.^{32–36}

For MVKO, there are four possible isomers/conformers.^{2, 32, 34–35} Similar to simpler CIs, the barrier of rotating the carbonyl C = O bond is high, resulting in non-interconverting *syn* and *anti* isomers (following the nomenclature of Barbar et al.).^{32, 37} However, the barrier of rotating the C–C single bond between the C = C and C = O bonds is low, giving essentially an equilibrium mixture of *cis* and *trans* conformers.^{31, 38–39} It has been predicted that *anti-trans*-MVKO would quickly interconvert to *anti-cis*-MVKO ($> 10^6 \text{ s}^{-1}$),³¹ which decays quickly via fast 1,5-ring closure to form dioxole with a rate coefficient of 2140 s^{-1} .^{31–32, 40–41} As a result, *anti*-MVKO was not observed experimentally, presumably due to short lifetime and/or low yield.³⁵

Caravan et al. have found that *syn*-MVKO reacts with SO₂ and formic acid as fast as other alkyl CIs do. Furthermore, based on their global chemistry and transport model, they showed that *syn*-MVKO could significantly increase the atmospheric oxidation of SO₂ and the removal of formic acid, where the isoprene emission is high. The high impact of *syn*-MVKO is mostly due to the abundance of isoprene (its source) and its slow decay (slow unimolecular decay and slow reaction with water).³⁵ The slow decay of *syn*-MVKO is related to its resonance stabilized electronic structure,^{32,36} which would be disrupted at the transition state of the unimolecular reaction.³²

MACRO also has a resonance-stabilized electronic structure and two non-interconverting families of conformers (Fig. 1). It has also been predicted that *syn-trans*-MACRO (following the nomenclature of Vansco et al.)³³ would interconvert quickly ($> 10^6 \text{ s}^{-1}$) to *syn-cis*-MACRO, which would undergo fast unimolecular decay ($k_{\text{uni}} = 2500 \text{ s}^{-1}$) to form dioxole, while *anti* conformers are expected to have slow unimolecular decay (ca. 10 s^{-1}).³¹ However, similar to other *anti* types of CIs (CH₂OO and *anti*-CH₃CHOO),¹⁷ the reaction of *anti*-MACRO with water vapor was predicted to be fast ($k_{\text{eff}} = 7.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ by Anglada et al. at relative humidity (RH) = 70% and 298 K, considering both water monomer and dimer reactions).⁴² If so, the fast reaction with water vapor ($> 10^3 \text{ s}^{-1}$) would result in a very low steady-state concentration of *anti*-MACRO, diminishing its atmospheric impact. Nonetheless, as will be shown later, this picture is incorrect.

Very recently, Vansco et al. have reported the electronic spectroscopy and photochemistry of MACRO; as the authors mentioned, “*This UV-visible detection scheme will enable study of its unimolecular and bimolecular reactions under thermal conditions of relevance to the atmosphere.*”³³ Following their method, here we prepare MACRO starting from the photolysis of *E*-1,3-diiodo-2-methylprop-1-ene precursor (Fig. 1). The time-resolved UV-visible spectrum of MACRO was recorded by using a broadband cw light source and a grating spectrometer equipped with an ultrafast CMOS camera. Analyzing the time series of the spectra allows us to retrieve the spectrum of MACRO and its time profile.

To our surprise, the reaction of MACRO with water vapor was found to be much slower than previous predictions,^{31, 42} implying much higher steady-state concentrations for atmospheric MACRO. On the other hand, the resonance stabilized MACRO still reacts extremely fast with SO₂. Based on a recent global

chemistry and transportation model of MVKO,³⁵ our results suggest that the impact of MACRO on the oxidation of atmospheric SO₂ would also be substantial.

Results

Under the same experimental conditions, SO₂ was added to scavenge CIs (see Supplementary Figures 1-2). We found that the spectral feature (i) disappears, indicating its spectral carrier is a Criegee intermediate. We further subtracted the time-resolved spectra recorded at [SO₂] = 1×10¹⁴ cm⁻³ from those without adding SO₂ at each photolysis-probe delay time. This operation removed most of the absorption signals of IO and I₂ (and also other minor byproducts), and the resulted spectra are mainly from the Criegee intermediate. Considering that we were using the same precursor and preparation method of Vansco et al.,³³ we assigned this CI to MACRO.

The spectrum of MACRO can be well fitted with a Gaussian function (Figure 3). This spectrum is similar to that of Vansco et al. who reported a broad spectrum of MACRO peaked at 380 nm with weak oscillatory structure at long wavelengths ascribed to vibrational resonances.³³ However, we do not observe such oscillatory structure; the differences are presumably due to different temperatures of the MACRO samples, as Vansco et al. recorded their spectrum under a jet cool condition.³³

We may decompose the observed spectra into the contributions of MACRO, IO and I₂ (Figure 1 & see Supplementary Figure 4) with a least-squares fit. The resulted signal intensities of MACRO, IO and I₂ are plotted in Figure 2 (lower) as a function of the delay time. The intensities of IO and I₂ grow with time, indicating they are secondary products. While the kinetics of IO and I₂ formation may be interesting, we like to focus on MACRO in this work. We can see that the lifetime of MACRO in this particular experiment is ca. 3 ms, much longer than the predicted value for *syn*-MACRO (< 0.4 ms, based on its $k_{\text{uni}} = 2500 \text{ s}^{-1}$).³¹ And other chemical processes would further shorten the lifetime). Therefore we conclude the observed spectral carrier should be *anti*-MACRO, similar to the case of MVKO.³⁵ Note that the long lifetime conformer of MVKO is *syn*-MVKO (following the nomenclature of Barbar et al.)³² which has a structure similar to *anti*-MACRO. For simplicity, we will use MACRO to represent *anti*-MACRO in the following analysis.

The above analysis has been repeated for experiments adding various [SO₂]. The resulted MACRO signal intensities at each photolysis-probe delay time are plotted in Figure 4 (upper). The decay of MACRO signal can be fitted with a single exponential function to yield a pseudo-first-order rate coefficient, k_{obs} , at each [SO₂].

$$sL[\text{MACRO}](t) = sL[\text{MACRO}]_0 \exp(-k_{\text{obs}} t)$$

Where s is the absorption cross section of MACRO and L is the optical path length. Figure 4 (lower) shows that k_{obs} increases linearly with [SO₂].

$$k_{\text{obs}} = k_0 + k_{\text{SO}_2}[\text{SO}_2]$$

The slope would correspond to the rate coefficient k_{SO_2} of the bimolecular reaction of MACRO with SO_2 , while the intercept k_0 would account for other decay processes of MACRO that are independent on $[\text{SO}_2]$, like reactions with radical byproducts, unimolecular decay, etc.

Because that MACRO can be fully scavenged within 0.3 ms at a high $[\text{SO}_2]$ ($\geq 9.3 \times 10^{13} \text{ cm}^{-3}$), we may further improve the analysis by subtracting the high $[\text{SO}_2]$ spectrum (the average spectrum at the two highest $[\text{SO}_2]$) from other low $[\text{SO}_2]$ spectra to remove most of the byproduct contributions while some minor amounts of IO and I_2 may still remain (SO_2 scavenge method). The resulted spectra were then decomposed into the contributions of MACRO and IO and I_2 . The time profiles of MACRO are plotted in Supplementary Figure 2. When using this SO_2 scavenging method, we did not include the data point at the first delay time (0.18 ms) due to incomplete scavenging.

The kinetic results of MACRO + SO_2 reaction are summarized in Supplementary Table 1. The data at 150 Torr and 500 Torr do not show significant difference after considering the experimental uncertainties. For these 4 sets of experimental data, we report the rate coefficient to be $(1.5 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 298 K and 150–500 Torr ($\pm 1 \sigma$ uncertainty). The rate coefficients of SO_2 reactions with other CIs (CH_2OO ,^{5, 50} *anti*- and *syn*- CH_3CHOO ,^{20, 22} $(\text{CH}_3)_2\text{COO}$,^{29, 49} MVKO³⁵⁻³⁶) are in the range of $(0.4\text{--}2.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.¹⁶⁻¹⁷ It appears that the resonance-stabilization of *anti*-MACRO does not reduce its reaction rate with SO_2 .

The same method has been applied to investigate the kinetics of MACRO reaction with water vapor. To our surprise, the effect of water in the decay of MACRO is rather weak as shown in Figure 5 (upper), indicating slow reaction. From the plots of k_{obs} as a function of $[\text{H}_2\text{O}]$ (Figure 5), we can see that the slopes are quite insignificant; some of them are even negative, indicating that these rate measurements are close to our detection limit. See Supplementary Table 2. The highest $[\text{H}_2\text{O}]$ used is ca. $6 \times 10^{17} \text{ cm}^{-3}$ (ca. 18 Torr), which is a larger portion of the bath gas if the total pressure is only 150 Torr (N_2 balance). Thus, we think it may require some cautions to view the data of 150 torr, because the reaction environment (type of bath gas) changes at various $[\text{H}_2\text{O}]$. Nonetheless, no trend can be found for pressures from 150 to 500 Torr. Finally we chose the results of Exp #5 (500 Torr and 298 K, Supplementary Table 2), which have 14 data points of k_{obs} , to report the rate coefficient for the reaction of MACRO with water vapor, $k_{\text{water-eff}} = (8 \pm 6) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ ($\pm 1 \sigma$ uncertainty).

Discussion

MACRO isomers. As pointed out by Vereecken et al., the *cis-trans* interconversion (Supplementary Figure 5) ($> 10^6 \text{ s}^{-1}$) is orders-of-magnitude faster than other chemical processes, such that the *cis* and *trans* conformers will be in near-equilibrium and should be considered as a single pool of species.³¹ Following

this idea, we summarize the rate coefficients of the unimolecular processes and reactions with water monomer and dimer in Table 1 for relevant Cls.

Table 1. Summary of theoretically estimated unimolecular rate coefficient k_{uni} and bimolecular rate coefficients of the reactions with water monomer and dimer ($k_{\text{H}_2\text{O}}$ and $k_{(\text{H}_2\text{O})_2}$) at 298 K for selected Cls. Our experimental result for *anti*-MACRO reaction with water vapor is shown in square brackets.

Cl	$k_{\text{uni}} /$ s^{-1}	$k_{\text{H}_2\text{O}}$ $/\text{cm}^3 \text{s}^{-1}$	$k_{(\text{H}_2\text{O})_2}$ $/\text{cm}^3 \text{s}^{-1}$	$k_{\text{water-eff}}^{\text{a}}$ $/\text{cm}^3 \text{s}^{-1}$	Ref.
<i>syn</i> -MVKO	33	3.4×10^{-19}	9.2×10^{-16}	1.5×10^{-18}	35, 42
<i>anti</i> -MACRO	–	2.9×10^{-15}	3.3×10^{-12}	7.2×10^{-15}	42
	10	1.9×10^{-16}	3.6×10^{-13}	6.3×10^{-16}	31
	25	4.9×10^{-17}	1.6×10^{-14}	6.9×10^{-17}	theory ^b
	–	–	–	$[(8 \pm 6) \times 10^{-17}]$	exp. ^b
<i>syn</i> -MACRO	–	2.3×10^{-19}	2.4×10^{-15}	1.3×10^{-17}	42
	2500	1.5×10^{-19}	5.6×10^{-16}	8.4×10^{-19}	31
	2644	1.4×10^{-20}	4.1×10^{-17}	6.4×10^{-20}	theory ^b

^a $k_{\text{water-eff}} = (k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{(\text{H}_2\text{O})_2}[(\text{H}_2\text{O})_2]) / [\text{H}_2\text{O}]$ at RH = 70% and 298 K, in which $[(\text{H}_2\text{O})_2]$ is estimated with $K_{\text{eq}} = P_{\text{dimer}} / P_{\text{monomer}}^2 = 0.0556 \text{ bar}^{-1}$ reported by Anglada et al.⁵¹ ^bThis work.

As shown in Table 1, the predicted unimolecular rates are very different for *syn*- and *anti*-MACRO. *Syn*-MACRO would have a rather short lifetime of ca. $1/2500 = 4 \times 10^{-4} \text{ s}$,³¹ which means its steady-state concentration would be very low. The experimental lifetime of MACRO is found to depend on the signal intensity—the higher the signal is, the shorter the lifetime. This is due to the fact that the inevitable reactions of MACRO with radical byproducts, including I atoms, IO radicals, and the products from the fast decomposition of *syn*-MACRO (similar to the case of *anti*-MVKO)⁴¹ would shorten its lifetime. Supplementary Figure 3 shows the plot of k_0 against $[\text{MACRO}]_0$. The linear relationship supports the above mechanism. Extrapolating k_0 to zero $[\text{MACRO}]_0$ would effectively remove the bimolecular contributions and give an estimation for the unimolecular lifetime of MACRO. The preliminary data of Supplementary Figure 3 are consistent with $k_0([\text{MACRO}]_0=0) < 50 \text{ s}^{-1}$, which gives a lifetime $> 20 \text{ ms}$. This long-lived MACRO cannot be *syn*-MACRO. Thus, the observed signal should belong to *anti*-MACRO.

Compare of $k_{\text{water-eff}}$ with previous theory.

The value of $k_{\text{water-eff}}$ of *anti*-MACRO (Table 1) is smaller than those of CH₂OO and *anti*-CH₃CHOO¹⁶⁻¹⁷ by orders of magnitude, suggesting that the extended conjugation of *anti*-MACRO correlates with the lower reactivity towards water monomer and dimer. This resonance-stabilization electronic structure is lacking in the alkyl CIs.

Anglada et al. have predicted the rate coefficients for *anti*-MACRO reactions with water monomer and dimer, giving $k_{\text{water-eff}} = 7.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (Table 1).⁴² To our surprise, this value is ca. 90 times larger than our experimental value. However, Vereecken et al. have pointed out that the level of theory used by Anglada et al.⁴² tends to underestimate the barriers for the CI reactions with water monomer and dimer.³¹ Using “structure-activity relationship”, Vereecken et al. scaled the barrier heights of a number of CI reactions by considering the best known theoretical and experimental data (mainly for CH₂OO and *anti*/*syn*-CH₃CHOO).³¹ The resulted rate coefficients of MACRO are also shown in Table 1. We can see this “scaling” does reduce the gap (from 90 times to 8 times) between the theoretical predictions and our experimental data. Since the reference data in the work of Vereecken et al.³¹ do not contain trustable data for reactions of CIs having a conjugated C=C group (there is no good anchor point for the scaling), this difference may be reasonable.

With details given in Supplementary Note 2, we found that it is important to calculate the reaction barrier heights at a level of quantum chemistry theory like QCISD(T)/CBS//B3LYP/6-311+G(2d,2p) (CBS = complete basis set extrapolation).⁵²⁻⁵⁸ For example, the QCISD(T)/CBS barriers are ca. 1.4/2.0 kcal mol⁻¹ higher than those calculated at QCISD(T)/aug-cc-pVTZ (AVTZ) for various reactions between (CH₂=CH)CHOO conformers with H₂O monomer/dimer (Supplementary Figure 6 & Supplementary Table 3), indicating that only using the AVTZ barrier heights would overestimate the reaction rates significantly.

After properly scaling the effect of the basis sets (CBS Vs. AVTZ) by using the results of (CH₂=CH)CHOO, which has a similar structure to MACRO, as an anchor point, (Supplementary Figure 6),⁵² our calculation (Table 1) also predicts a slower rate compared to previous ones.

Compare of $k_{\text{water-eff}}$ with ozonolysis experiment.

Newland et al. have analyzed the effect of water vapor in the system of isoprene ozonolysis; in their two-CI model, the isoprene-derived non-CH₂OO CI (sum of MVKO and MACRO) has an effective reaction rate coefficient with water vapor of $(1.1 \pm 0.27) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$.⁵⁹ While all conformers of MVKO are expected to react with water vapor much slower ($k_{\text{water-eff}} \leq 7.7 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$),³¹ the value of Newland et al. is much larger than our $k_{\text{water-eff}}$ for MACRO. The reason for this difference is possibly due the complexity of the isoprene ozonolysis system. For example, CH₂OO, which is much more reactive towards water vapor than MVKO and MACRO, has a higher yield (ca. 58%) in the isoprene ozonolysis system.²⁻³ As a result, it would be hard to probe the reaction rates of MVKO and MACRO, which have much lower reactivity.

Atmospheric lifetime.

Because the unimolecular decay and reaction with water vapor are the predominant processes that determine the atmospheric lifetime of a CI, we may estimate the effective decay rate coefficient k_{atm} for atmospheric *anti*-MACRO.

$$k_{\text{atm}} = k_{\text{uni}} + k_{\text{water-eff}}[\text{H}_2\text{O}]$$

Taking that $k_{\text{uni}} = 10 \text{ s}^{-1}$ for *anti*-MACRO,³¹ $k_{\text{atm}} = 10 \text{ s}^{-1} + [(8 \pm 6) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}](5 \times 10^{17} \text{ cm}^{-3}) = 50 \pm 30 \text{ s}^{-1}$ (RH = 70%, 298 K). Note that this atmospheric lifetime (ca. 20 ms) is much longer than previously thought (< ms), indicating that the atmospheric concentration of *anti*-MACRO would be much higher than previously expected.

Impact of *anti*-MACRO on the oxidation of atmospheric SO₂.

This would depend on three factors: (i) the yield of *anti*-MACRO in the ozonolysis of atmospheric alkenes (mainly isoprene), (ii) the atmospheric lifetime of *anti*-MACRO, and (iii) the rate coefficient of *anti*-MACRO reaction with SO₂. Each factor is discussed below.

First, based on the recent analysis of Nguyen et al., *anti*-MACRO has a yield of 15% among all stabilized CIs in isoprene ozonolysis, which is very similar to that of *syn*-MVKO (14%).^{2, 16} In addition, an earlier study of Zhang and Zhang has shown that the activation energies of O₃ cycloaddition to the two double bonds of isoprene are comparable and the barrier heights from the primary ozonides to *syn*-MVKO and *anti*-MACRO are also similar, implying that the *syn*-MVKO and *anti*-MACRO pathways are both accessible.⁴

Second, given that *syn*-MACRO and *anti*-MVKO have much shorter lifetimes ($t < \text{ms}$), the oxidation of atmospheric SO₂ by the C4 CIs from isoprene ozonolysis would be mainly by *anti*-MACRO and *syn*-MVKO ($t > 10 \text{ ms}$).^{31, 35} The above estimated value of k_{atm} of *anti*-MACRO ($50 \pm 30 \text{ s}^{-1}$) is comparable with that of *syn*-MVKO ($k_{\text{atm}} @ k_{\text{uni}} = 33 \text{ s}^{-1}$; ³² $k_{\text{water-eff}} \sim 10^{-18} \text{ cm}^3 \text{ s}^{-1}$)^{31, 35} within a factor of ca. 2, suggesting these two CIs would have similar steady-state concentrations in the troposphere (due to similar production and removal rates).

Finally, the rate coefficient of SO₂ reaction with *anti*-MACRO, $(1.5 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, is larger than that with *syn*-MVKO, $(4.0\text{--}4.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$,³⁵⁻³⁶ by a factor of ca. 4. Overall, the oxidation rate of SO₂ by *anti*-MACRO would be larger than that by *syn*-MVKO by a factor of ca. $0.5 \times 4 = 2$, assuming that these two CIs are mainly from isoprene ozonolysis with similar yields.

Although CH₂OO has the highest yield (ca. 58%) among the stabilized CIs produced in the ozonolysis of isoprene,^{2, 16} its fast reaction with water vapor results in a rather short atmospheric lifetime (< 1 ms),¹⁶⁻²² too short for CH₂OO to reach any substantial concentration to oxidize atmospheric SO₂. Recently Caravan et al., who utilized the up-to-date data of MVKO kinetics, show that *syn*-MVKO has the largest modeled steady-state concentration among all stabilized CIs globally (33% by molecules, 49% by

weight).³⁵ The above analysis shows that *anti*-MACRO would have similar concentrations as those of *syn*-MVKO and an even larger impact on the SO₂ oxidation.

Conclusion

Following the method of Vansco et al.,³³ MACRO has been synthesized and its UV-visible spectroscopy and reaction kinetics have been investigated. Similar to MVKO, MACRO has two non-interconverting isomers, *syn* and *anti* forms. *Syn*-MACRO would undergo fast 1,5-ring closure with a predicted thermal lifetime of < 0.4 ms. In our experiments, a much longer lifetime ($\tau > 4$ ms) has been observed, indicating that the spectral carrier is *anti*-MACRO. The rate coefficient of *anti*-MACRO reaction with SO₂ has been determined to be $(1.5 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 298 K, which is substantially larger than that of the *syn*-MVKO + SO₂ reaction. However, the reaction of *anti*-MACRO with H₂O was found to be quite slow with an effective rate coefficient of $(8 \pm 6) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 298 K, which is smaller than previous theoretical values by 1 or 2 orders of magnitude. Theoretical calculations that properly treat the effect of conjugated C = C substitution may reproduce the experimental trend.

A recent global chemistry and transport modeling based on the most up-to-date knowledge of MVKO chemistry has shown that *syn*-MVKO is important in the tropospheric processes of SO₂ oxidation and formic acid removal.³⁵ Our results indicate that *anti*-MACRO has an atmospheric lifetime similar to that of *syn*-MVKO, resulting in a similarly substantial steady-state concentration. Combined with the larger rate coefficient of its reaction with SO₂, the impact of *anti*-MACRO on the oxidation of atmospheric SO₂ would be comparable to or larger than that of *syn*-MVKO.

As mentioned above, to serve as an efficient oxidant of SO₂, it is required to have a long-enough lifetime under atmospheric relevant conditions. Having a resonance stabilized electronic structure may be a new direction for searching for a long lived Cl.

Methods

MACRO preparation.

The experimental details have been published.^{18, 36} We prepared MACRO following Vansco et al.: $\text{ICH}(\text{CH}_3)\text{CH}_2\text{I}$ (1,3-diiodo-2-methylprop-1-ene, Accela, 97.8 % by gas chromatography) + $h\nu$ (248 nm) $\rightarrow$ $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHI}$ + I, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHI} + \text{O}_2 \rightarrow \text{CH}_2=\text{C}(\text{CH}_3)\text{CHOO} + \text{I}$.³³ See Supplementary Note 1.

CMOS camera spectrometer.

A grating spectrometer (Andor SR303i) and fast CMOS camera (Andor, Marana-4BU11) were used to obtain the time-resolved absorption spectra of the reaction system. A series of spectra (exposure time 0.21 ms (or 0.43 ms) each) were recorded for every photolysis event. The spectrum taken 0.13-0.33 ms (or 0.36-0.79 ms) before the photolysis laser pulse was used as the reference spectrum; therefore, the

change of absorbance caused by the photolysis laser pulse was recorded transiently. Accumulation of 256, 512 (0.43 ms exposure time), or 2560 (0.21 ms exposure time) laser pulses was performed to improve the signal-to-noise ratio.

A background spectrum (without adding the MACRO precursor 1,3-diiodo-2-methylprop-1-ene) was recorded under the same experimental condition. This background was due to the interaction between the photolysis laser beam and the used optics (mainly the long-pass filters that reflected the photolysis laser beam and transmitted the probe beam). All the reported spectra are background corrected.

Theoretical calculations.

We optimized the reactant and transition state geometries on the singlet ground electronic state using B3LYP/6-311+G(2d,2p).^{52, 56-57} The electronic energies were corrected at QCISD(T)/CBS level,⁵²⁻⁵⁸ except for the transition states of MACRO+2H₂O, of which the energies were estimated with a correction method detailed in Supplementary Note 2 (Supplementary Figures 6-8, Supplementary Tables 3-5). The rate coefficients were calculated using the conventional transition state theory method using rigid rotor harmonic oscillator approximations.

Declarations

Data availability

The data supporting the findings of this study are available within the article and its Supplementary Information and from the corresponding author upon reasonable request.

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Author contributions

JJML conceived the experiment. YHL set up the experiment, performed the measurements, and analyzed the experimental data. CY and KT performed the theoretical calculations. YHL, CY, KT, and JJML discussed the results. JJML wrote the paper.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Synthesis and conformers of methacrolein oxide (MACRO) following the method and nomenclature of Vansco et al.³³

Figure 2

Upper panel: The difference absorption spectrum recorded in the 1,3-diiodo-2-methylprop-1-ene/O₂ photolysis system at 298 K and 500 Torr at 1 ms photolysis-probe delay time (red line, the data is from Exp #1, see Supplementary Table 1). The absorption contributions of MACRO (green), IO (blue), and I₂ (cyan; black is the sum of MACRO, IO and I₂) are also shown. Lower panel: Average peak absorbance of MACRO, IO, and I₂ obtained by fitting the spectra of Exp #1 at [SO₂] = 0 at each delay time. The ranges for

the absorbance averaging are 391–401 nm for MACRO, 410–413 nm for IO, and 510–520 nm for I2. [IO] and [I2] are estimated with literature cross sections (see Supplementary Figure 4).⁴³⁻⁴⁴

Figure 3

Height-normalized spectra of MACRO. The spectra of MACRO are obtained from the difference spectra between the spectra without SO₂ and the spectra with [SO₂] ~ 1014 cm⁻³ at 0.18 ms delay time. Four spectra obtained from Exp #1–4 are plotted as gray lines, and their average is plotted as a black line. The red curve shows the Gaussian fit of the average spectrum with peak position 397 nm and full width at half-maximum (FWHM) 77 nm.

Figure 4

Upper panel: The time profiles of absorbance changes of MACRO obtained by fitting the spectra at each delay time under various $[\text{SO}_2]$ at 298 K and 500 Torr. The data are from Exp #1. The black curves show the fitting results of single exponential decay. Lower panel: The pseudo-first-order plot of the reaction of MACRO with SO_2 at 298 K.

Figure 5

Upper panel: Time profiles of the MACRO absorption signal obtained by fitting the spectra at each delay time under various $[H_2O]$ at 298 K and 501 Torr. The data are from Exp #5 (Supplementary Table 2). The black curves show the fitting results of a single exponential decay function. Lower panel: The pseudo-first-order plot of the reaction of MACRO with H_2O at 298 K. The experiments with two data points (dashed lines) are shown only for comparison purpose.

Supplementary Files

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- [MACROSI1006.pdf](#)