

Unimolecular Kinetics of Stabilized CH₃CHOO Criegee Intermediates: *syn*-CH₃CHOO Decomposition and *anti*-CH₃CHOO Isomerization

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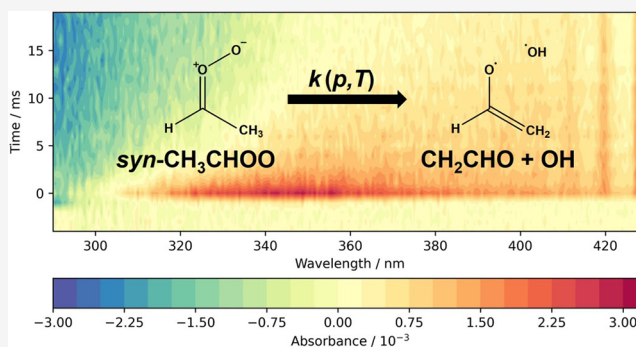
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ABSTRACT: The kinetics of the unimolecular decomposition of the stabilized Criegee intermediate *syn*-CH₃CHOO has been investigated at temperatures between 297 and 331 K and pressures between 12 and 300 Torr using laser flash photolysis of CH₃CH₂I/O₂/N₂ gas mixtures coupled with time-resolved broadband UV absorption spectroscopy. Fits to experimental results using the Master Equation Solver for Multi-Energy well Reactions (MESMER) indicate that the barrier height to decomposition is 67.2 ± 1.3 kJ mol⁻¹ and that there is a strong tunneling component to the decomposition reaction under atmospheric conditions. At 298 K and 760 Torr, MESMER simulations indicate a rate coefficient of 150⁺¹⁷⁶₋₈₁ s⁻¹ when tunneling effects are included but only 5⁺³₋₂ s⁻¹ when tunneling is not considered in the model. MESMER simulations were also performed for the unimolecular isomerization of the stabilized Criegee intermediate *anti*-CH₃CHOO to methyldioxirane, indicating a rate coefficient of 54⁺³⁴₋₂₁ s⁻¹ at 298 K and 760 Torr, which is not impacted by tunneling effects. Expressions to describe the unimolecular kinetics of *syn*- and *anti*-CH₃CHOO are provided for use in atmospheric models, and atmospheric implications are discussed.



INTRODUCTION

Criegee intermediates (R₂COO) are zwitterionic species produced in the atmosphere during the ozonolysis of unsaturated hydrocarbons and play a number of key roles in atmospheric oxidation processes. The high exothermicity (~250 kJ mol⁻¹)¹ of ozonolysis reactions leads to the production of nascent excited Criegee intermediates with high internal energy which facilitates the production of atmospheric oxidants including the hydroxyl radical (OH), the hydroperoxy radical (HO₂), and other peroxy radicals (RO₂). Such processes have been recognized as important sources of OH, the primary oxidizing agent in the atmosphere, particularly in winter and at night when photolytic routes to OH production are limited by low or zero solar intensity^{2,3} but are in competition with collisional stabilization, which leads to the production of stabilized Criegee intermediates (SCIs). Once stabilized, SCIs can undergo bimolecular reactions with water and water dimers and can act as atmospheric oxidants in bimolecular reactions with species including SO₂, NO₂, and organic acids.^{4–8} There is also growing recognition that unimolecular SCI decomposition can be a significant loss

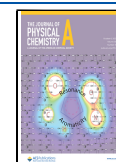
mechanism for certain SCIs in the atmosphere, enhancing the production of OH from ozonolysis reactions beyond that achieved through the decomposition of nascent excited Criegee intermediates.^{6–9}

The Criegee intermediate CH₃CHOO exists as two conformers: *syn*-CH₃CHOO, in which the methyl group is *syn* to the terminal oxygen, and *anti*-CH₃CHOO, in which the methyl group is *anti* to the terminal oxygen. Interconversion between the two conformers is precluded under atmospheric conditions by a significant barrier of ~160 kJ mol⁻¹ because of the double-bond character of the C–O bond resulting from the zwitterionic nature of Criegee intermediates,^{10,11} with the conformers displaying differences in spectra and reactivity.^{11,12}

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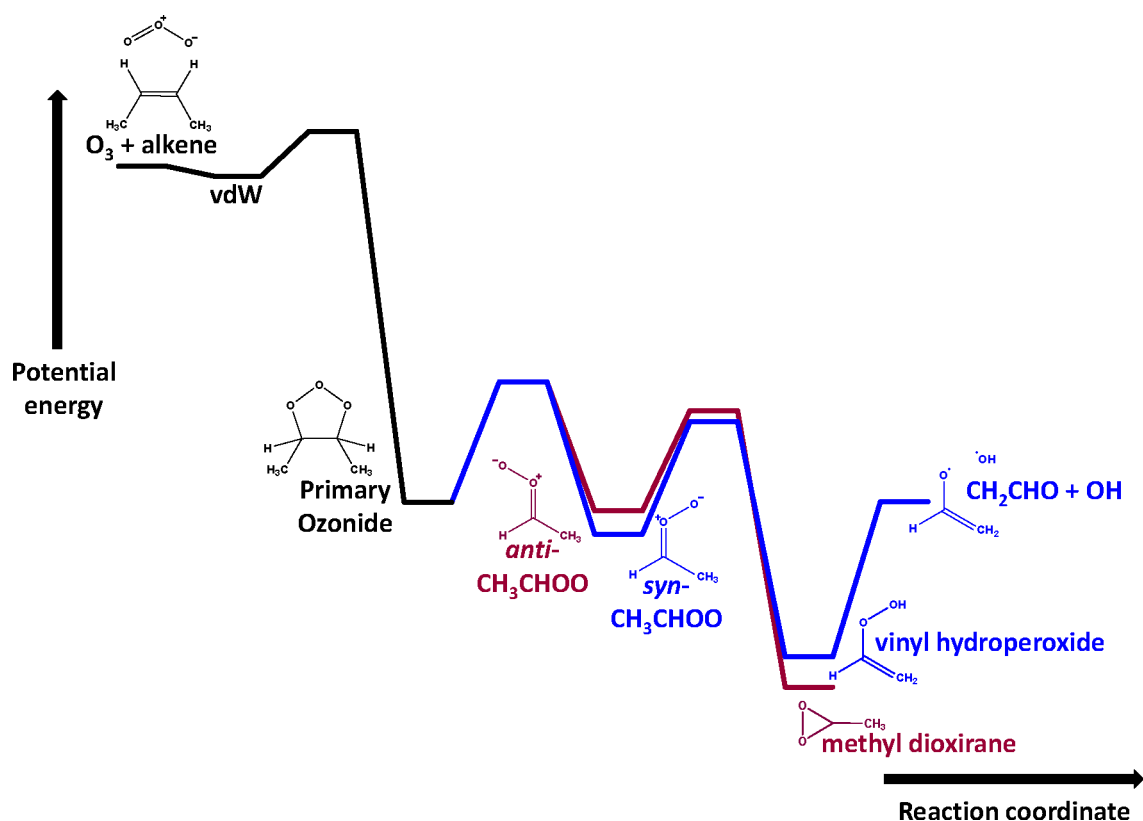


Figure 1. Typical potential energy surfaces describing the decomposition of *syn*-CH₃CHOO and isomerization of *anti*-CH₃CHOO (not to scale). Structures and labels refer to the species in the wells; vdW = van der Waals complex.

For *syn*-CH₃CHOO, and other Criegee intermediates with α hydrogen atoms *syn* to the COO Criegee group, decomposition is facilitated by a 1,4-H transfer of the α -H atom to the terminal oxygen atom of the COO group, resulting in a rapid process that is expected to dominate the atmospheric chemistry of such SCIs.^{7–9,13} The 1,4-H transfer in *syn*-CH₃CHOO leads to the production of vinyl hydroperoxide (CH₂CHOOH, VHP) which can undergo decomposition to OH radicals and vinyloxy radicals (CH₂CHO) (R1).^{7,13} Other unimolecular pathways such as 1,3-cyclization of the COO group are expected to be slower than the 1,4-H transfer for *syn*-CH₃CHOO.¹³ For *anti*-CH₃CHOO, the 1,4-H transfer mechanism is limited by the restricted rotation around the C–O bond, and instead 1,3-cyclization of the COO Criegee group leads to the production of methyl dioxirane (CH₃CHO₂) (R2).^{7,13} However, this process is expected to be relatively slow compared to the bimolecular reactions of *anti*-CH₃CHOO.

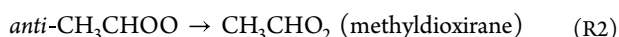


Figure 1 shows the typical potential energy surface summarizing the key features in the atmospheric formation and unimolecular chemistry of CH₃CHOO Criegee intermediates.⁴ The kinetics of *syn*-CH₃CHOO decomposition (R1) are key to determining the atmospheric fate and impact of *syn*-CH₃CHOO and potentially other substituted SCIs with α -H atoms *syn* to the Criegee group, while the atmospheric losses of SCIs such as *anti*-CH₃CHOO are expected to be dominated by bimolecular reactions, particularly the reactions with water vapor and water dimers.^{7,13}

Studies of ozonolysis reactions in flow reactors and atmospheric simulation chambers have enabled estimates of the unimolecular kinetics of the stabilized Criegee intermediate CH₃CHOO.^{14–18} However, such studies are typically unable to identify conformer-specific behavior and are subject to significant uncertainties because of the use of indirect measurements to infer the chemistry of Criegee intermediates. A number of such indirect studies have been used to approximate non-conformer-specific decomposition kinetics for CH₃CHOO on the basis of relative rate arguments, giving rate coefficients ranging over several orders of magnitude ($\sim 10^{-3}$ to $\sim 10^2$ s⁻¹) at room temperature and atmospheric pressure,^{14–17} while the first absolute, but indirect, measurements reported a value of 76 s⁻¹ with an accuracy within a factor of 3.¹⁸

Conformer-specific kinetics for *syn*-CH₃CHOO decomposition have been reported following observations of OH formation in the ozonolysis of propene and *trans*-but-2-ene, with results for k_1 ranging between 3 and 30 s⁻¹ at ~ 2.6 Torr and 293 K.¹⁹ Relative rate studies of CH₃CHOO in ozonolysis experiments at ambient temperature and atmospheric pressure, involving reactions of CH₃CHOO conformers with SO₂ and measurements of either H₂SO₄ products¹⁶ or SO₂,¹⁷ have also been used to estimate conformer-specific kinetics for *syn*- and *anti*-CH₃CHOO. These studies indicate values for k_1 of 86 ± 13 s⁻¹¹⁶ and 310 ± 290 s⁻¹,¹⁷ and a value of 38 ± 24 s⁻¹ for k_2 ,¹⁶ using current IUPAC recommendations²⁰ for the kinetics of reactions of CH₃CHOO conformers with SO₂. However, these values are associated with large uncertainties, and the results are potentially affected by differences in pressure between the ozonolysis experiments and those performed to measure the kinetics of CH₃CHOO + SO₂.

Table 1. Summary of Theoretical Studies of Reactions R1 and R2^a

T/K	p/ Torr	k_1/s^{-1}	barrier height (R1)/ kJ mol ⁻¹	k_2/s^{-1}	barrier height (R2)/ kJ mol ⁻¹	methods	ref
298	∞	24.2	74.9	67.2	64.4	MCG3//QC1SD/MG3	Kuwata et al. ¹⁰
298	∞	209	69.5	57.6	64.4	RRKM, VTST & Eckart tunneling model CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ	Nguyen et al. ²¹
298	760	166	71.5			RRKM & Eckart tunnelling model CCSD(T) cc-pVTZ & CCSD(T)-F12 CBS	Fang et al. ²²
298	760	122	71.5			RRKM & Eckart tunneling model CCSD(T) cc-pVTZ & CCSD(T)-F12 CBS	Fang et al. ²³
298	∞	328	71.2	55.4	65.4	RRKM & adjusted Eckart tunneling model W3X-L//CCSD(T)-F12a/DZ-F12	Long et al. ²⁴
298	760	124	72			MP-CVT SCT mHEAT-345(Q) SCTST & VPT2	Nguyen et al. ²⁵
298	∞	182	69.8	72.5	64.4	QCISD(T)/CBS//B3LYP/6-311+G(2d,2p) SCTST & VPT2	Vin & Takahashi ²⁶
298	∞	136	70.3	53	65.7	CCSD(T)/aug-cc-pVTZ//M06-ZX MC-CTST & Eckart tunneling model	Vereecken et al. ¹³
291	∞	137	71.1			MP2/aug-cc-pVTZ & CCSD(T)/aug-cc-pVTZ	Burd et al. ²⁷
291	∞	155	71.1			1D-SCTST MP2/aug-cc-pVTZ & CCSD(T)/aug-cc-pVTZ	Burd et al. ²⁷
291	∞	136	71.1			FD-SCTST (MP2 x matrix) MP2/aug-cc-pVTZ & CCSD(T)/aug-cc-pVTZ FD-SCTST (B3LYP x matrix)	Burd et al. ²⁷

^aTemperatures and pressures are given for the conditions at which the rate coefficients are calculated.

The potential energy surfaces and kinetics for reactions R1 and R2 have also been studied by a number of groups using theoretical methods.^{10,13,21–27} The mechanism for (R1) is expected to proceed via 1,4-H atom transfer from the methyl substituent to the terminal oxygen atom in a cyclic five-membered transition state, while that for (R2) involves bending of the O–O bond and 1,3-cyclization of the COO Criegee group. Table 1 summarizes the methods used, calculated barriers, and the predicted kinetics. Despite a higher barrier, the predicted rate coefficients for *syn*-CH₃CHOO (k_1) are larger than those for *anti*-CH₃CHOO (k_2) in most studies because of expected effects of quantum mechanical tunneling. For *syn*-CH₃CHOO, the availability of the 1,4-H transfer pathway facilitates quantum mechanical tunneling through the reaction barrier, leading to a significant enhancement in the rate of reaction which is not possible for *anti*-CH₃CHOO since pathways involving H atom transfer are inaccessible because of the restricted rotation around the C–O bond. The impact of quantum mechanical tunneling on the decomposition of *syn*-CH₃CHOO has been investigated in a series of experiments involving vibrational activation of jet-cooled *syn*-CH₃CHOO, generated via photolysis of CH₃CHI₂/O₂, and detection of the OH radical decomposition product.^{9,22,23,28–31} Activation of specific vibrational modes in *syn*-CH₃CHOO using tunable infrared laser excitation, while remaining below the energy barrier to decomposition, has demonstrated that there is a significant tunneling component to the reaction, with a combination of experimental results and application of theory leading to an expected rate coefficient of 122 s⁻¹ at 298 K and atmospheric pressure.²³ Experiments using *syn*-CD₃CHOO have also indicated that the decomposition of *syn*-CH₃CHOO

proceeds predominantly by a tunneling mechanism, with a kinetic isotope effect of over 50.³²

Direct measurements of the kinetics of *syn*-CH₃CHOO decomposition have been made at 298 K at pressures between 10 and 100 Torr, with CH₃CHOO produced following photolysis of CH₃CHI₂/O₂/Ar gas mixtures at 248 nm.³³ The kinetics for *syn*-CH₃CHOO were determined through detection of OH radicals by high repetition rate (10 kHz) laser-induced fluorescence at 282 nm, based on the assumption that any OH in the system is formed exclusively from decomposition of the *syn*-conformer. Analysis of the temporal profiles for OH required not only consideration of the kinetics for the decomposition of the Criegee intermediate but also its reactions with other species in the reaction mixture, including the CH₃CHI₂ precursor, IO radicals, and its self-reaction, as well as the kinetics of the processes leading to the removal of OH from the system. Knowledge of the initial concentrations of *syn*-CH₃CHOO was also required and was estimated to be on the order of 10¹²–10¹³ cm⁻³ from the laser fluence, the CH₃CHI₂ precursor concentration, the yield of CH₃CHOO from the reaction between CH₃CHI and O₂, which was assumed to be 0.9 for all pressures investigated based on previous measurements at 4 Torr,¹¹ and the ratio of *syn*:*anti* conformers, which was assumed to be 7:3.¹² The impact of wall losses and diffusion of *syn*-CH₃CHOO were assumed to be negligible. Determination of the decomposition kinetics using measurements of OH thus requires a complex analysis which necessitates a number of assumptions, although application of the approach to measure the kinetics of *syn*-CH₃CHOO + SO₂ gave similar results to others reported in the literature.^{11,12,34} The results for the decomposition kinetics of *syn*-CH₃CHOO indicated a rate coefficient of 182 ± 66 s⁻¹

between 25 and 100 Torr, with no significant pressure dependence in this range, although a lower value of $\sim 70 \text{ s}^{-1}$ was obtained at 10 Torr.³³

Experiments using time-resolved UV absorption spectroscopy have also been performed to make direct measurements of the decomposition kinetics of *syn*-CH₃CHOO, enabling investigation of the pressure dependence between 100 and 700 Torr at 298 K and of the temperature dependence between 278 and 318 K at a pressure of 300 Torr.³⁵ Photolysis of CH₃CHI₂/O₂/N₂ at 248 nm was used to generate CH₃CHOO, with the absorption monitored at 340 nm. While both *syn*- and *anti*-CH₃CHOO display significant absorption at 340 nm, high concentrations of water vapor were added to ensure the rapid removal of *anti*-CH₃CHOO. The change in absorption at 340 nm was thus dominated by changes in the concentration of *syn*-CH₃CHOO, with minor contributions from CH₃CHI₂, which are approximately constant on the time scale of the experiment, and IO. Compared to the experiments involving detection of OH,³³ direct monitoring of *syn*-CH₃CHOO simplifies the analysis, although determination of the decomposition kinetics still required consideration of the *syn*-CH₃CHOO self-reaction, which was assumed to be negligible for initial concentrations on the order of 10^{11} cm^{-3} , and of the reactions involving CH₃CHI₂, IO, and, for these experiments, water vapor. The reaction of *syn*-CH₃CHOO with its di-iodo precursor was demonstrated to be significant, with similar effects observed at high temperatures in our previous investigation of the decomposition kinetics of CH₂OO.³⁶ The effects of physical losses such as diffusion and wall loss were estimated on the basis of measurements for the CH₂OO Criegee intermediate under similar conditions and were highlighted as being potentially underestimated in the previous work³³ involving detection of OH. Results indicated a weak pressure dependence in the decomposition kinetics of *syn*-CH₃CHOO at 298 K, with the rate coefficient varying from $\sim 120 \text{ s}^{-1}$ at 100 Torr to $\sim 170 \text{ s}^{-1}$ at 700 Torr, and an increase in the rate coefficient at 300 Torr from $67 \pm 15 \text{ s}^{-1}$ at 278 K to $146 \pm 31 \text{ s}^{-1}$ at 298 K and $288 \pm 81 \text{ s}^{-1}$ at 318 K.³⁵

There are thus a range of estimates for CH₃CHOO Criegee intermediate decomposition kinetics obtained from various theoretical and experimental approaches, with significant uncertainties remaining. However, there is agreement within the literature that quantum mechanical tunneling plays an important role in the decomposition of *syn*-CH₃CHOO under ambient conditions and that the reaction is likely to dominate its atmospheric chemistry, with potentially significant consequences for tropospheric OH production.

In this work we report a direct investigation of the conformer-specific kinetics of *syn*-CH₃CHOO decomposition. Experiments were conducted at pressures between 12 and 300 Torr and temperatures between 297 and 331 K using flash photolysis of CH₃CHI₂/O₂/N₂, coupled with time-resolved broadband UV absorption spectroscopy. Experimental results are supported by Master equation calculations performed using the Master Equation Solver for Multi-Energy well Reactions (MESMER) to provide a full parametrization of the kinetics as a function of temperature and pressure suitable for inclusion in atmospheric models.

EXPERIMENTAL SECTION

The decomposition kinetics of *syn*-CH₃CHOO were studied using flash photolysis of CH₃CHI₂/O₂/N₂ gas mixtures,

coupled with broadband UV absorption spectroscopy. The experimental apparatus has been described in detail elsewhere;^{37–40} therefore, only a brief description is given here.

Precursor and bath gases were mixed in a gas manifold at known flow rates controlled by calibrated mass flow controllers (MKS Instruments), with CH₃CHI₂ entrained into the flow by passing a known flow of N₂ through a bubbler containing liquid CH₃CHI₂ held at a constant temperature in an ice bath. The precursor gas mixture was passed into a jacketed Pyrex reaction cell (100 cm in length, 3 cm internal diameter) which was sealed with fused silica windows at each end. The total flow rate through the reaction cell was maintained at 4000 standard cm³ per minute (sccm) at 100 Torr and adjusted accordingly with pressure to maintain a constant residence time in the cell of $\sim 6 \text{ s}$. The total pressure in the cell was measured by a capacitance manometer (MKS Instruments) and controlled by a rotary pump (EM2, Edwards) by throttling the exit to the reaction cell. The temperature of the gas mixture was maintained by flowing liquid from a recirculating thermostating unit (Huber Unistat 360) through the jacket surrounding the cell and calibrated through measurements of the temperature in the cell made by a K-type thermocouple placed at a series of positions along the length of the cell in separate experiments using flowing N₂ gas under otherwise identical conditions.⁴⁰

Chemistry in the cell was initiated by an excimer laser (KrF, Lambda-Physik CompEx 210) operating at a wavelength of $\lambda = 248 \text{ nm}$, which was aligned along the length of the reaction cell using a dichroic turning mirror (Edmund Optics). The timing of the photolysis laser was controlled by a delay generator (SRS DG535) with a pulse repetition rate of 0.15 Hz such that a fresh gas mixture was photolyzed on each pulse. The typical laser fluence was $\sim 25 \text{ mJ cm}^{-2}$, giving [*syn*-CH₃CHOO]₀ on the order of $\sim 10^{11} - 10^{12} \text{ cm}^{-3}$.

Absorption of UV/vis radiation by species within the cell was monitored using a laser-driven light source (LDLS, Energetiq EQ-99X), which provides $\sim 10 \text{ mW cm}^{-2}$ of light at wavelengths between 200 and 800 nm with near constant radiance across the spectral range. Output from the lamp was directed onto an off-axis parabolic mirror (ThorLabs) to collimate the beam. The probe light was aligned in a seven-pass arrangement described previously, resulting in a total effective path length of $443 \pm 21 \text{ cm}$.^{37–39} The beam exiting the cell was passed through a sharp cut-on filter (248 nm RazorEdge ultrasteepest long-pass edge filter, Semrock) to minimize the impacts of scattered excimer light and focused onto a fiber optic via a fiber launcher (Elliot Scientific).

For experiments at $T = 297 \text{ K}$, the output from the fiber optic was directed onto a spectrograph (CP140-103 Imaging Spectrograph, Horiba) and imaged onto a line-scan charge-coupled device (CCD) detector (S7030-1006 FFT, Hamamatsu), giving a spectral resolution (FWHM) of 1.5 nm and a time resolution of 1 ms achieved by transfer of data from the CCD to a PC for analysis in real time at 1 ms intervals.^{37,38}

For experiments at $T > 297 \text{ K}$, the output from the fiber optic was directed through a 25 μm slit onto a spectrograph equipped with a diffraction grating of 300 grooves/mm and imaged onto an integrated thermoelectrically cooled charge-coupled device (CCD) detector (FER-SCI-1024BRX, Princeton Instruments) with a spectral resolution (FWHM) of 1 nm and a variable time resolution on the order of hundreds of microseconds. The improved time resolution for experiments at $T > 297 \text{ K}$ was necessary because of the more rapid

chemistry occurring at such temperatures and required use of charge transfer from an illuminated region of the CCD (1024×10 pixels) to an optically masked storage region (1024×265 pixels) on the CCD prior to transfer to the PC for analysis. Charge transfer on the CCD, which can take place more rapidly than the communication between the CCD and the PC, requires the illumination of multiple rows on the CCD and results in an instrument response function which is also applied to the model used to obtain kinetic data during analysis (further details are given in the Supporting Information).³⁹

For experiments at all temperatures, the CCDs provide a series of sequential, time-resolved broadband transmission spectra before, during, and after photolysis. Wavelength calibration was performed via measurements of the well-known Hg emission spectrum from a low pressure Hg Pen-Ray lamp (Oriel). Timing of the CCD cameras was controlled by the same delay generator used to control the firing of the excimer laser. Intensity data recorded by the cameras were typically averaged for 100–400 photolysis shots and were transferred to a PC for analysis.

Experiments were performed in N₂ (BOC oxygen free, 99.998%) at temperatures between 297 and 331 K and pressures between 12 and 300 Torr. Concentrations of CH₃CHI₂ (Sigma-Aldrich, 98%) were varied in the range 4.33×10^{12} – 2.80×10^{14} cm⁻³ to enable characterization of the kinetics of CH₃CHI₂ + CH₃CHOO, while also ensuring low concentrations of photolysis products to minimize the effects of possible Criegee–Criegee and Criegee–radical chemistry. Concentrations of O₂ (BOC, 99.5%) were varied between 9.15×10^{16} and 5.89×10^{17} cm⁻³, while maintaining the requirement for rapid production of CH₃CHOO following photolysis of CH₃CHI₂. Gases and chemicals were used as supplied.

RESULTS

Absorbance spectra were determined at each time point during the course of the reaction from the measured transmission spectra using the Beer–Lambert law eq 1:

$$A_{\lambda,t} = \ln \left(\frac{I_{\lambda,0}}{I_{\lambda,t}} \right) = \sum_i \sigma_{i,\lambda} c_{i,t} l \quad (1)$$

where $A_{\lambda,t}$ is the total absorbance at wavelength λ and time t , $I_{\lambda,0}$ is the average pre-photolysis light intensity at wavelength λ , $I_{\lambda,t}$ is the post-photolysis light intensity at wavelength λ and time t , $\sigma_{i,\lambda}$ is absorption cross section of species i at wavelength λ , $c_{i,t}$ is the concentration of species i at time t , and l is the effective path length, which has a value of 443 ± 21 cm.

Reference absorption cross sections for CH₃CHI₂,⁴¹ *syn*-CH₃CHOO,¹² *anti*-CH₃CHOO,¹² and IO⁴² were least squares fit to the absorbance spectra to obtain concentrations for each species throughout the reaction. Figure 2 shows a typical fit to the post-photolysis absorbance, with typical concentration–time profiles shown in Figure 3. Experimental time scales and precursor concentrations were optimized to obtain kinetics for *syn*-CH₃CHOO, which resulted in small contributions to the absorbance signal from *anti*-CH₃CHOO because of lower yields of the *anti*-conformer from CH₃CHI + O₂^{11,12,34} and, presumably, more rapid reaction of the *anti*-conformer with the CH₃CHI₂ precursor. Experimental results reported in this work focus on the observations of *syn*-CH₃CHOO, for which conditions were optimized.

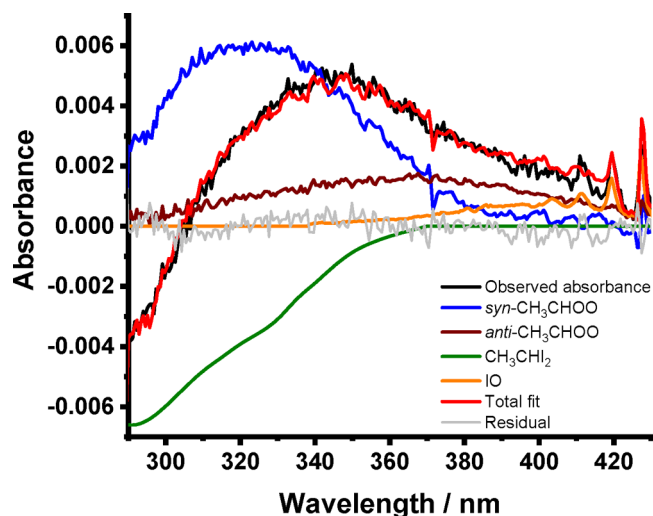


Figure 2. Observed absorbance (black), total fit (red), and the individual contributions from *syn*-CH₃CHOO (blue), *anti*-CH₃CHOO (purple), CH₃CHI₂ (green), and IO (orange) determined by fitting reference spectra to the observed absorbance using eq 1. For these data, $T = 297$ K, $p = 12$ Torr, $t = 1.0$ ms, and $[\text{CH}_3\text{CHI}_2] = 2.6 \times 10^{13}$ cm⁻³. The fit to the observed absorbance for these data gave $\Delta[\text{CH}_3\text{CHI}_2] = 3.97 \times 10^{12}$ cm⁻³, $[\text{syn-CH}_3\text{CHOO}] = 1.14 \times 10^{12}$ cm⁻³, $[\text{anti-CH}_3\text{CHOO}] = 3.00 \times 10^{11}$ cm⁻³, and $[\text{IO}] = 1.95 \times 10^{11}$ cm⁻³.

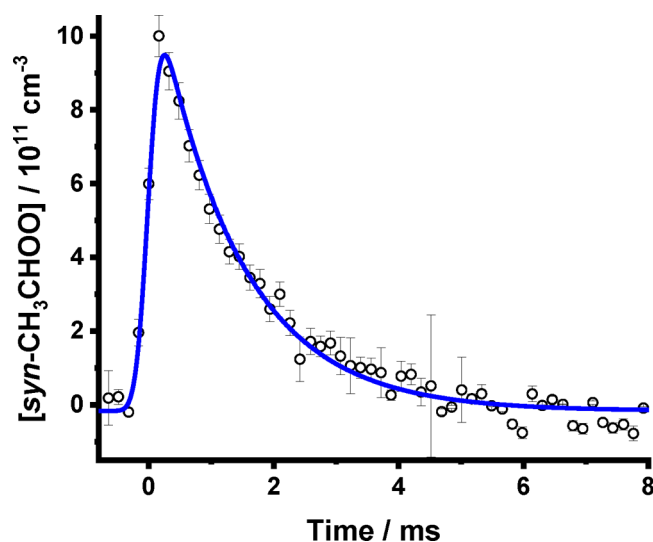
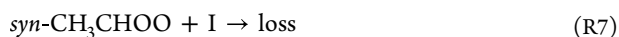
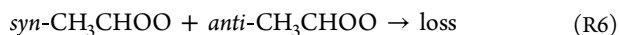
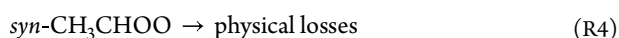
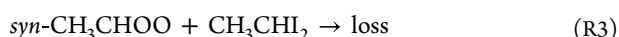


Figure 3. Observed concentration–time profile for *syn*-CH₃CHOO (open circles). For these data, $T = 318$ K, $p = 160$ Torr, and $[\text{CH}_3\text{CHI}_2] = 2.4 \times 10^{13}$ cm⁻³. Uncertainties in the *syn*-CH₃CHOO concentrations are given by the uncertainties in the fits to the observed absorbance at each time point combined with the uncertainty in the effective path length. The fit to eq 3 (coupled with the instrument response function as detailed in the Supporting Information) (solid line) gave $[\text{syn-CH}_3\text{CHOO}]_0 = (1.24 \pm 0.08) \times 10^{12}$ cm⁻³ and $k' = 756 \pm 79$ s⁻¹ (with the instrument response parameters $w = (1.52 \pm 0.04) \times 10^{-4}$ s and $t_c = -(8.9 \pm 3.2) \times 10^{-6}$ s). Errors are 1σ .

The kinetics of *syn*-CH₃CHOO removal from the system are controlled by its decomposition (R1), reaction with the CH₃CHI₂ precursor (R3), physical losses such diffusion out of the probe region and wall loss (R4), self-reaction (R5), and reaction with *anti*-CH₃CHOO (R6) or iodine atoms (R7).



The observed decays are also influenced by an instrument response function, details of which are given in the [Supporting Information](#). Of the processes contributing to *syn*-CH₃CHOO removal, the reaction with the precursor is pseudo-first-order because of the higher concentrations of CH₃CHI₂ compared to *syn*-CH₃CHOO, decomposition is first-order, and physical losses can be approximated as first-order, while the *syn*-CH₃CHOO self-reaction and reactions with *anti*-CH₃CHOO or iodine atoms are second-order. Concentration–time profiles for *syn*-CH₃CHOO can therefore be fit with a mixed first- and second-order kinetic model (eq 2), which can be coupled with the instrument response function where necessary (see the [Supporting Information](#)).

$$C_t = \frac{C_0 k'}{k' \exp(k't) - 2k''C_0 + 2k''C_0 \exp(k't)} \quad (2)$$

where C_t is the concentration of *syn*-CH₃CHOO at time t , C_0 is the initial concentration of *syn*-CH₃CHOO, k' represents the sum of first-order (or pseudo-first-order) losses of *syn*-CH₃CHOO, and k'' represents the sum of second-order losses of *syn*-CH₃CHOO.

Fits to eq 2 were performed with k'' treated as a global parameter at each temperature and pressure and all other parameters treated locally. At 297 K, the fits gave an average value of $k'' = (7.8 \pm 3.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, with no significant dependence on pressure (see the [Supporting Information](#)). At temperatures above 297 K, fits to eq 2 were found to be insensitive to the second-order component, indicating minimal effects of Criegee–Criegee and Criegee–iodine reactions for the initial concentrations used in these experiments (see the [Supporting Information](#) for further details). Similar behavior was also observed in our previous study of CH₂OO Criegee decomposition³⁶ and in a previous study of *syn*-CH₃CHOO decomposition.³⁵ For data obtained at temperatures above 297 K, the *syn*-CH₃CHOO profiles were thus analyzed with a model based on first-order loss kinetics (eq 3), which was coupled with the instrument response function where necessary as detailed in the [Supporting Information](#).

$$C_t = C_0 \exp(-k't) \quad (3)$$

where C_t is the concentration of *syn*-CH₃CHOO at time t , C_0 is the initial concentration of *syn*-CH₃CHOO, and k' is the rate coefficient describing the sum of first-order loss of *syn*-CH₃CHOO.

For fits to eq 2 or 3, the observed first-order rate coefficient describing the loss of *syn*-CH₃CHOO from the system, k' , is equal to $k_1 + k_3[\text{CH}_3\text{CHI}_2] + k_4$, and a plot of k' against the concentration of the CH₃CHI₂ precursor yields a slope equal to k_3 and an intercept equal to $k_1 + k_4$. At each temperature and pressure investigated the concentration of CH₃CHI₂ was varied sufficiently to determine k_3 . Figure 4 shows an example plot of k' against $[\text{CH}_3\text{CHI}_2]$ used to determine $(k_1 + k_4)$ and k_3 . Although there is some variability in determinations of k_3 , potentially because of uncertainties in $[\text{CH}_3\text{CHI}_2]$, the

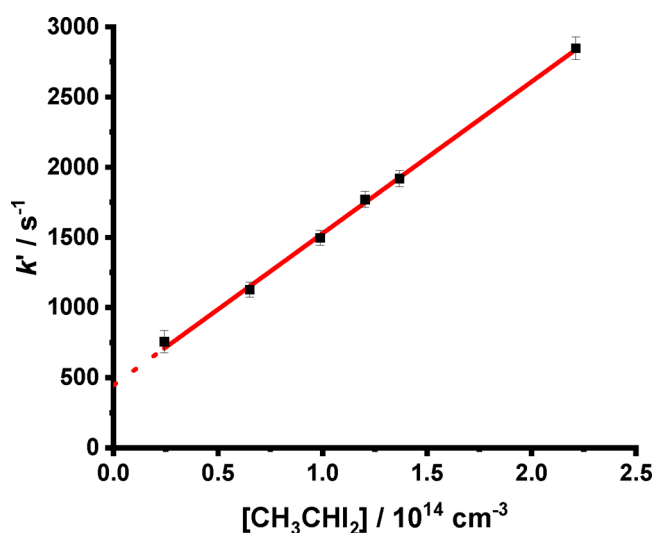


Figure 4. k' against $[\text{CH}_3\text{CHI}_2]$ at $T = 318 \text{ K}$ and $p = 160 \text{ Torr}$ (black points). The fit to the data (solid line) gave $(k_1 + k_4) = 446 \pm 115 \text{ s}^{-1}$ (intercept) and $k_3 = (10.81 \pm 0.98) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (slope). Errors are 1σ .

gradients and intercepts of the plots of k' against $[\text{CH}_3\text{CHI}_2]$ are well-defined, and thus $(k_1 + k_4)$ is well-defined. Results for k_3 indicate no significant dependence on pressure and a temperature dependence described by $k_3 = (3.2 \pm 0.7) \times 10^{-10} \exp((-1230 \pm 70)/T) \text{ cm}^3 \text{ s}^{-1}$, with a mean value of $(5.1 \pm 2.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 297 K (see the [Supporting Information](#) for further details).

Effects of physical losses were estimated from experiments in which the physical losses of the Criegee intermediate CH₂OO were measured via photolysis of CH₂I₂/O₂/N₂ mixtures,³⁸ in a similar manner to that described by Li et al.³⁵ in their study of *syn*-CH₃CHOO decomposition. Li et al. demonstrated that calculations of physical losses of *syn*-CH₃CHOO via diffusion likely underestimate the total physical losses because of effects of turbulence and that measurements of CH₂OO can be used to better estimate the total physical losses because the decomposition kinetics of CH₂OO is slow.³⁶ For pressures above 12 Torr, the rate coefficient describing physical losses obtained from measurements of CH₂OO showed no significant dependence on pressure, with a mean value of $3.2 \pm 1.7 \text{ s}^{-1}$, while at a pressure of 12 Torr a value of $10.6 \pm 5.9 \text{ s}^{-1}$ was obtained. A similar value of $9 \pm 6 \text{ s}^{-1}$ was reported by Li et al.³⁵ for a similar experimental setup, with no significant dependence on temperature in the range 278–318 K or pressure in the range 100–700 Torr. The decomposition kinetics for *syn*-CH₃CHOO was subsequently obtained by subtracting the estimated rate coefficients for physical losses (k_4) from the intercepts of the plots of k' against the concentration of CH₃CHI₂ (equal to $k_1 + k_4$) to obtain rate coefficients for *syn*-CH₃CHOO decomposition (k_1). Physical losses were significantly lower than chemical losses through decomposition for all conditions (i.e., $k_4 \ll k_1$). Further details are given in the [Supporting Information](#).

Figure 5 shows the rate coefficients for *syn*-CH₃CHOO decomposition, k_1 , as a function of temperature and pressure. A summary is given in Table 2. At 297 K, k_1 varies from $98.1 \pm 16.9 \text{ s}^{-1}$ at 12 Torr to $200.6 \pm 43.1 \text{ s}^{-1}$ at 297 Torr, with results in agreement with previous measurements using photolysis of CH₃CHI₂/O₂ to generate *syn*-CH₃CHOO,^{33,35} although the results obtained by Zhou et al.,³³ based on

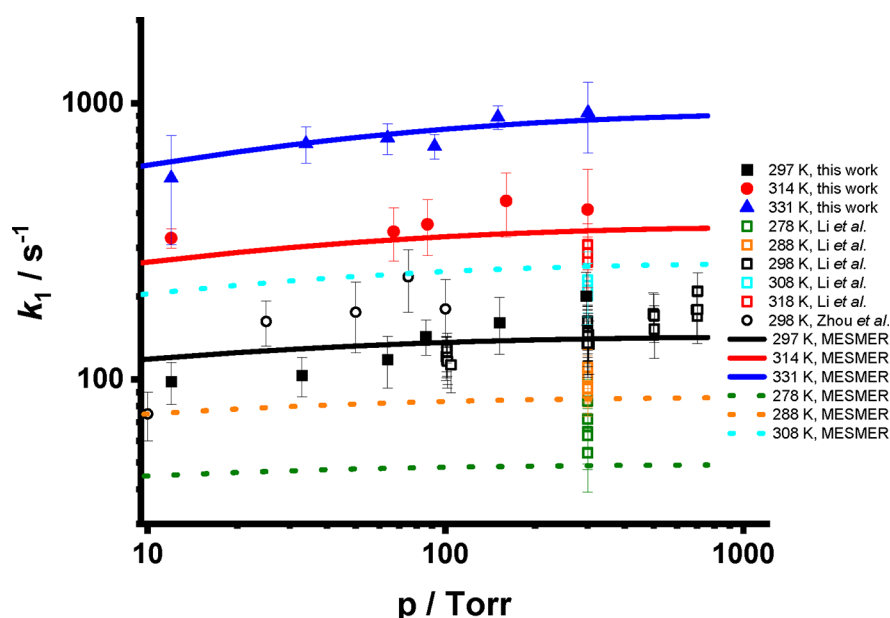


Figure 5. k_1 as a function of temperature and pressure. Results from this work are shown by the solid symbols; those obtained by Zhou et al.³³ and Li et al.³⁵ are shown by the open symbols. MESMER simulations using the parameters obtained from fits to this work are shown by the solid lines, with simulations using the fitted parameters for conditions used in previous work shown by the dotted lines. Errors are 1σ .

Table 2. Summary of Experimental Conditions and Results (Errors Are 1σ)

T/K	p/Torr	$(k_1 + k_4)/\text{s}^{-1}$	$k_3/10^{-12} \text{ cm}^3 \text{ s}^{-1}$	k_1/s^{-1}
297	12	109 ± 16	4.82 ± 0.37	98 ± 17
297	33	107 ± 17	5.21 ± 0.44	103 ± 17
297	64	121 ± 25	5.54 ± 0.49	118 ± 25
297	86	146 ± 21	1.52 ± 1.12	143 ± 21
297	152	164 ± 37	4.76 ± 0.86	161 ± 37
297	297	204 ± 43	9.03 ± 2.98	201 ± 43
314	12	335 ± 26	4.83 ± 0.37	325 ± 27
314	67	346 ± 75	1.78 ± 0.59	343 ± 75
314	87	367 ± 83	3.85 ± 0.83	364 ± 83
314	160	446 ± 115	10.81 ± 0.98	443 ± 115
314	300	415 ± 163	12.02 ± 1.23	412 ± 163
331	12	546 ± 228	8.38 ± 2.46	535 ± 228
331	34	716 ± 108	9.23 ± 0.75	713 ± 108
331	64	752 ± 95	8.99 ± 0.62	749 ± 96
331	92	701 ± 72	8.76 ± 0.59	698 ± 72
331	150	893 ± 87	8.00 ± 0.71	890 ± 87
331	301	927 ± 265	4.13 ± 2.07	924 ± 265

detection of OH, are systematically higher than those obtained in this work and by Li et al.,³⁵ which both monitor *syn*-CH₃CHOO directly. Results are also in good agreement with theoretical predictions at ~ 298 K (Table 1) and measurements obtained at 300 Torr and 318 K by Li et al.³⁵

Master Equation Analysis. Master equation calculations were performed to rationalize the observed decomposition kinetics for *syn*-CH₃CHOO, and to predict the isomerization kinetics for *anti*-CH₃CHOO, using the Master Equation Solver for Multi-Energy well Reactions (MESMER), which has been described in detail in previous work.^{36,40,43,44} MESMER uses an energy-grained master equation in which the rovibrational energy states for reactants, transition states, intermediates, and products are partitioned into a number of grains that contain a defined number of states. Energy grains representing initial reactants are assigned populations based on a Boltzmann

distribution, with grains representing other species assigned a population of zero. Changes in the population distribution among the grains can occur through collisional energy transfer via interactions with a thermal bath gas or through reactive transformation of one species to another. Transformations of one species to another are controlled by the microcanonical rate coefficients in the system, which are described by RRKM theory, while collisional energy transfer is described by an exponential down model in which the average energy transferred between grains on collision is determined by the parameter $\langle \Delta E \rangle_{\text{down}}$. In this work, $\langle \Delta E \rangle_{\text{down}}$ was assumed to be independent of temperature because of the relatively narrow range of temperatures investigated.

Pressure- and temperature-dependent rate coefficients for k_1 were calculated in MESMER using a rigid rotor harmonic oscillator approximation, with the effects of quantum mechanical tunneling determined using the asymmetric Eckart tunneling model.⁴⁵ Relevant energies, geometries, vibrational frequencies, and rotational constants were provided by the calculations reported by Vereecken et al.,¹³ which were performed at the CCSD(T)/aug-cc-pVTZ//M06-ZX level of theory. Collision parameters were obtained from the work of Long et al.²⁴ The input file for MESMER is given in the Supporting Information.

MESMER provides the potential to fit simulations for k_1 to the observed values by varying the barrier height to decomposition, $\langle \Delta E \rangle_{\text{down}}$, and the imaginary frequency for the transition state. However, it was not possible to achieve a good unique fit to the data by varying all three parameters simultaneously. To fit to the data, a series of fits were performed in which the barrier height to decomposition was varied for a range of fixed values for $\langle \Delta E \rangle_{\text{down}}$ and the imaginary frequency. The best fit was determined by comparing the reduced χ^2 statistic for the fits (shown in the Supporting Information), with the optimum fit using a value for $\langle \Delta E \rangle_{\text{down}}$ of 300 cm^{-1} and giving a barrier height of $67.2 \pm 1.3 \text{ kJ mol}^{-1}$ (compared to the calculated value¹³ of 70.3 kJ

mol^{-1}) using an imaginary frequency of $1480 \pm 45 \text{ cm}^{-1}$ (compared to the calculated value¹³ of 1619 cm^{-1}).

Figure 5 shows the MESMER fit to the experimental data using the optimized values for $\langle \Delta E \rangle_{\text{down}}$, the barrier height, and the imaginary frequency. The impact of tunneling on the overall rate coefficients for *syn*-CH₃CHO decomposition is significant under atmospheric conditions. At 298 K and 760 Torr, the MESMER simulations indicate a rate coefficient of $150_{-81}^{+176} \text{ s}^{-1}$ when tunneling effects are included but only $5_{-2}^{+3} \text{ s}^{-1}$ when tunneling is not considered in the model. The MESMER simulations give a high pressure rate-limiting coefficient of $152_{-83}^{+183} \text{ s}^{-1}$ at 298 K.

Simulations were performed in MESMER to determine k_1 using the optimized values for $\langle \Delta E \rangle_{\text{down}}$, the barrier height, and the imaginary frequency for (R1) at pressures between 1 and 7600 Torr and temperatures between 200 and 800 K. Simulations were also performed for k_2 using the potential energy surface for *anti*-CH₃CHO isomerization (R2) provided by Vereecken et al.¹³ at the CCSD(T)/aug-cc-pVTZ//M06-ZX level of theory, with $\langle \Delta E \rangle_{\text{down}} = 300 \text{ cm}^{-1}$ and the barrier height to isomerization adjusted by the same difference as that required for the fit to the experimental data for *syn*-CH₃CHO decomposition (i.e., using a barrier height of 62.6 kJ mol^{-1} for (R2) compared to the calculated value¹³ of 65.7 kJ mol^{-1}). The difference in transition state structure for the unimolecular reactions of *syn*- and *anti*-CH₃CHO has a significant impact on the atmospheric chemistry of the two conformers, with quantum mechanical tunneling leading to decomposition being the major pathway for *syn*-CH₃CHO loss in the atmosphere but isomerization having limited importance for *anti*-CH₃CHO. Effects of tunneling were thus included in the simulations for (R1) but not for (R2), and the imaginary frequency for (R2) was not adjusted in the simulations compared to the calculated value reported by Vereecken et al.¹³ At 298 K and 760 Torr, the MESMER simulations indicate $k_2 = 54_{-21}^{+34} \text{ s}^{-1}$. The high-pressure rate-limiting coefficient is $64_{-26}^{+35} \text{ s}^{-1}$ at 298 K.

The rate coefficients calculated by MESMER using the optimized potential energy surface were parametrized using the Troe expression⁴⁶ for use in kinetic models:

$$k = \frac{k_0[M]k_\infty}{k_0[M] + k_\infty} F \quad (4)$$

The low- and high-pressure limiting rate coefficients, k_0 and k_∞ in eq 4, are given by eqs 5 and 6:

$$k_0 = A_0 \left(\frac{T}{298} \right)^n \exp \left(-\frac{E_{a,0}}{RT} \right) \quad (5)$$

$$k_\infty = A_\infty \left(\frac{T}{298} \right)^m \exp \left(-\frac{E_{a,\infty}}{RT} \right) \quad (6)$$

The broadening factor, F , in eq 4 is given by eq 7:

$$\log F = \frac{\log F_c}{1 + \left[\frac{\log \left(\frac{k_0[M]}{k_\infty} \right)}{N} \right]^2} \quad (7)$$

where N is given by eq 8:

$$N = 0.75 - 1.27 \times \log F_c \quad (8)$$

The tunneling component to k_1 was parametrized by the inclusion of an additional term given by

$$k_{\text{tunnel}} = \alpha \left(\frac{T}{298} \right)^\mu \exp(-\beta T) \quad (9)$$

Parametrization of k_1 was thus achieved by the addition of eqs 4 and 9, while k_2 was parametrized by eq 4, with terms in eq 4 defined by eqs 5–8. It should be noted that the variables provided by these parametrizations are not intended to provide physical insight into the reactions, which is provided by the Master equation calculations, but rather to provide descriptions of the kinetics that can be readily implemented in atmospheric models. Table 3 summarizes the fit parameters

Table 3. Summary of Fit Parameters to Describe MESMER Simulations for k_1 (Eqs 4–9) and k_2 (Eqs 4–8)

	k_1/s^{-1}	k_2/s^{-1}
$A_0/\text{cm}^3 \text{ s}^{-1}$	$(1.9 \pm 1.8) \times 10^{-4}$	$(7.1 \pm 2.6) \times 10^{-4}$
n	-8.08 ± 0.60	-7.78 ± 0.24
$E_{a,0}/\text{kJ mol}^{-1}$	63.5 ± 2.8	73.8 ± 1.0
A_∞/s^{-1}	$(4.2 \pm 4.0) \times 10^9$	$(1.0 \pm 0.4) \times 10^{14}$
m	3.10 ± 0.64	-2.64 ± 0.31
$E_{a,\infty}/\text{kJ mol}^{-1}$	43.7 ± 2.6	69.7 ± 1.0
F_c	0.729 ± 0.015	0.785 ± 0.015
α/s^{-1}	801 ± 316	
μ	12.18 ± 0.46	
β/K^{-1}	$(8.8 \pm 1.2) \times 10^{-3}$	

determined in eqs 4–9 to describe k_1 and eqs 4–8 to describe k_2 . The MESMER simulations for k_1 and k_2 and fits to the eqs 4–9 (for k_1) or eqs 4–8 (for k_2) are shown in the Supporting Information.

Atmospheric Implications. Table 4 gives the current IUPAC recommendations²⁰ for the kinetics of stabilized *syn*- and *anti*-CH₃CHO with water vapor, water dimers, and SO₂ at 298 K and 760 Torr, with typical concentrations for these species in the lower atmosphere and the resulting pseudo-first-order loss rates associated with each reaction.²⁰ For *syn*-CH₃CHO, the pseudo-first-order loss for reaction with water vapor has an upper limit of 62 s^{-1} , with the reaction of SO₂ having a pseudo-first-order loss of 0.65 s^{-1} . Decomposition is thus expected to dominate the atmospheric loss of stabilized *syn*-CH₃CHO, with the rate coefficient of 150 s^{-1} determined in this work for 298 K and 760 Torr, giving a lower limit of 70% for the loss of *syn*-CH₃CHO via decomposition for typical tropospheric conditions when considering the competition with water vapor and SO₂. Quantum mechanical tunneling, which increases the rate coefficient for *syn*-CH₃CHO from 5_{-2}^{+3} to $150_{-81}^{+176} \text{ s}^{-1}$ at 298 K and 760 Torr, thus dominates the atmospheric chemistry of *syn*-CH₃CHO, shifting the balance of the main atmospheric loss process from reaction with water to unimolecular decomposition. The production of OH radicals following the decomposition of *syn*-CH₃CHO, through the vinyl hydroperoxide mechanism, has potentially significant impacts on tropospheric oxidizing capacity at night and in low-light conditions when photolytic sources are OH are low.^{2,3} At low temperatures, the tunneling component to the decomposition of *syn*-CH₃CHO will dominate the fate of *syn*-CH₃CHO in the atmosphere; however, there are currently no experimental measurements of the kinetics of *syn*-CH₃CHO with water dimers which may increase atmospheric losses through

Table 4. Current IUPAC Recommendations for Kinetics of *syn*- and *anti*-CH₃CHOO with Water Vapor, Water Dimers, and SO₂ at 298 K and 760 Torr,²⁰ with Pseudo-First-Order Loss Rate Coefficients for Typical Atmospheric Concentrations Compared to the Kinetics for *syn*-CH₃CHOO Decomposition and *anti*-CH₃CHOO Isomerization determined at 298 K and 760 Torr in This Work^a

reaction	conc ^a of reaction partner/cm ⁻³	$k/\text{cm}^3 \text{ s}^{-1}$ or s^{-1}	pseudo-first-order loss/ s^{-1}	% of total loss
<i>syn</i> -CH ₃ CHOO + H ₂ O	3.08×10^{17}	$<2 \times 10^{-16}$	<62	<29.02
<i>syn</i> -CH ₃ CHOO + (H ₂ O) ₂	1.96×10^{14}			
<i>syn</i> -CH ₃ CHOO + SO ₂	2.50×10^{10}	2.6×10^{-11}	0.65	>0.31
<i>syn</i> -CH ₃ CHOO decomposition		150	150	>70.67
<i>anti</i> -CH ₃ CHOO + H ₂ O	3.08×10^{17}	1.3×10^{-14}	4000	31.56
<i>anti</i> -CH ₃ CHOO + (H ₂ O) ₂	1.96×10^{14}	4.4×10^{-11}	8600	67.98
<i>anti</i> -CH ₃ CHOO + SO ₂	2.50×10^{10}	1.4×10^{-10}	3.5	0.03
<i>anti</i> -CH ₃ CHOO isomerization		54	54	0.43

^aConcentrations of reaction partners used are those adopted by IUPAC for the lower troposphere.²⁰

channels other than decomposition at higher temperatures. For *anti*-CH₃CHOO, atmospheric losses are expected to be dominated by reactions with water vapor and water dimers, for which the pseudo-first-order losses are orders of magnitude faster than isomerization. For both *syn*- and *anti*-CH₃CHOO the products of reactions with water and water dimers are currently uncertain, limiting full assessment of the atmospheric impacts of these reactions.

CONCLUSIONS

The kinetics of the unimolecular decomposition of the stabilized Criegee intermediate *syn*-CH₃CHOO (k_1) have been investigated at temperatures between 297 and 331 K and pressures between 12 and 300 Torr using laser flash photolysis of CH₃CHI₂/O₂/N₂ gas mixtures coupled with time-resolved broadband UV absorption spectroscopy.

Master equation fits to experimental results for k_1 were performed using MESMER. The fits required a decrease in the calculated¹³ barrier height of 70.3 to 67.2 kJ mol⁻¹ and in the calculated¹³ imaginary frequency for the reaction from a value of 1619 to 1480 cm⁻¹, using an exponential down model to describe collisional energy transfer with $\langle \Delta E \rangle_{\text{down}} = 300 \text{ cm}^{-1}$. The effects of quantum mechanical tunneling were included in MESMER using the asymmetric Eckart tunneling model, indicating significant impacts under atmospheric conditions. MESMER simulations using the optimized barrier height and imaginary frequency indicate a rate coefficient for decomposition of stabilized *syn*-CH₃CHOO of $150^{+176}_{-81} \text{ s}^{-1}$ when tunneling effects are included but only $5^{+3}_{-2} \text{ s}^{-1}$ when the effects of tunneling are not considered.

MESMER simulations were also performed for the unimolecular isomerization of the stabilized Criegee intermediate *anti*-CH₃CHOO using a calculated¹³ barrier height adjusted by the same difference required to fit the experimental results for *syn*-CH₃CHOO, indicating a rate coefficient of $54^{+34}_{-21} \text{ s}^{-1}$ at 298 K and 760 Torr.

Under atmospheric conditions, the impact of tunneling is expected to make decomposition the dominant loss mechanism for stabilized *syn*-CH₃CHOO, while the isomerization of stabilized *anti*-CH₃CHOO is expected to be a minor loss process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.2c05461>.

Description of the instrument response function; comparison of first- and mixed-order fits; temperature dependence of *syn*-CH₃CHOO + CH₃CHI₂; physical losses of *syn*-CH₃CHOO; optimization of the potential energy surface for (R1) using MESMER; MESMER analysis of k_1 and k_2 ; MESMER input files (PDF)

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Notes

The authors declare no competing financial interest.

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