Unimolecular Kinetics of Stabilized CH$_3$CHOO Criegee Intermediates: syn-CH$_3$CHOO Decomposition and anti-CH$_3$CHOO Isomerization

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ABSTRACT: The kinetics of the unimolecular decomposition of the stabilized Criegee intermediate syn-CH$_3$CHOO has been investigated at temperatures between 297 and 331 K and pressures between 12 and 300 Torr using laser flash photolysis of CH$_3$CH$_2$/O$_2$/N$_2$ 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$^{+81}_{−81}$ 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-CH$_3$CHOO 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-CH$_3$CHOO are provided for use in atmospheric models, and atmospheric implications are discussed.

INTRODUCTION

Criegee intermediates (R$_2$COO) 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$^{-1}$) 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 (HO$_2$), and other peroxo radicals (RO$_2$). 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 SO$_2$, NO$_2$, and organic acids.$^{1−8}$ 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 CH$_3$CHOO exists as two conformers: syn-CH$_3$CHOO, in which the methyl group is syn to the terminal oxygen, and anti-CH$_3$CHOO, 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.$^{11,12}$
For syn-CH$_2$CHOO, and other Criegee intermediates with $\alpha$ hydrogen atoms syn to the COO Criegee group, decomposition is facilitated by a 1,4-H transfer of the $\alpha$-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. The 1,4-H transfer in syn-CH$_2$CHOO leads to the production of vinyl hydroperoxide (CH$_3$CHOOH, VHP) which can undergo decomposition to OH radicals and vinoxy radicals (CH$_3$CHO) (R1). 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-CH$_2$CHOO. For anti-CH$_2$CHOO, 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 (CH$_3$CHO$_2$) (R2). However, this process is expected to be relatively slow compared to the bimolecular reactions of anti-CH$_2$CHOO.

\[
\text{syn-CH}_2\text{CHOO} \rightarrow \text{OH} + \text{CH}_3\text{CHO} \quad (R1)
\]

\[
\text{anti-CH}_2\text{CHOO} \rightarrow \text{CH}_3\text{CHO}_2 \quad \text{(methyl dioxirane)} \quad (R2)
\]

Figure 1 shows the typical potential energy surface summarizing the key features in the atmospheric formation and unimolecular chemistry of CH$_2$CHOO Criegee intermediates. The kinetics of syn-CH$_2$CHOO decomposition (R1) are key to determining the atmospheric fate and impact of syn-CH$_2$CHOO and potentially other substituted SCIs with $\alpha$-H atoms syn to the Criegee group, while the atmospheric losses of SCIs such as anti-CH$_2$CHOO are expected to be dominated by bimolecular reactions, particularly the reactions with water vapor and water dimers.

Studies of ozonolysis reactions in flow reactors and atmospheric simulation chambers have enabled estimates of the unimolecular kinetics of the stabilized Criegee intermediate CH$_2$CHOO. 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 CH$_2$CHOO on the basis of relative rate arguments, giving rate coefficients ranging over several orders of magnitude ($\sim 10^{-3}$ to $10^2$ s$^{-1}$) at room temperature and atmospheric pressure, while the first absolute, but indirect, measurements reported a value of 76 s$^{-1}$ with an accuracy within a factor of 3.

Conformer-specific kinetics for syn-CH$_2$CHOO 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 $\sim$2.6 Torr and 293 K. Relative rate studies of CH$_2$CHOO in ozonolysis experiments at ambient temperature and atmospheric pressure, involving reactions of CH$_2$CHOO conformers with SO$_2$ and measurements of either H$_2$SO$_4$ products or SO$_2$, have also been used to estimate conformer-specific kinetics for syn- and anti-CH$_2$CHOO. These studies indicate values for $k_1$ of 86 $\pm$ 13 s$^{-1}$ and 310 $\pm$ 290 s$^{-1}$, and a value of 38 $\pm$ 24 s$^{-1}$ for $k_2$, using current IUPAC recommendations for the kinetics of reactions of CH$_2$CHOO conformers with SO$_2$. 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 CH$_2$CHOO + SO$_2$. 

Figure 1. Typical potential energy surfaces describing the decomposition of syn-CH$_2$CHOO and isomerization of anti-CH$_2$CHOO (not to scale). Structures and labels refer to the species in the wells; vdW = van der Waals complex.

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

| T/K  | p/Torr | \(k_i\)/s\(^{-1}\) | barrier height (R1)/kJ mol\(^{-1}\) | \(k_i\)/s\(^{-1}\) | barrier height (R2)/kJ mol\(^{-1}\) | methods | ref |
|------|--------|-----------------|-----------------|-----------------|-----------------|--------|-----|
| 298  | ∞      | 24.2            | 74.9            | 67.2            | 64.4            | MCG3/QC15D/MG3 | Kuwata et al. \(^{10}\) |
| 298  | ∞      | 209             | 69.5            | 57.6            | 64.4            | RRRM, VTST & Eckart tunneling model | Nguyen et al. \(^{21}\) |
| 298  | 760    | 166             | 71.5            |                 |                 | CCSD(T)/aug-cc-pVTZ/B3LYP/aug-cc-pVTZ | Nguyen et al. \(^{21}\) |
| 298  | 760    | 122             | 71.5            |                 |                 | RRRM & Eckart tunneling model | Nguyen et al. \(^{21}\) |
| 298  | ∞      | 328             | 71.2            | 55.4            | 65.4            | W3X-L/CCSD(T)-F12a/DZ-F12 | Long et al. \(^{24}\) |
| 298  | 760    | 124             | 72              |                 |                 | MP-CVT SCT | Nguyen et al. \(^{25}\) |
| 298  | ∞      | 182             | 69.8            | 72.5            | 64.4            | QC15D(T)/CBS/B3LYP/6-311+G(2d,2p) | Vin & Takahashi \(^{16}\) |
| 298  | ∞      | 136             | 70.3            | 53              | 65.7            | CCSD(T)/aug-cc-pVTZ/M06-2X | Vereecken et al. \(^{13}\) |
| 298  | ∞      | 137             | 71.1            |                 |                 | MC-CTST & Eckart tunneling model | Burd et al. \(^{27}\) |
| 298  | ∞      | 155             | 71.1            |                 |                 | MP2/aug-cc-pVTZ & CCSD(T)/aug-cc-pVTZ | Burd et al. \(^{27}\) |
| 298  | ∞      | 136             | 71.1            |                 |                 | 1D-SCTST | Burd et al. \(^{27}\) |
| 298  | ∞      | 136             | 71.1            |                 |                 | FD-SCTST (MP2 x matrix) | Burd et al. \(^{27}\) |

\(^{a}\)Temperatures 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-CH\(_2\)CHOO \((k_i)\) are larger than those for anti-CH\(_2\)CHOO \((k_i)\) in most studies because of expected effects of quantum mechanical tunneling. For syn-CH\(_2\)CHOO, 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-CH\(_2\)CHOO 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-CH\(_2\)CHOO has been investigated in a series of experiments involving vibrational activation of jet-cooled syn-CH\(_2\)CHOO, generated via photolysis of CH\(_3\)CH\(_2\)/O\(_2\) and detection of the OH radical decomposition product.\(^{27,22,25,28–31}\) Activation of specific vibrational modes in syn-CH\(_2\)CHOO 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-CD\(_2\)CHOO have also indicated that the decomposition of syn-CH\(_2\)CHOO proceeds predominantly by a tunneling mechanism, with a kinetic isotope effect of over 50.\(^{32}\)

Direct measurements of the kinetics of syn-CH\(_2\)CHOO decomposition have been made at 298 K at pressures between 10 and 100 Torr, with CH\(_2\)CHOO produced following photolysis of CH\(_3\)CH\(_2\)/O\(_2\)/Ar gas mixtures at 248 nm.\(^{33}\) The kinetics for syn-CH\(_2\)CHOO 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 CH\(_2\)CH\(_2\) 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-CH\(_2\)CHOO was also required and was estimated to be on the order of 10\(^{12}\)–10\(^{13}\) cm\(^{-3}\) from the laser fluence, the CH\(_3\)CH\(_2\) precursor concentration, the yield of CH\(_2\)CHOO from the reaction between CH\(_3\)CH\(_2\) and O\(_2\), 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.\(^{32}\) The impact of wall losses and diffusion of syn-CH\(_2\)CHOO 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-CH\(_2\)CHOO + SO\(_2\) gave similar results to others reported in the literature.\(^{11,12,25}\) The results for the decomposition kinetics of syn-CH\(_2\)CHOO indicated a rate coefficient of 182 ± 66 s\(^{-1}\).
The decomposition kinetics of $\text{CH}_3\text{CHO}_2$ was obtained at 10 Torr. Experiments using time-resolved UV absorption spectroscopy have also been performed to make direct measurements of the decomposition kinetics of $\text{syn-CH}_3\text{CHO}_2$, 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.\textsuperscript{55} Photolysis of $\text{CH}_2\text{CH}_2\text{O}_2/N_2$ at 248 nm was used to generate $\text{CH}_3\text{CHO}_2$, with the absorption monitored at 340 nm. While both $\text{syn}$- and $\text{anti-CH}_3\text{CHO}_2$ display significant absorption at 340 nm, high concentrations of water vapor were added to ensure the rapid removal of $\text{anti-CH}_3\text{CHO}_2$. The change in absorption at 340 nm was thus dominated by changes in the concentration of $\text{syn-CH}_3\text{CHO}_2$, with minor contributions from $\text{CH}_2\text{CH}_2\text{O}_2$, which are approximately constant on the time scale of the experiment, and $\text{IO}$. Compared to the experiments involving detection of $\text{OH}$,\textsuperscript{33} direct monitoring of $\text{syn-CH}_3\text{CHO}_2$ simplifies the analysis, although determination of the decomposition kinetics still required consideration of the $\text{syn-CH}_3\text{CHO}_2$ self-reaction, which was assumed to be negligible for initial concentrations on the order of $10^{11}$ cm$^{-3}$, and of the reactions involving $\text{CH}_2\text{CH}_2\text{O}_2$ and $\text{IO}$, and, for these experiments, water vapor. The reaction of $\text{syn-CH}_3\text{CHO}_2$ 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 $\text{CH}_2\text{OO}$.\textsuperscript{36} The effects of physical losses such as diffusion and wall loss were estimated on the basis of measurements for the $\text{CH}_2\text{OO}$ Criegee intermediate under similar conditions and were highlighted as being potentially underestimated in the previous work\textsuperscript{33} involving detection of $\text{OH}$. Results indicated a weak pressure dependence in the decomposition kinetics of $\text{syn-CH}_3\text{CHO}_2$ at 298 K, with the rate coefficient varying from $\sim 120$ s$^{-1}$ at 100 Torr to $\sim 170$ s$^{-1}$ at 700 Torr, and an increase in the rate coefficient at 300 Torr from $67 \pm 15$ s$^{-1}$ at 278 K to $146 \pm 31$ s$^{-1}$ at 298 K and $288 \pm 81$ s$^{-1}$ at 318 K.\textsuperscript{55}

There are thus a range of estimates for $\text{CH}_3\text{CHO}_2$ 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 $\text{syn-CH}_3\text{CHO}_2$ 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 $\text{syn-CH}_3\text{CHO}_2$ decomposition. Experiments were conducted at pressures between 12 and 300 Torr and temperatures between 297 and 331 K using flash photolysis of $\text{CH}_2\text{CH}_2\text{O}_2/N_2$ 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 $\text{syn-CH}_3\text{CHO}_2$ were studied using flash photolysis of $\text{CH}_2\text{CH}_2\text{O}_2/N_2$ gas mixtures, coupled with broadband UV absorption spectroscopy. The experimental apparatus has been described in detail elsewhere,\textsuperscript{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 $\text{CH}_2\text{CH}_2\text{O}_2$ entrained into the flow by passing a known flow of $\text{N}_2$ through a bubbler containing liquid $\text{CH}_2\text{CH}_2\text{O}_2$ 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 cm$^3$ per minute (scm) at 100 Torr and adjusted accordingly with pressure to maintain a constant residence time in the cell of $\sim 6$ 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 thermostatting 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 $\text{N}_2$ gas under otherwise identical conditions.\textsuperscript{40}

Chemistry in the cell was initiated by an excimer laser (KrF, Lambda-Physik CompEx 210) operating at a wavelength of $\lambda = 248$ 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 DGS35) 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 $\sim 25$ mJ cm$^{-2}$, giving $[\text{syn-CH}_3\text{CHO}_2]_0$ on the order of $10^{11}$–$10^{12}$ 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 $\sim 10$ 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 a spectrometer (Horiba Jobin Yvon), resulting in a total effective path length of 443 cm.\textsuperscript{37–39} The beam exiting the cell was passed through a sharp cut-on filter (248 nm RazorEdge ultrasteep 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 $T = 297$ K, the output from the fiber optic was directed onto a spectograph (CP140-103 Imaging Spectrograph, Horiba) and imaged onto a line-scan charge-coupled device (CCD) detector (S7030-1006 FFP, 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.\textsuperscript{37,38}

For experiments at $T > 297$ K, the output from the fiber optic was directed through a 25 µm slit onto a spectograph 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 $T > 297$ 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 \times 10 pixels) to an optically masked storage region (1024 \times 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 photoysis. 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 photoysis shots and were transferred to a PC for analysis.

Experiments were performed in N\(_2\) (BOC oxygen free, 99.998\%) at temperatures between 297 and 331 K and pressures between 12 and 300 Torr. Concentrations of CH\(_3\)CH\(_2\)_I (Sigma-Aldrich, 98\%) were varied in the range 4.33 \times 10^{12}–2.80 \times 10^{14} \text{ cm}^{-3} to enable characterization of the kinetics of CH\(_3\)CH\(_2\)I + CH\(_2\)CHOO, while also ensuring low concentrations of photoysis products to minimize the effects of possible Criegee–Criegee and Criegee–radical chemistry. Concentrations of O\(_2\) (BOC, 99.5\%) were varied between 9.15 \times 10^{16} and 5.89 \times 10^{17} \text{ cm}^{-3}, while maintaining the requirement for rapid production of CH\(_2\)CHOO following photolysis of CH\(_3\)CH\(_2\)_I. 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:

\[
A_{\lambda,t} = \ln \left( \frac{I_{\lambda,0}}{I_{\lambda,t}} \right) = \sum_i \sigma_{\lambda,i} c_i \sigma_i t
\]

where \( A_{\lambda,t} \) is the total absorbance at wavelength \( \lambda \) and time \( t \), \( I_{\lambda,0} \) is the average pre-photoysis light intensity at wavelength \( \lambda \), \( I_{\lambda,t} \) is the post-photoysis light intensity at wavelength \( \lambda \) and time \( t \), \( \sigma_i \) is absorption cross section of species \( i \) at wavelength \( \lambda \), \( c_i \) is the concentration of species \( i \) at time \( t \), and \( l \) is the effective path length, which has a value of 443 \pm 21 cm.

Reference absorption cross sections for CH\(_3\)CH\(_2\)_I, syn-CH\(_2\)CHOO, \(^{12}\) anti-CH\(_2\)CHOO, \(^{12}\) and IO \(^{42}\) \ 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-photoysis absorbance, with typical concentration–time profiles shown in Figure 3. Experimental time scales and precursor concentrations were optimized to obtain kinetics for syn-CH\(_2\)CHOO, which resulted in small contributions to the absorbance signal from anti-CH\(_2\)CHOO because of lower yields of the anti-conformer from CH\(_3\)CH\(_2\)_I + O\(_2\),\(^{1,12,13}\) \ and, presumably, more rapid reaction of the anti-conformer with the CH\(_3\)CH\(_2\)_I precursor. Experimental results reported in this work focus on the observations of syn-CH\(_2\)CHOO, for which conditions were optimized.

![Figure 2. Observed absorbance (black), total fit (red), and the individual contributions from syn-CH\(_2\)CHOO (blue), anti-CH\(_2\)CHOO (purple), CH\(_3\)CH\(_2\)_I (green), and IO (orange) determined by fitting reference spectra to the observed absorbance using eq 1. For these data, \( T = 297 \text{ K}, p = 12 \text{ Torr}, t = 1.0 \text{ ms, and [CH}\(_3\)CH\(_2\)_I] = 2.6 \times 10^{13} \text{ cm}^{-3}. \) The fit to the observed absorbance for these data gave \( \Delta[\text{CH}\(_3\)CH\(_2\)_I] = 3.97 \times 10^{12} \text{ cm}^{-3}, [\text{syn-CH}_2\text{CHOO}] = 1.14 \times 10^{12} \text{ cm}^{-3}, [\text{anti-CH}_2\text{CHOO}] = 3.00 \times 10^{12} \text{ cm}^{-3}, \text{ and [IO]} = 1.95 \times 10^{11} \text{ cm}^{-3}. \) ![Figure 3. Observed concentration–time profile for [syn-CH\(_2\)CHOO] (open circles). For these data, \( T = 318 \text{ K}, p = 160 \text{ Torr, and [CH}\(_3\)CH\(_2\)_I] = 2.4 \times 10^{15} \text{ cm}^{-3}. \) Uncertainties in the syn-CH\(_2\)CHOO 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 \( \text{[syn-CH}_2\text{CHOO]} = (1.24 \pm 0.08) \times 10^{12} \text{ cm}^{-3} \text{ and } k' = 756 \pm 9 \text{ s}^{-1}. \) (with the instrument response parameters \( w = (1.52 \pm 0.04) \times 10^{-4} \text{ s and } t_s = (8.9 \pm 3.2) \times 10^{-6} \text{ s). Errors are 1\sigma.} \) ](https://doi.org/10.1021/acs.jpca.2c05461)

The kinetics of syn-CH\(_2\)CHOO removal from the system are controlled by its decomposition (R1), reaction with the CH\(_3\)CH\(_2\)_I precursor (R3), physical losses such diffusion out of the probe region and wall loss (R4), self-reaction (R5), and reaction with anti-CH\(_2\)CHOO (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 the instrument response function where necessary (see the Supporting Information). Similar behavior 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 decomposition and in a previous study of syn-CH₂CHO decomposition. For data obtained at temperatures above 297 K, the syn-CH₂CHO 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.

\[ C_i = C_0 \exp(-k't) \]  

where \( C_i \) is the concentration of syn-CH₂CHO at time \( t \), \( C_0 \) is the initial concentration of syn-CH₂CHO, \( k' \) represents the sum of first-order (or pseudo-first-order) losses of syn-CH₂CHO, and \( k'' \) represents the sum of second-order losses of syn-CH₂CHO.

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 decomposition and in a previous study of syn-CH₂CHO decomposition. For data obtained at temperatures above 297 K, the syn-CH₂CHO 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.

\[ C_i = \frac{C_0 k'}{k' \exp(k't) - 2k'' C_0 + k'' C'_0 \exp(k't)} \]  

where \( C_i \) is the concentration of syn-CH₂CHO at time \( t \), \( C_0 \) is the initial concentration of syn-CH₂CHO, \( k' \) represents the sum of first-order (or pseudo-first-order) losses of syn-CH₂CHO, and \( k'' \) represents the sum of second-order losses of syn-CH₂CHO.

For fits to eq 2 or 3, the observed first-order rate coefficient describing the loss of syn-CH₂CHO from the system, \( k' \), is equal to \( k_1 + k_2 \text{[CH}_2\text{CH}_1\text{I]} + k_3 \), and a plot of \( k' \) against the concentration of the CH₂CH₃ precursor yields a slope equal to \( k_1 \) and an intercept equal to \( k_1 + k_3 \). At each temperature and pressure investigated the concentration of CH₂CH₃ was varied sufficiently to determine \( k_3 \). Figure 4 shows an example plot of \( k' \) against [CH₂CH₃] used to determine \( k_1 \) and \( k_3 \). Although there is some variability in determinations of \( k_3 \), potentially because of uncertainties in [CH₂CH₃], the gradients and intercepts of the plots of \( k' \) against [CH₂CH₃] are well-defined, and thus \( k_1 + k_3 \) is well-defined. Results for \( k_1 \) indicate no significant dependence on pressure and a temperature dependence described by \( k_1 = (3.2 \pm 0.7) \times 10^{-10} \exp((−1230 ± 70)/T) \text{ cm}^3 \text{ s}^{-1} \), with a mean value of \((5.1 ± 2.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) 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 CH₂I/CH₃OO/N₂ mixtures, in a similar manner to that described by Li et al. in their study of syn-CH₂CHO decomposition. Li et al. demonstrated that calculations of physical losses of syn-CH₂CHO 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. 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 \((3.2 ± 1.7) \text{ s}^{-1} \), while at a pressure of 12 Torr a value of \((10.6 ± 5.9) \text{ s}^{-1} \) was obtained. A similar value of \((9 ± 6) \text{ s}^{-1} \) was reported by Li et al. 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-CH₂CHO was subsequently obtained by subtracting the estimated rate coefficients for physical losses (\( k_3 \)) from the intercepts of the plots of \( k' \) against the concentration of CH₂CH₃I (equal to \( k_1 + k_3 \)) to obtain rate coefficients for syn-CH₂CHO decomposition (\( k_1 \)). Physical losses were significantly lower than chemical losses through decomposition for all conditions (i.e., \( k_3 \ll k_1 \)). Further details are given in the Supporting Information.

Figure 5 shows the rate coefficients for syn-CH₂CHO 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 ± 16.9 s⁻¹ at 12 Torr to 200.6 ± 43.1 s⁻¹ at 297 Torr, with results in agreement with previous measurements using photolysis of CH₂I/CH₃/O₂ to generate syn-CH₂CHO, although the results obtained by Zhou et al. based on
detection of OH, are systematically higher than those obtained in this work and by Li et al., 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 | (k₁ + k₂)/s⁻¹ | k₁/10⁻¹² cm³ s⁻¹ | k₂/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    | 466 ± 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 |

Figure 5. k₁ as a function of temperature and pressure. Results from this work are shown by the solid symbols; those obtained by Zhou et al. 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.

**Supporting Information.** Relevant energies, geometries, vibrational frequencies, and rotational constants were provided by the calculations reported by Vereecken et al., which were performed at the CCSD(T)/aug-cc-pVTZ//M06-2X level of theory. Collision parameters were obtained from the work of Long et al. The input file for MESMER is given in the Supporting Information.
The low- and high-pressure limiting rate coefficients, \( k_1 \) and \( k_\infty \), in eq 4, are given by eqs 5 and 6:

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

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

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

\[
\log F = \frac{\log F_i}{1 + \left( \log \left( \frac{F_i}{a} \right) \right)^2}
\]

where \( N \) is given by eq 8:

\[
N = 0.75 - 1.27 \times \log F_i
\]

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

\[
k_{\text{tunnel}} = a \left( \frac{T}{298} \right)^n \exp(-\beta T)
\]

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.

| \( k_0/\text{s}^{-1} \) | \( k_\infty/\text{s}^{-1} \) |
|-------------------|-------------------|
| \( 1.9 \pm 1.8 \times 10^{10} \) | \( 7.1 \pm 2.6 \times 10^{10} \) |
| \( 8.08 \pm 0.60 \) | \( -7.78 \pm 0.24 \) |
| \( 63.5 \pm 2.8 \) | \( 73.8 \pm 1.0 \) |
| \( 4.2 \pm 4.0 \times 10^{0} \) | \( 1.0 \pm 0.4 \times 10^{4} \) |
| \( 3.10 \pm 0.64 \) | \( -2.64 \pm 0.31 \) |
| \( 43.7 \pm 2.6 \) | \( 69.7 \pm 1.0 \) |
| \( 0.729 \pm 0.015 \) | \( 0.785 \pm 0.015 \) |
| \( 801 \pm 316 \) | \( 12.18 \pm 0.46 \) |
| \( 8.8 \pm 1.2 \times 10^{-3} \) |

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Atmospheric Implications. Table 4 gives the current IUPAC recommendations\(^{20}\) for the kinetics of stabilized syn- and anti-\(CH\text{OOH} \) with water vapor, water dimers, and \( \text{SO}_2 \) 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-\(\text{CHOOH} \), the pseudo-first-order loss rate with water vapor has an upper limit of 62 \( \text{s}^{-1} \), with the reaction of \( \text{SO}_2 \) having a pseudo-first-order loss rate of 0.65 \( \text{s}^{-1} \). Decomposition is thus expected to dominate the atmospheric loss of stabilized syn-\(\text{CHOOH} \), with the rate coefficient of 150 \( \text{s}^{-1} \) determined in this work for 298 K and 760 Torr, giving a lower limit of 70% for the loss of syn-\(\text{CHOOH} \) via decomposition for typical tropospheric conditions when considering the competition with water vapor and \( \text{SO}_2 \). Quantum mechanical tunneling, which increases the rate coefficient for syn-\(\text{CHOOH} \) from \( 150 \pm 30 \) \( \text{s}^{-1} \) to \( 150 \pm 76 \) \( \text{s}^{-1} \) at 298 K and 760 Torr, thus dominates the atmospheric chemistry of syn-\(\text{CHOOH} \), shifting the balance of the main atmospheric loss process from reaction with water to unimolecular decomposition. The production of \( \text{OH} \) radicals following the decomposition of syn-\(\text{CHOOH} \), 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 low.\(^{25}\) At low temperatures, the tunneling component to the decomposition of syn-\(\text{CHOOH} \) will dominate the fate of syn-\(\text{CHOOH} \) in the atmosphere; however, there are currently no experimental measurements of the kinetics of syn-\(\text{CHOOH} \) with water dimers which may increase atmospheric losses through...
channels other than decomposition at higher temperatures. For anti-CH$_3$CHOO, 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-CH$_3$CHOO 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-CH$_3$CHOO ($k_i$) have been investigated at temperatures between 297 and 331 K and pressures between 12 and 300 Torr using laser flash photolysis of CH$_3$CHI/O$_2$/N$_2$ gas mixtures coupled with time-resolved broadband UV absorption spectroscopy.

Master equation fits to experimental results for $k_i$ were performed using MESMER. The fits required a decrease in the calculated barrier height of 70.3 to 67.2 kJ mol$^{-1}$ and in the calculated 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 $\langle \Delta E \rangle_{\text{down}} = 300$ 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-CH$_3$CHOO of 150$^{+34}_{-21}$ s$^{-1}$ when tunneling effects are included but only 54$^{+34}_{-21}$ 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-CH$_3$CHOO using a calculated barrier height adjusted by the same difference required to fit the experimental results for syn-CH$_3$CHOO, indicating a rate coefficient of 54$^{+34}_{-21}$ 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-CH$_3$CHOO, while the isomerization of stabilized anti-CH$_3$CHOO 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-CH$_3$CHOO + CH$_3$CHI$_2$ physical losses of syn-CH$_3$CHOO; optimization of the potential energy surface for (R1) using MESMER; MESMER analysis of $k_i$ and $k_j$; MESMER input files (PDF)

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### Table 4. Current IUPAC Recommendations for Kinetics of syn- and anti-CH$_3$CHOO with Water Vapor, Water Dimers, and SO$_2$ at 298 K and 760 Torr, with Pseudo-First-Order Loss Rate Coefficients for Typical Atmospheric Concentrations Compared to the Kinetics for syn-CH$_3$CHOO Decomposition and anti-CH$_3$CHOO Isomerization determined at 298 K and 760 Torr in This Work$^{20}$

| reaction | conc$^a$ of reaction partner/cm$^3$ | k/cm$^3$ s$^{-1}$ or s$^{-1}$ | pseudo-first-order loss/s$^{-1}$ | % of total loss |
|----------|-------------------------------------|------------------------------|---------------------------------|-----------------|
| syn-CH$_3$CHOO + H$_2$O | 3.08 $\times$ 10$^{17}$ | $<$2 $\times$ 10$^{-16}$ | $<$62 | $<$29.02 |
| syn-CH$_3$CHOO + (H$_2$O)$_2$ | 1.96 $\times$ 10$^{14}$ | 2.6 $\times$ 10$^{-11}$ | 0.65 | 0.31 |
| syn-CH$_3$CHOO decomposition | 2.50 $\times$ 10$^{10}$ | 150 | 150 | 70.67 |
| anti-CH$_3$CHOO + H$_2$O | 3.08 $\times$ 10$^{17}$ | 1.3 $\times$ 10$^{-14}$ | 4000 | 31.56 |
| anti-CH$_3$CHOO + (H$_2$O)$_2$ | 1.96 $\times$ 10$^{14}$ | 4.4 $\times$ 10$^{-11}$ | 8600 | 67.98 |
| anti-CH$_3$CHOO + SO$_2$ | 2.50 $\times$ 10$^{10}$ | 1.4 $\times$ 10$^{-10}$ | 3.5 | 0.03 |
| anti-CH$_3$CHOO isomerization | 54 | 54 | 54 | 0.43 |

“Concentrations of reaction partners used are those adopted by IUPAC for the lower troposphere.”$^{20}$

The authors declare no competing financial interest.

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