Selective deuteration illuminates the importance of tunneling in the unimolecular decay of Criegee intermediates to hydroxyl radical products

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Ozonolysis of alkenes, an important nonphotolytic source of hydroxyl (OH) radicals in the atmosphere, proceeds through unimolecular decay of Criegee intermediates. Here, we report a large kinetic isotope effect associated with the rate-limiting hydrogen-transfer step that releases OH radicals for a prototypical Criegee intermediate, CH3CHOO. IR excitation of selectively deuterated syn-CD3CHOO is shown to result in deuterium atom transfer and release OD radical products. Vibrational activation of syn-CD3CHOO is coupled with direct time-resolved detection of OD products to measure a 10-fold slower rate of unimolecular decay upon deuteration in the vicinity of the transition state barrier, which is confirmed by microcanonical statistical theory that incorporates quantum mechanical tunneling. The corresponding kinetic isotope effect of ~10 is attributed primarily to the decreased probability of D-atom vs. H-atom transfer arising from tunneling. Master equation modeling is utilized to compute the thermal unimolecular decay rates for selectively and fully deuterated syn methyl-substituted Criegee intermediates under atmospheric conditions. At 298 K (1 atm), tunneling is predicted to enhance the thermal decay rate of syn-CH3CHOO compared to the deuterated species, giving rise to a significant kinetic isotope effect of ~50.

Criegee intermediates | unimolecular decay | quantum mechanical tunneling | kinetic isotope effect | atmospheric chemistry

Ozonolysis of volatile alkenes originating from biogenic and anthropogenic sources is an important source of hydroxyl (OH) radicals, a key oxidant in the troposphere (1). The TORCH Campaign near London showed that ~1/3 of daytime OH and essentially all of nighttime OH are produced by alkene ozonolysis, while the PUMA field campaign near Birmingham, United Kingdom, attributed nearly half of OH radicals in the summertime and most of the OH radicals in wintertime to this mechanism (2–4). Alkene ozonolysis occurs by addition of ozone across the C=C double bond to form a primary ozonide, which rapidly decomposes to an energized Criegee intermediate (R1R2COO) and carbonyl coproduct in a highly exothermic process (1). Under atmospheric conditions, the Criegee intermediates may undergo unimolecular decay to OH and other products (1, 5–9). Alternatively, collisional stabilization and bimolecular reaction of the Criegee intermediates may occur with water vapor, SO2, and other atmospheric species (10–15). The relative importance of the unimolecular and bimolecular processes depends on the size and conformation of the Criegee intermediate as well as the atmospheric abundance of the reaction partners.

Unimolecular decay of syn alkyl-substituted Criegee intermediates, such as syn-CH2CHOO, proceeds via a 1,4-hydrogen atom transfer mechanism. An α-hydrogen on the syn-alkyl group transfers to the terminal O atom via a five-membered cyclic transition state (TS) to form vinyl hydroperoxide (VHP), which is followed by rapid homolysis of the O–O bond to release OH + vinoxyl radical products (6, 16, 17), as illustrated for syn-CH3CHOO in Fig. 1. For syn-CH3CHOO and (CH3)2COO, a combination of prompt and thermal unimolecular decay to OH products is the dominant atmospheric loss process (7, 18–20). For example, recent master equation modeling of 2,3-dimethyl-2-butenes ozonolysis under atmospheric conditions (1 atm, 298 K) showed that the calculated chemical activated (CH3)2COO (average energy of ~24 kcal-mol−1) that decays to OH products on prompt (10−13s) and thermal (10−9 s) timescales with comparable yields (7). On the other hand, Criegee intermediates that lack a syn alkyl group (i.e., CH2OO and anti-CH3CHOO) are predicted to decay via a ring closure pathway through a dioxiranine intermediate (three-membered cyclic peroxide) to a complex array of products including OH radicals (8, 21). For CH2OO and anti-CH3CHOO, bimolecular reaction with water dimer is the primary atmospheric decay pathway (12–14).

Recently, this laboratory carried out microcanonical rate measurements for the unimolecular decay of the more stable syn conformers of alkyl-substituted Criegee intermediates—namely, syn-CH2CHOO, (CH3)2COO, and syn-CH3CH2CHOO—to OH radical products at energies in the vicinity of the TS barrier (~6,000 cm−1) (20, 22). The experiments were conducted by IR activation of the Criegee intermediates in the CH stretch overtone region (2ν(C=H)) and time-resolved detection of the resultant OH products under collision-free conditions. The experimental OH appearance rates were in excellent agreement with complementary statistical Rice–Ramsperger–Kassel–Marcus (RRKM) theory that incorporates quantum mechanical tunneling (20). Subsequently, OH radical products were observed following vibrational

Significance

Ozonolysis of volatile biogenic and anthropogenic alkenes is a significant source of hydroxyl radicals, a key oxidant in the troposphere. A critical step in the generation of hydroxyl radicals is a hydrogen-atom transfer reaction involving a carbonyl oxide species, known as the Criegee intermediate. In this study, experimental and statistical theory reveal that selective deuteration of a Criegee intermediate results in deuterium atom transfer and slows the release of hydroxyl-d radicals. A large kinetic isotope effect is found at energies near the classical barrier to reaction and under thermal conditions relevant to the atmosphere. This demonstrates that quantum mechanical tunneling significantly enhances the rate of production of hydroxyl radicals in alkene ozonolysis reactions under atmospheric conditions.

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 activation of combination bands involving CH stretch and another lower-frequency mode of \( \text{syn-CH}_3\text{CHOO} \) and \((\text{CH}_3)\text{C}O\text{O}\) at energies as much as \( \sim 2,000 \text{ cm}^{-1} \) below the TS barrier (18, 19). At these energies, the 1,4 H-atom transfer reaction is classically forbidden and must proceed exclusively via quantum mechanical tunneling. Direct IR-UV time-domain measurements revealed much slower rates of appearance for OH products, which were generally in very good agreement with statistical RRKM theory, including tunneling. In addition, the experimentally validated microcanonical decay rates \( k(E) \) for the syn alkyl-substituted Criegee intermediates were extended by using master equation modeling to derive thermal decay rates \( k(T) \) in the high pressure limit. The resultant thermal decay rates (18–20, 22), which are in accord with other recent experimental and computational studies (23–26), were also found to have significant contribution from tunneling under atmospheric conditions.

The quintessential assessment to verify the role of tunneling in a chemical reaction is via isotopic (H/D) substitution, which increases the mass of the particle and slows tunneling through the TS barrier. When tunneling is important, deuteration of the syn methyl-substituted Criegee intermediate is expected to significantly slow the rate of 1,4 D-atom transfer, leading to OD products. Deuteration decreases the imaginary frequency along the reaction coordinate, effectively increasing the breadth of the barrier (in mass-weighted coordinates), and slightly increases the barrier height due to zero-point energy (ZPE) effects, both of which slow tunneling. Deuteration also lowers the frequencies of other vibrational modes—e.g., CD stretches \( \sim 2,200 \text{ cm}^{-1} \) compared with CH stretches \( \sim 3,000 \text{ cm}^{-1} \)—which increases the density of reactive states at a given energy \( N(E) \) and slows unimolecular decay (27). In addition, deuteration slows the thermal decay rate (23, 24, 28).

The present study examines the importance of tunneling in the unimolecular decay of \( \text{syn-CD}_3\text{CHOO} \) by using selectively deuterated \( \text{syn-CD}_3\text{CHO} \), which maintains a CH stretch \( (\nu_1) \) and associated vibrational overtone transition \( (2\nu_1) \) at \( \sim 6,000 \text{ cm}^{-1} \) in the vicinity of the TS barrier, as shown in Fig. 1. As will be shown, the vibrationally activated \( \text{syn-CD}_3\text{CHOO} \) undergoes 1,4 D-atom transfer from the \( \text{CD}_3 \) group to the terminal O atom, resulting in release of OD products. A direct time-domain measurement of the \( \nu_1 \) (or OD) region at a fixed IR pump–UV probe delay of 100 ns, and a significant kinetic isotope effect, KIE = \( k_D/k_H \), is elucidated (27), demonstrating the importance of quantum mechanical tunneling in the unimolecular decay of \( \text{syn-CH}_3\text{CHOO} \) to hydroxyl radical products.

**Results**

Unimolecular decay of selectively deuterated \( \text{syn-CD}_3\text{CHOO} \) Criegee intermediates to OD + vinoxy radical products is examined experimentally and theoretically. Two types of experiments are performed: (i) An IR action spectrum of \( \text{syn-CD}_3\text{CHOO} \) is obtained by scanning the IR pump laser in the \( (\nu_3) \) region at a fixed IR pump–UV probe delay of 100 ns; and (ii) direct time-domain measurements of the rate of appearance of OD products are recorded following vibrational activation of \( \text{syn-CD}_3\text{CHOO} \). In this case, the IR-UV time delay is stepped in 2- or 50-ns increments. In both types of experiments, the OD \( \nu_3 = \nu_1 = 3.5 \) (or \( \nu_3 \)) products are detected by laser-induced fluorescence (LIF) on the OD \( \nu_3 \) (or \( \nu_1 \)) transition. Complementary theoretical calculations are carried out to predict the IR absorption spectrum of selectively deuterated \( \text{syn-CD}_3\text{CHOO} \) and fully deuterated \( \text{syn-CD}_3\text{CDOO} \), which are extended by master equation modeling. Finally, a significant kinetic isotope effect, KIE = \( k_D/k_H \), is elucidated (27), demonstrating the importance of quantum mechanical tunneling in the unimolecular decay of \( \text{syn-CH}_3\text{CHOO} \) to hydroxyl radical products.
deuterated syn-CD$_3$CHOO Criegee intermediate. As shown in Fig. 4, scanning the IR-UV time delay in 2-ns steps reveals a slower exponential appearance of OD products from unimolecular decay of IR-activated syn-CD$_3$CHO at the rate of appearance being much slower than that of IR-activated syn-CH$_3$CHO at a similar energy (5.709.0 cm$^{-1}$) (20).

The OD product temporal profile from IR-activated syn-CD$_3$CHO is also measured with 50-ns IR-UV time-delay increments to capture the long-time behavior as shown in Fig. S1. The overall temporal profile is well represented by a dual exponential function that encompasses the rise ($k_{\text{rise}}$) and fall ($k_{\text{fall}}$) rate constants, as well as the laser time resolution of 5.0 ± 0.1 ns (20). $k_{\text{rise}}$ is the rate constant for appearance of OD products and corresponding unimolecular decay of syn-CD$_3$CHO. $k_{\text{fall}}$ is purely experimental in nature, which arises from the molecules moving out of the UV probe volume due to the terminal velocity of the free jet expansion and the kinetic energy release to the OD products following unimolecular decay (33, 34). At long time delays, the temporal profile is dominated by the exponential fall-off term. Repeated measurements yield $k_{\text{fall}} = 8.0 \pm 0.5 \times 10^{-5}$ s$^{-1}$, which is fixed in the subsequent determination of $k_{\text{rise}}$. The exponential rise rate constant is then separately determined to be $k_{\text{rise}} = 3.0 \pm 0.3 \times 10^{2}$ s$^{-1}$, corresponding to an OD appearance time of 33.3 ± 2.8 ns. The uncertainty ($\pm 1\sigma$) in $k_{\text{rise}}$ is derived from repeated measurements and takes into account the uncertainty ($\pm 1\sigma$) in $k_{\text{fall}}$.

The microcanonical dissociation rate constants $k(E)$ for the selectively deuterated syn-CD$_3$CHO Criegee intermediate are also computed with RRKM theory. Tunneling is taken into account by using semiclassical TS theory (SCTST) (35) and asymmetric Eckart (36) models that incorporate anharmonic frequencies. The D-atom transfer step is taken to be rate-limiting for unimolecular decay to OD products.

The RRKM calculations are based on previous high-level electronic structure calculations of the TS barrier for syn-CH$_3$CHO (20) and changes in the anharmonic frequencies and ZPE of the Criegee intermediate reactant and TS upon deuteration (Tables S1 and S3). Upon selective deuteration of syn-CD$_3$CHO, the TS barrier increases to 17.74 kcal mol$^{-1}$ (6.205 cm$^{-1}$), and the imaginary frequency associated with 1,4 D-atom transfer decreases to 1,325 cm$^{-1}$; see below for comparison of these parameters with other isotopologues. The computed RRKM rate coefficients using Eckart and SCTST tunneling models are predicted to be 2.94 × 10$^{-1}$ and 2.62 × 10$^{-1}$ s$^{-1}$ (corresponding to lifetimes of 34.0 and 38.2 ns), respectively, for selectively deuterated syn-CD$_3$CHO at 6.055.0 cm$^{-1}$, which are in very good agreement with the

Experimental, the IR action spectrum of syn-CD$_3$CHO was scanned in the 6,030- to 6,080-cm$^{-1}$ range with UV LIF detection of the resultant OD products with an IR-UV time delay of 100 ns. One feature is observed at 6,055.0 cm$^{-1}$, as shown in Fig. 3. Only one IR transition of syn-CD$_3$CHO is anticipated near 6,000 cm$^{-1}$ (Fig. 2), and thus the observed feature is ascribed to the strong CH stretch overtone (2$\nu_1$) transition predicted at 6,042.5 cm$^{-1}$. No OH products are detected upon excitation of syn-CD$_3$CHO at 6,055.0 cm$^{-1}$, confirming that unimolecular decay arises from D-atom transfer and leads exclusively to OD products.

The assignment is further validated by simulation of the rotational band contour by using the PGOPHER spectral simulation program (31). The simulation is generated by using calculated rotational constants for syn-CD$_3$CHO (A = 0.524 cm$^{-1}$, B = 0.208 cm$^{-1}$, C = 0.157 cm$^{-1}$), which differ only slightly from the experimental rotational constants for syn-CH$_3$CHO (32), and the hybrid a/b-type transition (a:b = 1:2) predicted by theory for 2$\nu_1$. As shown in Fig. 3, a simulation with band origin at 6,055.0 cm$^{-1}$, rotational temperature of ~10 K, and homogeneous broadening with a Lorentzian linewidth of 2.7 cm$^{-1}$ corresponding to an intramolecular vibrational redistribution (IVR) lifetime of ~2 ps, is in good accord with the experimental band contour.

The experimental rate of appearance of OD products is obtained from direct time-domain measurements following CH stretch overtone (2$\nu_1$) excitation at 6,055.0 cm$^{-1}$ of the selectively
Selective deuteration of syn-CD₃CHOO provides an effective means to examine the kinetic isotopic effect associated with H/D-atom transfer from the methyl group to the terminal O-atom. The energy-specific activation of syn-CD₃CHOO is afforded by IR excitation of a strong CH stretch overtone (2ν₁) transition at 6,055.0 cm⁻¹, which is followed by statistical unimolecular decay of syn-CD₃CHOO to OD + CD₂CHO products on a 33.3 ± 2.8-ns timescale with k(E) = 3.0 ± 0.3 × 10⁻⁸ s⁻¹. Additional IR transitions arising from CD stretch overtone and combination bands are predicted to occur in the 4,000- to 4,600-cm⁻¹ energy range. However, these excitation energies are in the deep tunneling regime, where RRKM calculations including tunneling indicate unimolecular decay rates for syn-CD₃CHOO to OD products that are orders of magnitude slower (10² to 10⁵ s⁻¹; Fig. 5 and Table S4). The latter are too slow to measure under the current experimental conditions, which is limited by the timescale (~1–2 µs) for molecules moving out of the probe laser detection region (18, 19) and will not be observed in the IR action spectrum. In addition, the weak IR transitions of syn-CD₃CHOO predicted in the 5,100- to 5,400-cm⁻¹ region will result in slow unimolecular decay (10⁵ to 10⁶ s⁻¹) and are not expected to be observable in the IR action spectrum.

Selectively deuterated syn-CD₃CHOO differs from the previously studied syn-CH₃CHOO system in that the rate-limiting H-atom transfer step leading to OH products is now a D-atom transfer process that yields OD products. At 6,055.0 cm⁻¹, the unimolecular decay time of syn-CD₃CHOO is 33.3 ± 2.8 ns, while that of syn-CH₃CHOO was limited by the laser time resolution (20). Since experiment and RRKM theory are in excellent accord for syn-CD₃CHOO at 6,055.0 cm⁻¹ and for syn-CH₃CHOO at slightly lower energies, we utilize RRKM theory with tunneling for the unimolecular decay time for syn-CH₃CHOO at 6,055.0 cm⁻¹ (3.7 ns) to deduce a 10-fold increase in lifetime upon selective deuteration of the methyl-substituted Criegee intermediate. Equivalently, this corresponds to a kinetic isotope effect (KIE) of ~10. A portion of this increase, specifically a factor of 3.4, can be explained by the increase in N(E) at 6,055.0 cm⁻¹ upon selective deuteration (Fig. S3). The balance is primarily due to the decreased probability of tunneling through the TS barrier for D-atom vs. H-atom transfer.

The rate of change of the unimolecular decay rate with energy is also greater for selectively deuterated syn-CD₃CHOO than syn-CH₃CHOO. As shown in Fig. 5, the unimolecular decay rate for syn-CD₃CHOO increases 10,000-fold from 3,900 to 6,300 cm⁻¹ (Table S4), while that for syn-CH₃CHOO increases by a factor of 400 (see Table S4 of ref. 19). The KIE changes from 8 to 200 across this energy range, with the largest KIE at energies significantly below the TS barrier in the deep tunneling regime. A small portion of this effect can be attributed to the increase in N(E) (by a factor of 2.8–3.4) upon selective deuteration at these energies.
Deuteration of the methyl-group of the Criegee intermediate results in changes in the TS barrier height and imaginary frequency. Fig. 6 shows an anharmonic ZPE-corrected asymmetric Eckart potential in mass-weighted coordinates to illustrate these changes. The TS barrier increases by ~4% from 17.05 kcal mol\(^{-1}\) (5,960 cm\(^{-1}\)) for syn-CH\(_3\)CHOO to 17.74 kcal mol\(^{-1}\) (6,205 cm\(^{-1}\)) for selectively deuterated syn-CD\(_3\)CHOO. This is a result of a larger reduction in the ZPE of the reactant than that of the TS upon deuteration. The imaginary frequency along the reaction coordinate for H/D atom transfer also decreases by ~22% from 1,696 cm\(^{-1}\) for syn-CH\(_3\)CHOO (20) to 1,325 cm\(^{-1}\) for syn-CD\(_3\)CHOO. The imaginary frequency is related to the curvature at the top of the barrier and results in an increase in the breadth of the Eckart potential (in mass-weighted coordinates) to illustrate these changes. The thermal unimolecular decay rates \(k(T)\) for the fully deuterated syn methyl-substituted Criegee intermediates have been computed under atmospheric conditions by using master equation modeling; thermal rates for syn-CH\(_3\)CHOO have been reported (19, 20, 25, 26). Under these conditions, the rates are predicted to be in the high pressure limit, where the thermal rate can be expressed as a Boltzmann-weighted average over \(k(E)\) and \(N(E)\), \(k(T) \propto \int k(E)N(E)\exp(-E/k_BT)dE\) (39). Note that the higher \(N(E)\) for the fully deuterated syn-CD\(_3\)CHOO compared with selectively deuterated syn-CD\(_3\)CDOO results in essentially the same thermal rates, aside from a minor effect due to their slightly different TS barriers arising from ZPE corrections. Over the 200–350 K (1 atm) range, the thermal rates for syn-CD\(_3\)CHOO (Fig. 7) and syn-CD\(_3\)CDOO are nearly indistinguishable. The thermal unimolecular decay rate of fully deuterated syn-CD\(_3\)CDOO to OD products makes it difficult to detect via IR action spectroscopy. The RRKM calculations indicate that syn-CD\(_3\)CDOO excited on IR transitions in the 4,200–4,600 cm\(^{-1}\) range (Fig. 2), assigned to transitions involving two quanta of CD stretch excitation, will decay too slowly to OD products (~10\(^{-4}\) to 10\(^{-7}\) s\(^{-1}\)) to be observed under the current experimental conditions. While syn-CD\(_3\)CDOO prepared with three quanta of CD stretch (e.g., 3\(\nu_3\)) near ~6,000 cm\(^{-1}\) would have appropriate unimolecular decay rates (~10\(^{-7}\) s\(^{-1}\)) for experimental observation, these IR transitions are anticipated to be at least an order of magnitude weaker than those involving two quanta of CD stretch excitation (e.g., 2\(\nu_3\)). Preliminary attempts to obtain an IR action spectrum of the fully deuterated syn-CD\(_3\)CDOO Criegee intermediate in the 2\(\nu_3\) and 3\(\nu_3\) energy regions were not successful.

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decay rates for syn-CH₃CHO (Fig. 7) are significantly faster than the deuterated systems, primarily due to enhanced tunneling for H-atom transfer. At 298 K, the thermal decay rates for both deuterated Criegee intermediates are ≈3 s⁻¹ compared with 166 s⁻¹ for syn-CH₃CHO (19, 20). By contrast, the effective first-order rate constants for syn- and anti-CH₃CHO with water vapor are estimated to be ∼10⁻⁴ and ∼10⁻⁸ s⁻¹, respectively, at typical atmospheric concentrations of [H₂O] = 1 × 10¹³ to 5 × 10¹⁷ cm⁻³ (14). Thus, thermal unimolecular decay will be the primary atmospheric loss process for syn-CH₃CHO, while bimolecular reaction with water vapor is expected to be the main atmospheric decay pathway for the less stable anti-CH₃CHO conformer.

As shown in Fig. 7, the thermal rates without tunneling follow similar Arrhenius behavior with slopes indicative of the TS barrier heights. Thermal rates incorporating tunneling show significantly enhanced rates with strong curvature evident in the Arrhenius plots at lower temperatures, which can be represented by modified Arrhenius expressions (SI Materials and Methods).

At 298 K, tunneling enhances the thermal decay rate of syn-CH₃CHO by a factor of 100 and to a lesser degree (10-fold) for syn-CD₃-CH₃ and syn-CD₂-CD₂O. The syn methyl-substituted Criegee intermediate is predicted to have a large KIE of 52 at 198 K upon deuteration and ranges from 15 (350 K) to >4,200 (200 K) at low temperatures in the troposphere.

This work demonstrates the importance of quantum mechanical tunneling in the energy-dependent (3,900 cm⁻¹) and thermal (200–350 K) unimolecular decay rates of syn-CH₃CHO to OH radical products. Selective deuteration of syn-CD₃-CH₃ is shown to slow the rate of unimolecular decay to OD products by 10-fold in the vicinity of the TS barrier, primarily due to the decreased probability of tunneling in D-atom vs. H-atom transfer. Moreover, deuteration is shown to give rise to a large KIE of ~50 in the thermal unimolecular decay rate of syn-CH₃CHO at 298 K. The large KIE emphasizes the importance of tunneling in enhancing the thermal decay rate of the syn methyl-substituted Criegee intermediate to OH products, which needs to be taken into account in atmospheric models of OH production.

Materials and Methods

The methods utilized for IR action spectroscopy and time-resolved dynamics of syn-CH₃CHO to OH radical products have been described (17, 19, 20). In the present study, the 1,1-diidoethane-2,2-d₂ (CD₂CD₂) precursor is prepared by using the general procedures of Friedman et al. (40), starting from acetaldehyde-2,2-d₂ (99.9% purity, 98% D, Sigma Aldrich). H₂, D₂, and 13C NMR and high-resolution mass spectrometry confirm selective deuteration of the methyl group. Additional details are given in SI Materials and Methods.