Observation of the simplest Criegee intermediate CH$_2$OO in the gas-phase ozonolysis of ethylene

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INTRODUCTION

Ozonolysis is one of the most common oxidation pathways for unsaturated hydrocarbons in the troposphere. It is the predominant sink for biogenic and anthropogenic alkenes and is a significant source of OH radicals (1), but many aspects of this complex reaction pathway remain poorly understood even after decades of study (1–4). It is generally understood, however, that the reaction proceeds via a concerted 1,3-cycloaddition of O$_3$ across the alkene double bond, through a van der Waals complex, to form a 1,2,3-trioxolane primary ozonide (denoted as a POZ, and shown in Fig. 1). This initial step is highly exothermic; consequently, the POZ is formed with high vibrational energy and promptly decomposes to form a carbonyl and a carbonyl oxide, which is commonly referred to as a Criegee intermediate (CI) (2). Although a portion of the internal energy in the POZ is lost to translational and rotational degrees of freedom of the two fragments, the CI is formed with a considerable amount of vibrational energy (5).

Nascent CIs are generally categorized as either “excited” CIs, which have sufficient vibrational energy to isomerize or dissociate rapidly, or “stabilized” CIs (SCIs), which had been initially formed with high vibrational energy but have been stabilized by collisional energy transfer. However, SCIs remain quite reactive owing to their zwitterionic character (6, 7) and undergo rapid bimolecular reaction with other atmospheric species; as such, only one instance of a SCI resulting from gas-phase ozonolysis has been reported, albeit at low resolution (8). Theoretical and indirect experimental studies (9) have determined the branching fraction to SCI to be as high as 0.54 for CH$_3$OO formed in the ozonolysis of ethylene (10). The branching fraction for larger SCIs is highly dependent on a number of factors, including temperature, pressure, and the nature of its substituents (11). A schematic of the initial reaction pathways for the ozonolysis of ethylene, the simplest alkene, is shown in Fig. 1.

Although the Criegee mechanism is now widely accepted (12), CIs eluded direct detection in the gas phase until 2008, when Taatjes et al. (13) measured the simplest CI, CH$_2$OO (2), by photolysis of dimethyl sulfoxide and photoionization mass spectroscopy. In 2012, the same group showed that the photolysis of diiodomethane (CH$_2$I$_2$) in the presence of excess molecular oxygen was a more efficient method for selectively generating CH$_2$OO (14). This production method has since been used by many groups to measure the vibrational (15), rotational (16–18), and electronic (19, 20) spectra of small CIs, as well as to study their reactivity with common atmospheric molecules (7, 8, 21–23). Although this method has been enormously valuable in characterizing the spectroscopy and kinetics of CH$_2$OO, a number of questions remain about the product branching of the nascent CIs formed directly from ozonolysis. Furthermore, the generation of larger CIs with the photolysis method is contingent on the availability of analogously larger diiodo-substituted precursors. For these reasons, we have studied the ozonolysis of ethylene at atmospheric pressure and temperature, using Fourier transform microwave (FTMW) spectroscopy and a modified pulsed nozzle. This work has resulted in the detection of species ranging from the pre-reactive complex to secondary reaction products. Most significantly, the simplest CI, CH$_2$OO, was detected in trace amounts.

RESULTS AND DISCUSSION

The first step of the O$_3$ + C$_2$H$_4$ reaction is highly exothermic ($\Delta H = -50$ kcal/mol) (24, 25), but the overall reaction rate coefficient is relatively small (1.45 $\times$ 10$^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) (19). Nascent CH$_2$OO is highly reactive with many species, including the O$_3$ and C$_2$H$_4$ reactants. For these reasons, detection of CH$_2$OO likely requires (i) large concentrations of O$_3$ and C$_2$H$_4$ to ensure a high reaction rate, (ii) rapid sampling after the two reactants are mixed to minimize secondary chemistry, and (iii) an exquisitely sensitive and selective detection method capable of measuring many different species at parts per billion concentrations (that is, $\sim$10$^{-9}$ molecules/pulse). The Balle-Flygare type cavity FTMW spectrometer used in these experiments (16, 26), described in Materials and Methods fulfills this last requirement. To address the second requirement, we constructed a nozzle source (see Fig. 2) based on the design of Lovas et al. (27, 28), who studied the O$_3$–C$_2$H$_4$ complex by “freezing” the products mid-reaction through supersonic expansion into a vacuum chamber.

In total, nine product species were detected in our experiment at room temperature and pressure. All required the presence of both O$_3$ and
Fig. 1. The initial reactions in the ozonolysis of ethylene. The reaction proceeds through a van der Waals complex and then forms a high-energy primary ozonide, which immediately decomposes into a Cl and formaldehyde. Depending on the energy available, the Cl may undergo unimolecular dissociation or bimolecular reactions with other atmospheric species. Shaded text boxes indicate species detected in our experiment.

Fig. 2. A schematic of a fast-flow reactor to rapidly sample products of the O₃ + C₂H₄ reaction. The reactants were passed through 1/16-inch inlets into the inner body of the nozzle. The armature, poppet, and spring in the center of the nozzle controlled the flow of 3.5% of the reacting mixture into the detector, while the remainder of the sample was exhausted to a fume hood. Further details may be found in Materials and Methods.

C₂H₄ and were sensitive to the flow rates and relative O₃ and C₂H₄ concentrations. The signal attributed to CH₂OO, shown in Fig. 3, was scrutinized carefully. Although weak, the frequency of this line matches the published high-resolution data (16, 17) to within 3 kHz, and we ensured that it was not an oscilloscope artifact or image by shifting the probe frequency. Additionally, the line vanished when a second microwave source, aligned perpendicularly to the cavity axis in a double resonance scheme, excited the 20a₂⁻10a₁ transition (16, 17). For these reasons, the line can be unequivocally attributed to CH₂OO. Its signal intensity corresponds to about 5.9 × 10⁶ molecules/pulse, which is close to the detection limit of the microwave spectrometer. Other detected species are listed in Table 1. All can be attributed to established secondary chemistry of the O₃ + C₂H₄ reaction, as illustrated in Figs. 4 and 5, and discussed below. A small number of the product species in the figures were not detected, because they either could not be detected in our spectrometer, were too reactive, or do not have published rotational lines.

Figure 4 illustrates the two unimolecular pathways available for excited CH₂OO, denoted as the “hot ester” and “hydrogen transfer” mechanisms. The hot ester pathway involves a ring-closing mechanism to form dioxirane (4), then O–O bond cleavage through an unstable dioxygen intermediate (5) to make formic acid (6). This pathway was experimentally verified by the matrix isolation FTIR experiments of Lovas et al. (32), and we detected dioxirane and formic acid in high relative concentrations: 50 and 3300 times that of CH₂OO, respectively. Dioxymethylene is very reactive and has not been studied in the microwave region and, consequently, was not measured here. Some fraction of formic acid was presumably formed with sufficient vibrational energy to isomerize to CO₂ + H₂ and CO + H₂O, but these two- and three-atom species do not have rotational frequencies in the 5 to 42 GHz range of our spectrometer. There is also some evidence of HCO + OH formation (38), but HCO cannot be measured in our spectrometer, and OH was not observed, likely because of its reactivity.

The second pathway available is the hydrogen transfer mechanism. In Cls with hydrocarbon substituents in the syn position, this pathway is a 1,4-hydrogen transfer and is highly favored, leading to either stabilized vinyl hydroperoxides or OH radicals (1, 3, 5). Indeed, this pathway is thought to be the dominant source of nighttime hydroxyl radicals in the troposphere (4). Because of the absence of β-hydrogens, CH₂OO may instead undergo a 1,3-hydrogen transfer to the unstable hydroperoxymethylene (7), which immediately decomposes to HCO + OH. The microwave spectrum of 7 has not been previously measured and was therefore not measured here. However, this pathway is believed to have a barrier height more than 13 kcal/mol higher than the hot ester pathway (39) and is thus expected to be a minor reaction.

Figure 5 shows the major bimolecular reaction pathways of CH₂OO in our experiment. Under true atmospheric conditions, the reaction of CH₂OO with water is believed to be its dominant pathway (1) because of the prevalence of water in the troposphere (40). Other key co-reactants include SO₂, NO₂, and the water dimer; the reactivity of CH₂OO with each has been well studied (23, 40–42). Reactions with ozone, alkenes, and carbonyl oxides have also been studied (43), but are less important in the atmosphere because of the relative scarcity of these molecules. Under our experimental conditions, however, O₃, C₂H₄, and CH₃OH are present in high abundance, and thus, the bimolecular chemistry with CH₂OO is dominated by the reactions of these three species.

CH₂OO is highly reactive with carbonyl groups, and formaldehyde (3) is the most prevalent carbonyl in our system, not only because it is the cofragment of POZ decomposition but also because many bimolecular reactions of CH₂OO yield formaldehyde. Indeed, Table 1 shows that formaldehyde is present in concentrations three orders of magnitude greater than any other product. The reaction with formaldehyde (reaction A; Fig. 5) proceeds through ethylene ozonide (8, also called 1,2,4-trioxolane or the secondary ozonide), which immediately decomposes to hydroxymethyl formate (9) or formaldehyde and formic acid.
Our experimental results are in good agreement with this mechanism, as evidenced by the detection of ethylene ozonide, but in trace amounts relative to formic acid. Because the rotational spectrum of hydroxymethyl formate is unknown, its abundance could not be determined. Taatjes and co-workers (22) measured the reaction rate of CH$_2$OO with acetaldehyde and found no evidence of secondary ozonide, but their experiments were done under low-pressure (4 torr) conditions, and secondary ozonide stabilization is likely pressure-dependent. The rate coefficient was recently estimated as \( k_A = 6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (22, 43), but older studies (42) have reported values between \( 10^{-12} \) and \( 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

The reaction of CH$_2$OO with C$_2$H$_4$ (reaction B) was studied both experimentally (21) and theoretically (43, 44) and found to yield 1,2-dioxolane (10) through a barrierless pathway, although Crehuet et al. (44) suggest that a minor pathway, leading to ethylene oxide (11) and formaldehyde, is also possible. A portion of the ethylene oxide may isomerize to the more stable acetaldehyde isomer (12). We detected both 11 and 12, but the microwave spectrum of 10 has yet to be measured. Vereecken et al. (43) suggest an overall rate coefficient of \( k_B = 5.45 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for this reaction, but the experimental work of Buras et al. (21) indicates a rate coefficient of \( k_B = 7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \) nearly an order of magnitude smaller.

The reactions of CH$_2$OO with ozone (reaction C) and with itself (reaction D) both yield formaldehyde and molecular oxygen. The former reacts with a rate coefficient of \( k_C = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (43), although there is some disagreement about whether the reaction proceeds through a biradical (43) or a cyclic (45, 46) intermediate. Neither intermediate would likely be sufficient for detection in our system, nor are there microwave spectral data available to test that hypothesis. Vereecken et al. (43) report that the CH$_2$OO self-reaction proceeds exothermically through a cyclic peroxide before decomposing to 2 CH$_2$O + O$_2$.

Buras and co-workers (47) have measured this rate coefficient as \( k_D = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Finally, CH$_2$OO may react with CO to form formic anhydride (reaction E), as suggested by Kühne et al. (48). As CO is a dissociation product of vibrationally excited formic acid, this reaction is certainly possible, and we see evidence of formic anhydride (13). However, no experimental or theoretical rate constants have been published for this reaction, and we cannot measure the concentration of CO; thus, the importance of this reaction in our experiments remains unclear. Formic anhydride has also been suggested to be a product of the reaction of CH$_2$OO with formic acid (49).

A simple kinetic model of the experimental CH$_2$OO abundance is in qualitative agreement with the theoretically published rate constants. In this model, [CH$_2$OO] was treated as a steady-state concentration, with its formation resulting from O$_3$ + C$_2$H$_4$ alone [\( k_{\text{form}} = 1.45 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (10)], and its destruction occurring
through unimolecular reaction $[k_{\text{uni}} = 75 \text{ s}^{-1} (22, 47)]$, and the bimolecular reactions listed in Fig. 5 involving species with large abundances ($k_A$ through $k_B$) only.

$$\frac{d[\text{CH}_2\text{OO}]}{dt} = k_{\text{form}}[O_3][\text{C}_2\text{H}_4] - k_{\text{uni}}[\text{CH}_2\text{OO}] - k_A[\text{CH}_2\text{OO}][\text{CH}_2\text{O}] - k_B[\text{CH}_2\text{OO}][\text{C}_2\text{H}_4] - k_C[\text{CH}_2\text{OO}][O_3] - k_D[\text{CH}_2\text{OO}]^2 \approx 0 \quad (1)$$

The concentrations of O$_3$, C$_2$H$_4$, and CH$_2$O are large and were thus treated as constant. Equation 1 was solved for [CH$_2$OO] using the initial concentrations of [O$_3$] = 0.005 M and [C$_2$H$_4$] = 0.0003 M, and the experimentally measured [CH$_2$O] $\leq$ 0.002 M. Although several wide-ranging values of $k_A$ and $k_B$ have been published, neither has a large effect on [CH$_2$OO], and thus, the most recently published value was selected. Other bimolecular reactions, including reaction E, were not included in this model because their rate coefficients have not been measured. The margins of error of all rate constants were assumed to be no smaller than an order of magnitude. This zeroth-order assumption for some fraction of the steady-state CH$_2$OO abundance. For example, Wang et al. (50) calculated the energetic barriers and rate constants for the CH$_2$O + O$_3$ reaction, and found CH$_2$OO + O$_2$ to be a possible product channel. However, the barrier is higher than 60 kcal/mol, and the rate coefficient at 298 K was found to be on the order of $10^{-33}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Given the concentration of ozone and formaldehyde found in these experiments, we would expect the formation of only $10^2$ CH$_2$OO molecules/pulse from this mechanism. Similarly, the CH$_2$OO signal in our previous discharge studies of CH$_4$/O$_2$ (16) was tentatively attributed to a secondary reaction of excited CH$_2$OO (51). However, only trace amounts of CH$_2$OO were detected in the present discharge-free experiments, and thus, this reaction is not expected to significantly contribute to the CH$_2$OO signal.

Experiments are currently under way to detect the monosubstituted CI, CH$_2$CHO+O$_2$, via the reaction of O$_3$ with C$_3$H$_6$. Under similar experimental conditions, many of the analogs to the products in the O$_3$ + C$_3$H$_6$ reaction have been observed, including propylene ozonide, propylene oxide, $\text{syn}$-vinyl alcohol, propionaldehyde, acetic acid, and acetone, in addition to the formaldehyde, acetaldehyde, and formic acid found in the ethylene reaction. However, neither the O$_3$ + C$_3$H$_6$ van der Waals complex nor methylformic acid-$c$-(OOC)-CH$_3$ has been studied in the microwave region. Because detection of O$_3$ + C$_3$H$_6$ (1) and dioxirane (4) was a critical step in optimizing the experimental conditions in this study, our inability to optimize the experimental conditions in the O$_3$ + C$_3$H$_6$ system using these analogs has made it difficult to definitively assign any signal to CH$_3$CHOO.
CONCLUSIONS

We have reported the first detection of CH2OO in the gas-phase ozonolysis of ethylene at atmospheric temperature and pressure, using FTMW spectroscopy and a modified nozzle designed for rapid sampling. Although the signal was weak, it can be unequivocally attributed to CH2OO. Other products were detected in relative amounts that qualitatively support the established reaction pathways of the nascent excited and stabilized CIs in the literature. Although it is conceivable that an alternative mechanism is responsible for the CH2OO signal, the detected signals match very well with the kinetic model, and no other plausible mechanism has been suggested in the literature. Our results appear to confirm this long postulated oxidation mechanism. With improvements to the experimental methods described here, including developing a more consistent ozone source and increasing the steady-state concentration of CH2OO, this direct ozonolysis method may allow for the formation and characterization of larger CIs under atmospheric conditions. Direct formation from O3 + alkenes greatly simplifies the formation kinetic analysis and can yield important information about branching and OH radical formation, which are key questions for understanding the critical role of ozonolysis in atmospheric chemistry.

MATERIALS AND METHODS

In our nozzle design, two 1/16-inch-diameter holes were drilled into the inner body of a Parker-Hannifin Series 9 pulsed nozzle in a V-shape (Fig. 2). Stainless steel tubing (inner diameter 1/16 inch) was welded to each inlet, and O3 and ethylene were separately passed into the nozzle, using mass flow controllers to regulate carefully their flow. In one inlet, 2% C2H4 in neon flows at a rate of 50 sccm (cm3/min at STP), whereas a ~10% mixture of O3 in argon flows through the second inlet at 100 sccm. The O3 is obtained by trapping the ozone from a Welsbach ozonator on a silica gel trap maintained at ~60°C and then flowing argon through the trap. Ozone is explosive in high concentrations, so for safety we collected very small samples of ozone on the trap (<500 mg) and refilled it every 2 hours. The rate of desorption of O3 is roughly proportional to the trapped concentration; thus, a high initial ozone concentration is observed (quantified by sodium thiosulfate titration), followed by a steady decrease over 2 hours. The concentration of O3 inside the nozzle can therefore only be estimated.

The reactants mix at 1 atm and 298 K inside the 1.6-cm3 body of the nozzle, and the pulsed nozzle injects ~3.5% of the resulting mixture into the FTMW spectrometer; the remainder of the gas vents through the rear of the nozzle. We estimate that the products are sampled within the first 0.5 s of the reaction because there is a high steady gas flow and sampling occurs at a rate of 6 Hz. The signal levels began to diminish after about 2 hours, ostensibly owing to the buildup of a thin film of organic material on the inside of the nozzle, which required manual cleaning. The microwave spectrum obtained by flowing an inert gas over this material indicates the presence of formic acid and formaldehyde, but the low volatility of the material suggests the additional presence of larger oligomers.

A portion of the reaction mixture is supersonically expanded ($T_{rot} \approx 3$ K) into a vacuum chamber maintained at 10-6 torr, and probed by a 5 to 42 GHz cavity FTMW spectrometer. A tunable microwave synthesizer generates ~1 μs microwave pulses, which excites all rotational transitions that fall within the bandwidth of the pulse. Coherently rotating molecules undergo free induction decay, which is detected using a sensitive microwave receiver; a Fourier transform of this signal yields a power spectrum. Products in the O3 + C2H4 reaction are detected by monitoring known low-J rotational transitions of each. No attempt was made to detect species whose microwave transitions have yet to be measured. The species detected are shown in Table 1, along with their molecular abundances, estimated by calibrating with a stable molecule of known abundance [0.04% carbonyl sulfide (OCS) in Ar] and corrected for differences in dipole moments, rotational partition functions, and the spectrometer instrument response function.

REFERENCES


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