Kinetics of the Simplest Criegee Intermediate CH₂OO Reacting with CF₃CF═CF₂†

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CF₃CF═CF₂ is a potential source of atmospheric trifluoroacetic acid (CF₃C(O)OH). The kinetics of the reaction of the simplest Criegee intermediate (CH₂OO) with CF₃CF═CF₂ was studied by using the OH laser-induced fluorescence method. At 10 torr, the rate coefficients were measured to be (1.45±0.14)×10⁻¹³, (1.18±0.11)×10⁻¹³, (1.11±0.08)×10⁻¹³, and (1.04±0.08)×10⁻¹³ cm³·molecule⁻¹·s⁻¹ at 283, 298, 308 and 318 K, respectively. The activation energy of (−1.66±0.21) kcal/mol was derived from the Arrhenius equation. No obvious pressure dependence was observed.

Key words: Criegee Intermediate, Reaction kinetics, Rate coefficient

I. INTRODUCTION

Ozonolysis of alkenes is one of the most important reactions in the troposphere. Its mechanism was first postulated by Rudolf Criegee et al. [1], according to which, O₃ adds across the double bond of alkenes to form a primary ozone with a five-membered ring structure. This complex further decomposes to highly energized carbonyl oxide, which is called Criegee intermediate (CI). The newly formed CI isomerizes or is stabilized by the bath gases, or decomposes to species such as OH, HO₂, and organic radicals [2–11]. The OH radicals are essential to the oxidative ability of the atmosphere. The formation of OH from thermal decomposition of stabilized Criegee intermediates (SCIs) is a significant source of OH in cold or dark environments, such as during night-time or in winter. Under these conditions, the well-recognized source of OH—namely the reaction of H₂O with O¹(1D) which is generated from the photolysis of ozone—is limited either by the low concentration of water or by the lack of the UV light [12]. The SCIs thus have long enough lifetime to react with atmospheric species, e.g., H₂O (monomer or dimer), SO₂, alcohols, and carboxylic acids [13–18]. These reactions are relevant to the formation of atmospheric aerosols [12].

Despite the theoretical predictions, the kinetics of CIs reactions were lack of direct experimental observation, due to the difficulty in producing a sufficient amount of CIs in the lab. A substantial breakthrough was made when Welz et al. prepared the simplest CI, CH₂OO by photolyzing CH₃I in the presence of O₂ [13]. Subsequently, various detection methods, including photolysis mass spectrometry, ultraviolet (UV) absorption, infrared (IR) absorption, laser-induced fluorescence (LIF), and microwave spectroscopy, were applied to its spectroscopy, structure and kinetics study [13, 14, 19–23].

The fate of SCIs, and their influence on the earth’s atmosphere, are among the most significant scientific issues about SCIs. The reaction of water, the third most abundant species in the troposphere, with CH₂OO has been extensively studied, both theoretically and experimentally [24–30]. Benefiting from the method of directly preparing CIs in the lab, recent experiments showed good consistency in terms of values of rate coefficient: 6.5×10⁻¹²–7.5×10⁻¹² cm³·molecule⁻¹·s⁻¹ for CH₃OO reacting with water dimer, and 2.4×10⁻¹⁶–3.2×10⁻¹⁶ cm³·molecule⁻¹·s⁻¹ for CH₂OO reacting with water monomer [14, 17, 24.

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The theoretical calculations predicted similar values of $5.44 \times 10^{-12}$ and $2.41 \times 10^{-18} - 1.06 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the two reactions, respectively [28, 30]. The reactions of CH$_2$OO with some organic and inorganic acids, e.g., HCOOH, CH$_3$COOH, and HNO$_3$ are very fast, with rate coefficients in the vicinity of $2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [16, 31]. Those values for CH$_2$OO reacting with SO$_2$ and NO$_2$ are approximately $3.9\times 10^{-11}$ and $7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively [13, 17, 32]. The consumption rate of CH$_2$OO is determined by both the rate coefficient of the reaction and the concentration of the co-reactant. According to these criteria, water consumes the majority of atmospheric CH$_2$OO. Species mentioned above, as well as NH$_3$, H$_2$S, CO$_2$, alcohol, and so forth, only play minor roles in the consumption of CH$_2$OO [15, 33-35].

The impact of CH$_2$OO on the atmosphere also depends on the reaction products. Though reactions, such as CH$_2$OO with NO$_2$ and SO$_2$, consume a fraction of CH$_2$OO in the atmosphere, they are potentially important in terms of the impact of reaction products on the atmosphere. For example, the reaction products SO$_3$, NO$_3$, and CH$_2$OONO$_2$ could either alter the oxidizing capacity of the atmosphere or contribute to the formation of aerosols [36].

Hexafluoropropylene (CF$_3$CF=CF$_2$) is a photolysis product of some perfluorinated polymers, such as polytetrafluoroethylene (PTFE) and polytetrafluoroalkyl ethers (FEP) [37]. The oxidation of CF$_3$CF=CF$_2$ by OH radicals, Cl atoms or O$_3$ could produce trifluoroacetic acid (CF$_3$C(O)OH), a compound with no clear loss mechanism [38]. It is unlikely that CF$_3$CF=CF$_2$ could compete with water in the consumption of CH$_2$OO in the atmosphere, due to the high concentration of water there. As the concentration of SCIs is comparable with that of OH in certain circumstances [39, 40], the title reaction may play a role in the oxidation of atmospheric CF$_3$CF=CF$_2$, depending on its rate coefficient. If this value is comparable or even larger than that of OH+CF$_3$CF=CF$_2$ reaction, it is worthwhile to investigate the product of the title reaction in the future study to see if its major product is more environmentally friendly than trifluoroacetic acid. In the present work, we measured the temperature- and pressure-dependent rate coefficients of CH$_2$OO+CF$_3$CF=CF$_2$ reaction by using the OH laser-induced fluorescence method.

II. EXPERIMENTS

We are using the OH LIF to measure the rate coefficient of CH$_2$OO reacting with CF$_3$CF=CF$_2$. The details of our experimental instrumentance have been described in our previous work [5], and a brief description was introduced here. O$_2$ (99.995%), CF$_3$CF=CF$_2$ (3% seeded in Ar), buffer gas Ar (99.999%), and CH$_2$I$_2$ (Sigma-Aldrich, 99%) flowed continuously through a pre-mixed manifold to a 75-cm-long flow tube reactor. The flow rate of these gases was controlled by a set of calibrated mass flow controllers (MKS, GM50A Series). CH$_2$I$_2$, kept in a bubbler which was stabilized at 25 °C by water bath, was seeded by Ar. A capacity manometer (MKS Baratron), together with an exhaust throttle valve (MKS, 653B), was utilized to actively control the pressure of the flow reactor.

CH$_2$OO was prepared by photolyzing CH$_2$I$_2$ in the presence of O$_2$ with a 248 nm pulsed KrF excimer laser (Coherent, COMPexPro 50). The typical pulse energy was 35 mJ/cm$^2$. The probe UV radiation (2 mm diameter, 40 nJ), frequency doubling of the output of a dye laser (Narrow Scan High Rep, with Rhodamine 590 dye) which was pumped by the second harmonic of a Nd:YAG laser (Edgewave INNOSLAB: IS1211-ET, 10 kHz), intersected the photolysis beam perpendicularly. The time delay between the photolysis and probe radiation was controlled by a delay generator (Stanford Research System, DG535). The probe wavelength of 282 nm corresponds to the P$(1,1)$ line of the (1,0) band of the OH $(A^2\Sigma^+ - X^2\Pi)$ transition. The OH fluorescence, collected by a quartz lens in the direction perpendicular to both the photolysis and the probe beam, was amplified by a photomultiplier tube (PMT, Electron PDM9111-CF-TTL) and recorded in a computer. Normally, about 1200 decay profiles were accumulated for further analysis. The stray light was filtered out by three filters, i.e., Semrock FF01-315/15-25, Schott UG11, and Semrock FF02-320/40-25.

The concentration of CH$_2$I$_2$ was determined by the UV absorption method. A deep UV LED (DUV325-H46, Roithner Lasertechnik) and an amplified photodetector (PDB450A, Thorlabs) were used to monitor the absorbance of CH$_2$I$_2$, and its concentration was deduced based on the known absorption cross-section and the measured LED emission profile.

III. RESULTS AND DISCUSSION

CH$_2$OO is generated from the following reactions:

$$\text{CH}_2\text{I}_2 + h\nu \xrightarrow{k_1} \text{CH}_2\text{I} + \text{I} \quad (1)$$
$$\text{CH}_2\text{I} + \text{O}_2 \xrightarrow{k_2} \text{CH}_2\text{OO} + \text{I} \quad (2)$$
$$\text{CH}_2\text{I} + \text{X} \xrightarrow{k_3} \text{other products} \quad (3)$$

The consumption of CH$_2$OO and OH arises from the following reactions:

$$\text{CH}_2\text{OO} \xrightarrow{k_4} \text{OH} \quad (4)$$
$$\xrightarrow{k_5} \text{other products} \quad (5)$$
$$\text{CH}_2\text{OO} + \text{X} \xrightarrow{k_6} \text{products} \quad (6)$$
$$\text{CH}_2\text{OO} + \text{CH}_2\text{OO} \xrightarrow{k_7} \text{products} \quad (7)$$
$$\text{OH} + \text{Y} \xrightarrow{k_8} \text{products} \quad (8)$$
$$\text{CH}_2\text{OO} + \text{CF}_3\text{CF}=\text{CF}_2 \xrightarrow{k_9} \text{products} \quad (9)$$

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X denotes species that react with CH$_2$OO—except for CF$_3$CF=CF$_2$—in the reactor, such as I and CH$_2$I; Y denotes the species that consume OH, e.g., I and CH$_2$I; $k$ is the rate coefficient.

In the current experiment, the concentration of CF$_3$CF=CF$_2$ is massive in comparison with that of CH$_2$OO; thus, the reaction of CH$_2$OO with CF$_3$CF=CF$_2$ is under pseudo-first-order approximation condition.

The time-dependent OH signal could be described by Eq.(10) when the above reactions are considered (see our previous publication for details) [5]:

$$S_{OH}(t) = \frac{C}{D} - A_1e^{-k'dt}$$

$$C = A_0(k_3 + k'_4 + k'_5)$$

$$D = (k_3 + k'_4 + k'_5)e^{(k_3 + k'_4 + k'_5)t} - 2k_3[CH_2OO]_0 + 2k_3[CH_2OO]_0e^{(k_3 + k'_4 + k'_5)t}$$

$$k_3 = k_{3a} + k_{3b}$$

$$k'_4 = k_4[X]$$

$$k'_5 = k_5[Y]$$

$$k'_7 = k_7[CF_3CF = CF_2]$$

$$A_0 = \gamma \left( \frac{k_{3a}}{k_6 - (k_3 + k'_4 + k'_5)} \right) [CH_2OO]_0$$

$$A_1 = \gamma \left( \frac{k_{3a}}{k_6 - (k_3 + k'_4 + k'_5)} \right) [CH_2OO]_0 - [OH]_0$$

where $\gamma$ is the detection efficiency of OH. During fitting the OH decay profiles, $A_0$, $A_1$, $(k_3 + k'_4 + k'_5)$ and $k'_6$ were allowed to vary; $k_5$ was fixed at 8.0 x 10^{-11} cm$^3$-molecule$^{-1}$-s$^{-1}$, in reference to the results of Ting et al. [41]; [CH$_2$OO]$_0$ was fixed to the values calculated according to the known [CH$_2$I$_2$], fluence of the photolysis radiation and the yield of CH$_2$OO from reactions (Eq.(2) and Eq.(3)).

FIG. 1 shows the selected decay traces of the OH signals at 10 torr and 298 K. [CH$_2$OO] was fixed to 9.19 x 10^{12} cm$^{-3}$ and [CF$_3$CF=CF$_2$] was varied from 0.09 x 10^{15} cm$^{-3}$ to 2.75 x 10^{15} cm$^{-3}$. Solid lines are the fit of experimental data (hollow points) with Eq.(10) by using First Optimization software (1stOpt 7.0, 7Dsoft High Technology Inc.). According to Eq.(10), the decrease of OH signals with time indicates the consumption of CH$_2$OO. That the OH signals decline faster as the initial [CF$_3$CF=CF$_2$] increases shows that the consumption of CH$_2$OO by CF$_3$CF=CF$_2$ is conspicuous in the current experimental conditions. It is also obvious that the peak values of the OH signals decrease while [CF$_3$CF=CF$_2$] increases. This is possible because the quenching cross-section of OH ($A^2\Sigma^+$) by CF$_3$CF=CF$_2$ is larger than that by Ar. In the current experiment, the variation of [CF$_3$CF=CF$_2$] was balanced by [Ar]. The quenching cross-section of Ar to OH ($A^2\Sigma^+$) is 0.05 Å$^2$ [42]. Although the corresponded value for CF$_3$CF=CF$_2$ is not available, a value of 90 Å$^2$ for isobutane could roughly be taken as a reference [43].

As mentioned above, fitting OH decay traces with Eq.(10) could derive $(k_3 + k'_4 + k'_5)$. Because $k_3$ and $k'_4$ are irrelevant to [CF$_3$CF=CF$_2$], when plotting $(k_3 + k'_4 + k'_5)$ against [CF$_3$CF=CF$_2$], the intercept is $(k_3 + k'_5)$; thus, $k'_5$ could be extracted. FIG. 2 shows the $k'_5$ at various [CF$_3$CF=CF$_2$] and four temperatures of 283, 298, 308, and 318 K. The linear relationship between $k'_5$ and [CF$_3$CF=CF$_2$] at each temperature is shown with a solid line. The slope of the linear fitting corresponds to the bimolecular reaction rate coefficient of CH$_2$OO reacting with CF$_3$CF=CF$_2$. By averaging over 31 sets of experimental data at each temperature from different days, we obtained the bimolecular reaction rate coefficients, which are $(1.45\pm0.14)\times10^{-13}$, $(1.18\pm0.11)\times10^{-13}$, $(1.11\pm0.08)\times10^{-13}$ and $(1.04\pm0.08)\times10^{-13}$ cm$^3$-molecule$^{-1}$-s$^{-1}$ at 283, 298, 308, and 318 K, respectively. This reaction at room temperature is faster than O$_2$+CF$_3$CF=CF$_2$ reaction—upper limit rate coefficient of which is $3\times10^{-21}$ cm$^3$-molecule$^{-1}$-s$^{-1}$ at 296 K—but slower
than OH+CF$_3$CF=CF$_2$ and Cl+CF$_3$CF=CF$_2$ reaction, the rate coefficients of which are 2.4×10^{-12} and 2.7×10^{-11} cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively [38]. According to the observed rate coefficients, CF$_3$CF=CF$_2$ is indiscernible in the consumption of CH$_2$OO in the atmosphere. But CH$_2$OO might compete with OH in reacting with CF$_3$CF=CF$_2$, especially during the night time or winter, when the OH concentration is low.

The activation energy—the minimum energy that is required for a reaction to occur—could be derived from the temperature-dependent rate coefficients of the title reaction by applying the Arrhenius expression

$$k(T) = A \exp \left( \frac{-E_a}{RT} \right)$$

Here, $A$ is the pre-exponential factor, $E_a$ is the activation energy, and $R$ is the universal gas constant. The Arrhenius plot of the bimolecular rate coefficients for CH$_2$OO+CF$_3$CF=CF$_2$ reaction at 10 torr is shown in FIG. 3. From the linear fitting, the activation energy of (-1.66±0.21) kcal/mol was derived. Similar to some reactions, e.g., CH$_2$OO with (H$_2$O)$_2$, H$_2$S and CF$_3$COOH, which show negative temperature dependence, the negative activation energy of the title reaction might be explained with a complex-formation mechanism [34, 44, 45]. Take the CH$_2$OO+(H$_2$O)$_2$ reaction, which has an activation energy of ~8.1 kcal/mol, for example. A reactive complex CH$_2$OO−(H$_2$O)$_2$ is bound by about 11 kcal/mol with respect to the separated reactants. Due to a low barrier, arising from small geometry change between the complex and the transition state, the transition state lies about 6 kcal/mol below the energy of the separated reactants [45]. For the title reaction, we postulate that the transition state—formed from a prereactive complex via a submerged barrier—locates at energy slightly lower than that of the separated reactants, similar to the CH$_2$OO+H$_2$S reaction [34]. Similarly, the OH+CF$_3$CF=CF$_2$ reaction is also negative temperature dependent, with an activation energy of about ~0.8 kcal/mol [46].

The pressure dependence of CH$_2$OO reacting with CF$_3$CF=CF$_2$ was measured at five pressures ranging from 6.3 torr to 70 torr, as shown in FIG. 4. Due to the collisional quenching of OH(A$^2\Sigma^+$), the OH signals at pressures higher than 70 torr are too small to provide reliable information. For the same reason, the $k_T$ at 70 torr has a relatively larger deviation. The data in FIG. 4. suggest that the title reaction may reach the high-pressure limit at a pressure as low as 6 torr. This result is similar to the CH$_2$OO+SO$_2$ reaction, which achieves the high-pressure limit at a pressure lower than 1.5 torr [47]. To evaluate the atmospheric effect of the CH$_2$OO+CF$_3$CF=CF$_2$ reaction, the information about the reaction product, which is currently not available, is indispensable.

IV. CONCLUSION

The OH laser-induced fluorescence method was applied to the measurement of the rate coefficient for CH$_2$OO reacting with CF$_3$CF=CF$_2$. At 10 torr, the bimolecular reaction rate coefficients are (1.45±0.14)×10^{-13}, (1.18±0.11)×10^{-13}, (1.11±0.08)×10^{-13}, and (1.04±0.08)×10^{-13} cm$^3$ molecule$^{-1}$ s$^{-1}$ at 283, 298, 308, and 318 K, respectively. The activation energy of (-1.66±0.21) kcal/mol was derived based on the Arrhenius equation. No obvious pressure dependence was observed in the range from 6.3 torr to 70 torr. The title reaction may play a minor role in the consumption of atmospheric CH$_2$OO but could compete with OH in the oxidization of CF$_3$CF=CF$_2$, especially under the conditions that the OH concentration is low, such as winter and night-time.

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