Reaction kinetics of O(^1D) with CF\textsubscript{3}CN

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The rate constant for removal of O(^1D) by reaction with CF\textsubscript{3}CN has been measured to be (1.3 ± 0.2) × 10^{-10} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at room temperature by a time-resolved laser induced fluorescence (LIF) technique. The quantum yield for the electronic quenching O(^1D) to O(^3P) has been also measured to be 0.14 ± 0.02. The O(^1D) and O(^3P) atoms were detected by LIF using a vacuum ultraviolet laser as a probe laser. CN(X 2Σ\textsuperscript{+}) and NCO(X 2Π) products were also detected by LIF using ultraviolet and visible lasers, respectively. The CN(X) radical was observed as a primary product, while the NCO(X 2Π) radical was not observed as a primary product in the present reaction.

1. Introduction

Reactions of electronically excited oxygen atoms O(^1D) are a significant chemical channel for the removal of the mixed halogenated methane derivatives CF\textsubscript{x}X\textsubscript{4-x} (X = Cl, Br, I) in the stratosphere.\textsuperscript{1–4} The kinetics for the production of O(^3P), ClO and Cl radicals following the O(^1D) reaction with the chlorofluoromethane CF\textsubscript{3}Cl\textsubscript{4-x} (CF\textsubscript{3}-1n) have been well determined,\textsuperscript{5,6} because it is important to estimate the production rate of ClO \textsuperscript{6} destroying the ozone layer.\textsuperscript{7–9} The dominant pathways of these reactions are the production of O(^3P) and ClO, while the reaction channel of Cl production is a quite small contribution.\textsuperscript{5} It is interesting that the Cl atom is hardly produced in the reaction CF\textsubscript{3}Cl + O(^1D) in spite of the largest reaction energy released. The reason for this phenomenon is not yet understood.

In the present study, the decay of O(^1D) and rise of O(^3P) were monitored to measure the total reaction rate constant, \(k_{\text{total}}\). The signal of O(^1D) was detected by LIF using a tunable vacuum ultraviolet laser (VUV) laser. The O(^3P), CN(X) and NCO(X) radical products were also detected by LIF using VUV, UV and VIS lasers, respectively. The quantum yield of the quenching reaction, \(\phi_q\), was measured by comparison between the O(^3P) signal intensity formed in the present reaction and that in the quenching reaction

\[ \text{N}_2 + \text{O}^1D \rightarrow \text{N}_2 + \text{O}^3P, \]

in which the quantum yield is defined as unity.\textsuperscript{11} From the observed quenching reaction rate constant, \(k_q = k_{\text{total}}\phi_q\), and the time profile of the LIF signals of CN(X) and NCO(X), the reaction mechanism is discussed.

2. Experimental

The experimental setup was essentially the same as in the previous studies.\textsuperscript{12} The reaction cell (60 × 60 × 60 mm\textsuperscript{3}) was evacuated by a rotary pump through a liquid-N\textsubscript{2} trap. Sample gas mixtures containing N\textsubscript{2}O as an O(^1D) source, CF\textsubscript{3}CN or N\textsubscript{2} as a reactant, and He as a buffer were flowed slowly through the reaction cell where the pressure was measured by a Baratron gauge. The N\textsubscript{2}O, CF\textsubscript{3}CN, N\textsubscript{2} and He gases were obtained commercially and used without further purification. The O(^1D) was generated in the reaction cell by the photolysis of N\textsubscript{2}O at 193 nm using an ArF laser (Lambda Physik, Compex; 50 mJ). The initial concentration of O(^1D) is estimated to be \(\sim 10^9 \) molecule cm\textsuperscript{-3}. Because translationally hot O(^1D) atoms are thermalized rapidly by collisions with buffer gas,\textsuperscript{13} the hot atom effect can be ignored under the present experimental conditions. The probe laser beam for the detection of O(^1D) or reaction products was also introduced in the reaction cell after the delay. The reaction time is defined as this delay time, \(t\), between the photolysis and probe laser pulses, which is controlled by a pulse generator (Stanford Research Systems, DG535).

The O(^1D) and O(^3P) atoms were detected by LIF for the 3s 1D–2p 1D transition at 115.22 nm and 3s 2S–2p 3P\textsubscript{2} transition at 130.22 nm, respectively. The VUV wavelengths of 115.22 and 130.22 nm were generated by frequency tripling (3o) of a dye laser (Lambda Physik, FL3002, 5 mJ pulse\textsuperscript{-1}) at 345.6 nm in Xe (50 Torr) and Ar (130 Torr) gas mixture and

\[ \text{N}_2 + \text{O}^1D \rightarrow \text{N}_2 + \text{O}^3P, \]
by four-wave difference mixing ($2\omega_1 - \omega_2$) using two dye lasers (Lambda Physik, FL3002 and Scanmate) in Kr gas (20 Torr), respectively. The dye laser output was frequency doubled by a BBO crystal for the $\omega_2$ light of wavelength 212.56 nm, which was two-photon resonant with Kr $5p[1/2]_0$. The dye lasers were pumped by a XeCl excimer laser (Lambda Physik, Lextra-50). The wavelength of $\omega_2$ was tuned around 578.1 nm. The laser beams were focused into a Xe or Kr gas cell by a lens with a focal length of 200 mm. The VUV light generated in the Xe or Kr gas cell was introduced into the reaction cell through a LiF window in a direction orthogonal to the photolysis laser direction. The intensity of the VUV beam was monitored by the photo-current measurement in an NO ionization cell located behind the reaction cell. The resonant LIF signal was detected by a photomultiplier tube (EMR, Model 5473-08-17) at right angles to both the photolysis and probe laser beams. The CN($3\Sigma^+$) and NCO($3\Sigma^+$) radicals were also detected by LIF for the CN($B^2\Sigma^--X^2\Sigma^+$) transition around 390 nm and NCO($A^2\Sigma^--X^2\Pi$) transition around 440 nm, respectively, using the dye laser (Lambda Physik, FL3002) pumped by the XeCl excimer laser (Lambda, Lextra-50). The UV (390 nm) or VIS (440 nm) probe laser beam was introduced into the reaction cell in a direction counter-propagated to the photolysis laser beam. The intensities of the UV and VIS beams were monitored by a photodiode. LIF signals of CN($B^2\Sigma-X^2\Sigma$) and NCO($A-X$) transitions were detected by a dynode-gated photomultiplier tube (Hamamatsu, 1P28 and C1392-56) with a high speed amplifier (Hamamatsu C5594) to separate the resonance fluorescence and the strong laser scattering.

3. Results

3.1. Total rate constant for the removal of O($^3D$)

The temporal profiles of O($^3D$) and O($^3P$) were recorded in order to measure the total reaction rate constant. Fig. 1 shows the temporal profile of O($^3D$) obtained when the pressures of $N_2O$, CF$_3$CN and He are 2.3, 23 and 455 mTorr, respectively. Fig. 2 shows the temporal profile of O($^3P$) obtained when the pressures of $N_2O$, CF$_3$CN and He are 9, 91 and 1900 mTorr, respectively. The intensities of the UV and VIS beams were limited by a certain concentration of $N_2O$ needed in order to see the signal and therefore they needed high concentrations of CF$_3$CN to ensure the dominance of the target reaction. The diffusion of the O($^3D$)

\[
k = k_{N_2O}[N_2O] + k_{CF_3CN}[CF_3CN],
\]

where $k_{N_2O}$ and $k_{CF_3CN}$ are the rate constants for the removal of O($^3D$) by the reactants $N_2O$ and CF$_3$CN, respectively, and [N$_2$O] and [CF$_3$CN] are the concentrations of $N_2O$ and CF$_3$CN, respectively. The removal by interaction with $N_2O$ can be estimated according to the concentrations and the reported rate constant of $k_{N_2O} = 1.6 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Under the present conditions, the ratio of the contributions of $k_{N_2O}[N_2O]$ to $k_{CF_3CN}[CF_3CN]$ were less than 0.1. The plots of the reduced decay rate, i.e. $k = k_{CF_3CN}$, were measured at different pressures in the reaction cell, because they are the function of reactant concentrations, i.e.

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k = k_{N_2O}[N_2O] + k_{CF_3CN}[CF_3CN],
\]

where $k_{N_2O}$ and $k_{CF_3CN}$ are the rate constants for the removal of O($^3D$) by the reactants $N_2O$ and CF$_3$CN, respectively, and [N$_2$O] and [CF$_3$CN] are the concentrations of $N_2O$ and CF$_3$CN, respectively. The removal by interaction with $N_2O$ can be estimated according to the concentrations and the reported rate constant of $k_{N_2O} = 1.6 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Under the present conditions, the ratio of the contributions of $k_{N_2O}[N_2O]$ to $k_{CF_3CN}[CF_3CN]$ were less than 0.1. The plots of the reduced decay rate, i.e. $k = k_{N_2O}[N_2O]$, were measured at different pressures in the reaction cell, because they are the function of reactant concentrations, i.e.

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\[
k = k_{N_2O}[N_2O] + k_{CF_3CN}[CF_3CN],
\]
3.2. Quantum yield for the electronic quenching of O(1D)

Since in the reaction with N₂, the O(1D) atom is quenched to O(3P) [eqn. (9)] with unit efficiency,¹ the asymptotic signal intensity measured in the reaction O(1D) + CF₃CN can be normalized by comparison with that in the reaction O(1D) + N₂ under the same initial concentration of O(1D). The ratio obtained by this comparison is the quantum yield, ϕₑ, for the electronic quenching of O(1D). The O(3P) signal intensities for O(1D) + CF₃CN and O(1D) + N₂ were compared at a delay of 15 μs when the O(3P) signals reached plateau levels and the reactions were completed. In the ϕₑ measurements, the partial pressures of CF₃CN and N₂ were determined so that the rise rates of the O(3P) signals had the almost identical values between the O(1D) + CF₃CN and O(1D) + N₂ reaction systems. The pressures of CF₃CN and N₂ were 72 and 360 mTorr, and the total pressure with the He buffer gas was 2 Torr. The rise time of the O(3P) signals was about 0.3 μs⁻¹. Since the pressure of He buffer gas was 5 times higher than those of reactants and hot atoms effects should be negligibly small, the value of ϕₑ measured thus was 0.14 ± 0.02, then the quenching rate constant, kₑ = k₁CF₃CN ϕₑ, is calculated to be (1.8 ± 0.4) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The uncertainty of ϕₑ is estimated from the standard deviation (1σ) of five measurements and systematic errors.

3.3. CN(X Σ⁺) formation

The CN(X Σ⁺) radical products were observed in the reaction of O(1D) with CF₃CN. Fig. 4 shows the LIF excitation spectrum of the CN(B Σ⁺ – X Σ⁺) transition measured in the present reaction process at the delay time of 15 μs. The pressures of CF₃CN and N₂O were 45 and 10 mTorr, respectively, and the total pressure was 1 Torr with He buffer gas. The temporal profile of CN(X) with the excitation laser wavelength fixed at the R(5) line of the B-X 0–0 transition is shown in Fig. 5. The simulation spectrum in the upper part of Fig. 4 indicates that the CN(X) radicals are rotationally relaxed (Tₚ₀ = 300 K) but still vibrationally excited (Tᵥ₀ = 3000 K) at a delay of 15 μs. The LIF spectrum of CN in Fig. 4 was taken in the plateau region of the time profile as shown in Fig. 5. The rotational relaxation rate should be faster than 1 μs⁻¹ at the total pressure of 1 Torr. Therefore, the rise of the time profile shown in Fig. 5 reflects the reactive formation rate of the CN(X) radicals. The rise rate of this profile, i.e. 0.33 ± 0.07 μs⁻¹, is consistent with the O(1D) decay rate of 0.26 ± 0.04 μs⁻¹ which is estimated from the reaction rates of O(1D) + CF₃CN and O(1D) + N₂O under the experimental conditions of Fig. 5. This suggests that the CN(X) radicals are produced by the direct reaction between O(1D) and CF₃CN, eqn. (7). Because no standard value of the quantum yield for the

Table 1 Total rate constants for the removal of O(1D), kₑ, quantum yields for the electronic quenching of O(1D), ϕₑ, and calculated rate constants for the electronic quenching, kₑ = ϕₑ kₑ total, at room temperature

<table>
<thead>
<tr>
<th>Substance</th>
<th>kₑ total/10⁻¹¹ cm³ molecule⁻¹ s⁻¹</th>
<th>ϕₑ</th>
<th>kₑ/10⁻¹¹ cm³ molecule⁻¹ s⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃CN</td>
<td>13 ± 2</td>
<td>0.14 ± 0.02</td>
<td>1.8 ± 0.4</td>
<td>This work</td>
</tr>
<tr>
<td>CF₃Cl</td>
<td>8.7</td>
<td>0.16 ± 0.05</td>
<td>1.4 ± 0.5</td>
<td>11, 5</td>
</tr>
<tr>
<td>N₂</td>
<td>2.6</td>
<td>1</td>
<td>2.6</td>
<td>11</td>
</tr>
</tbody>
</table>
CN(X) formation in the reaction of O(1D) has been determined, the branching ratio for this reaction pathway of eqn. (7) was not measured.

3.4. NCO(X 2Π) formation

Fig. 6 shows the LIF excitation spectrum of the NCO(A 3Σ+ − X 2Π) transition measured at a delay time of 100 μs after the irradiation of 193 nm laser pulse to the N2O + CF3CN gas mixture in the cell. The NCO(X 2Π) and NCO(A 3Σ+) radicals were not observed in the reaction of O(1D) with CF3CN on the same time scale as the production of O(3P) and CN(X) productions. The temporal profile of NCO(X) in the vibrationally ground state was measured as shown in Fig. 7. No significant signals of the vibrationally excited NCO(X) were detected in the present study. The NCO(X 2Πγ) and NCO(X 2Πα) radicals were detected by LIF signal at the Q1 and P2 band-heads of the A 3Σ+ − X 2Π transition, respectively. The LIF signal intensity did not reach an asymptotic value until the delay time of ca. 100 μs for a CF3CN pressure of 45 mTorr. This temporal profile was almost independent of the N2O concentration. Since this time scale is much larger than that of production rates of O(3P) and CN(X), the NCO(X) radical is not formed by the primary process of O(1D) + CF3CN.

4. Discussion

4.1. Electronic quenching process

The CF3CN molecule was used as a surrogate for CF3Cl. In the case of the reaction between CF3Cl and O(1D), it is supposed that the approach of O(1D) toward the F end of CF3Cl is not effective in the quenching process. That is suggested by the fact that the CF4 molecule is quite inert to quenching of O(1D). The quenching rate constant for CF4 is 2 × 10−14 cm3 molecule−1 s−1. Addison has suggested that the attractive interaction is effective between the vacant p-orbital of O(1D) and the lone-pair on the Cl atom end. On the other hand, molecular orbitals for the CN end in the CF3CN molecule are similar to those of N2 molecule by which the electronic quenching process of O(1D) is well known. The interaction of O(1D) with the CN end is expected to be strong enough to form stable CF3CNO species as well as that from the interaction of O(1D) with N2 forms the N2O molecule. The quenching rate constants of O(1D) by the reactants CF3CN, CF3Cl and N2 are summarized in Table 1. In the mechanism of quenching process by N2, the reaction proceeds via the collision complex N2O as an intermediate. The O(1D) atom approaches the N2 molecule on the potential energy surface (PES) of N2O(A′) leading from N2O(X 1Σg−) to N2O(X 1Σg−) + O(3P). This singlet PES crosses the triplet PESs of N2O(A′) and N2O(A′) to form the N2O(X 1Σg−) and O(3P) products at an N−O distance of ca. 0.19 nm. The collision complex can decompose to N2 + O(3P) through the crossing seam between these singlet and triplet PESs.

In the present case of the quenching process by CF3CN, the O(1D) atom can approach the N end on the singlet PES leading to CF3CNO(S1g). The triplet PES of CF3CNO(T1) correlating to CF3CN + O(3P) intersects this singlet PES. At the seam of the intersection the intersystem crossing, i.e. S1g → T1, should occur. Therefore it is proposed that the CF3CNO intermediate is formed in the quenching reaction process.

4.2. CN(X 3Σ+) production reaction

The mechanism of the similar reaction system O(1D) + HCN should provide us with useful information about the reaction O(1D) + HCN. The reaction of O(1D) with HCN has been studied by Carpenter et al.20 and Kreher et al.21 The main pathway of this reaction is

\[
\text{HCN} + \text{O(1D)} \rightarrow \text{NH} (a^1\Sigma^+) + \text{CO}(X 3\Sigma^+); \\
\Delta H = 195 \text{ kJ mol}^{-1}, \quad (11)
\]

and other dominant pathway is

\[
\text{HCN} + \text{O(1D)} \rightarrow \text{OH}(X 3\Pi) + \text{CN}(X 3\Sigma^+); \\
\Delta H = 100 \text{ kJ mol}^{-1}. \quad (12)
\]

The reaction channel of eqn. (12) can proceed through both the direct H atom elimination process by O(1D) and the insertion process forming the HOCN intermediate. Kreher et al.
suggested\textsuperscript{11} the reaction mechanism for the production of CN(X-2\Sigma^+), in which formation of the intermediates HOCN(X-1\Delta) and/or HOCN(A-1\Delta) followed by decomposition into the products OH(X-2\Pi) + CN(X-2\Sigma^+) occur by the direct insertion of O(1\Delta) into the H-C bond or the insertion process through the cyclic H-C(CNO), \textit{viz.}:

\[
\begin{array}{c}
\text{H} \quad \text{C} \quad \text{N} \\
\text{O}
\end{array}
\]

Based on the foregoing discussion, it is expected that the cyclic CF\textsubscript{3}-(CNO) intermediate, \textit{viz.}:

\[
\begin{array}{c}
\text{F}_2\text{C} \quad \text{C} \\
\text{N} \quad \text{O}
\end{array}
\]

could be formed in the reaction between O(1\Delta) and CF\textsubscript{3}CN. The highly excited vibrational energy of the cyclic intermediate CF\textsubscript{3}-(CNO) is not sufficient to cleave the C-C bond, \textit{i.e.} to produce the cyclic (CNO) radical, but is sufficient for isomerization to form CF\textsubscript{3}OCN* which dissociates to the products CF\textsubscript{3}O + CN(X-2\Sigma^+). Anyway, observing CN products in the present study, we conclude that the insertion process forming the CF\textsubscript{3}-O-(CN) intermediate occurs in the reaction of O(1\Delta) + CF\textsubscript{3}CN.

As described before, the coincidence between the CN(X) signal rise rate and the estimated reaction rate of O(1\Delta) + CF\textsubscript{3}CN suggests that the CN radicals are produced by direct reaction between O(1\Delta) and CF\textsubscript{3}CN. Another candidate for the CN(X) formation reaction is decay from the electronic excited state CN(A) produced by eqn. (7). The rate constant of the CN(A) is ca. 0.15 \mu s\textsuperscript{-1} which is much slower than the rise time of the CN(X) signal. The electronic quenching rates of CN(A) collisions with various gases were reported to be in the range (0.5 \sim 11) \times 10\textsuperscript{11} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}.\textsuperscript{12,22} However, the quenching rate of CN(A) is unknown under our experimental conditions. Thus, the possibility of the formation of CN(X) from CN(A) cannot be omitted.

\subsection*{4.3. Source of NCO(X-2\Pi) radical}

In the present reaction of CF\textsubscript{3}CN + O(1\Delta), the NCO(X-2\Pi) radical is not produced on the time scale of the reactions which produce O(3\Pi) and CN(X) productions. Carpenter \textit{et al.}\textsuperscript{20} observed LIF of NCO radicals in the reaction of O(1\Delta) + HCN. They also reported that the production process of NCO has a slow rise time and concluded that the NCO radicals were not primary products of O(1\Delta) + HCN. There are several possible processes which are responsible for the slow NCO formation. One may be a secondary reaction of the primary O(3\Pi) products, \textit{i.e.} O(3\Pi) + CF\textsubscript{3}CN, or CN products, \textit{i.e.} CN + O(1\Delta) + CN + N\textsubscript{2}O. Another is the collision-induced decomposition process of the long-lived intermediate (CF\textsubscript{3}CN-O)\textsuperscript{*} produced by the reaction of O(1\Delta) + CF\textsubscript{3}CN, \textit{i.e.}

\[
\begin{align}
\text{CF}_2\text{CN} + \text{O}(1\Delta) & \rightarrow \text{(CF}_3\text{CN-O)}^*, \\
(\text{CF}_3\text{CN-O})^* + \text{CF}_3\text{CN} & \rightarrow \text{CF}_2\text{CN} + \text{CF}_3 + \text{NCO}(X-2\Pi).
\end{align}
\]

The reaction of O(3\Pi) is expected to be slow, since the rate constant of the similar reaction,

\[
\text{HCN} + \text{O}(3\Pi) \rightarrow \text{Products,}
\]

is very slow, \textit{i.e.} \( k = 1.5 \times 10\textsuperscript{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K.\textsuperscript{11} It was suggested that all the reaction coordinates of HCN + O(3\Pi) have energy barriers.\textsuperscript{16,23} It was found in our experiments that the rise rates of the NCO LIF signal were not affected at all by increases in the N\textsubscript{2}O concentration, that is the concentration of O(1\Delta). This means that the NCO(X-2\Pi) product is unlikely to be formed by the reaction of the primary reaction products such as CN and O(3\Pi). Therefore, we suggest NCO formation by reactions (13) and (14). However, further experiments are required to elucidate the formation process of the NCO radical.

\section*{5. Summary}

The reaction processes of CF\textsubscript{3}CN with O(1\Delta) were studied using the time-resolved LIF detection of O(3\Pi), O(1\Delta), (CN) and NCO(X). CF\textsubscript{3}CN can be regarded as a pseudo-CF\textsubscript{3}Cl molecule. The total rate constant between O(1\Delta) and CF\textsubscript{3}CN was measured to be (1.3 \pm 0.2) \times 10\textsuperscript{-10} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at room temperature. This value is 1.5 times faster than the rate constant for the reaction of CF\textsubscript{3}Cl with O(1\Delta). The quantum yield of the electronic quenching process, \( \phi_q \) was determined by comparison with the reaction of N\textsubscript{2} + O(1\Delta). The value of \( \phi_q \) was measured to be 0.14 \pm 0.02 for O(1\Delta) + CF\textsubscript{3}CN, which is almost identical with that for O(1\Delta) + CF\textsubscript{3}Cl. The CN radical was observed as a primary product in the reaction of O(1\Delta) + CF\textsubscript{3}CN. The insertion process forming the CF\textsubscript{3}-O-(CN) intermediate may occur in this reaction, which results in the formation of CN. Since the rise rates of the LIF signal of the NCO(X-2\Pi) radical were much slower than the total reaction rates of O(1\Delta) + CF\textsubscript{3}CN, it is concluded that the NCO(X-2\Pi) radical is not a primary product.

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