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Kyoto University
Direct observation and reactions of Cl₃ radical

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The broad absorption of Cl₃ radical was observed between 1150 and 1350 nm using cavity ring-down spectroscopy at 213–265 K and 50–200 Torr with He, N₂, Ar, or SF₆ diluents. The absorption intensity of Cl₃ increased at lower temperature and higher pressure. SF₆ was the most efficient diluent gas. The temperature dependent equilibrium constants for Cl₃ formation from Cl+Cl₂ were theoretically calculated at the MP4SDQ/6-311+G(d) level. Observed decay time profiles of Cl₃ and the pressure dependence of Cl₃ formation are explained by the equilibrium reaction and a decay reaction of Cl+Cl₃.


INTRODUCTION

Trihalogens have been proposed to explain halogen atom recombination reactions.1–4 Crossbeam scattering experiments by Lee and co-workers5–8 suggested the existence of bound trihalogens in the gas phase reactions. Fluorine containing trihalogens were observed and characterized in rare gas matrices using infrared (IR) absorption and Raman spectroscopy.9–13 Hutton and Wright3 proposed a formation mechanism of trichloride radical Cl₃ from Cl atom recombination in the presence of Cl₂,

\[ \text{Cl} + \text{Cl}_2 + M \rightarrow \text{Cl}_3 + M, \]  
\[ \text{Cl} + \text{Cl}_2 + M \rightarrow \text{Cl}_2 + \text{Cl} + M, \]  
\[ \text{Cl}_3 + \text{Cl} \rightarrow 2\text{Cl}_2. \]

Existence of Cl₃ was reported experimentally2–4,14–16 and theoretically.17–23 Emission spectra attributable to Cl₃ were observed by Kawasaki et al.14 and Wright et al.15 These data were in reasonable agreement with each other. An IR spectrum of Cl₃ in a Kr matrix was reported by Nelson and Pimentel.24 However, Wight et al.25 indicated that the species they observed was not Cl₃ radical but Cl₃ anion.

An ab initio study by Kaledin et al.23 showed that the structure in the global minimum of the Cl₃ radical is linear \( ^2 \Sigma_g^+ \) with a bond dissociation energy \( D_b(\text{Cl}_2\text{−Cl}) \) of 280 cm⁻¹. Kaledin et al.23 reported that the energies and transition moments of the low-lying excited states are not consistent with the experimental electronic ultraviolet and visible spectra that have been assigned to Cl₃. They also suggested that the low-lying doublet excited state is a bound symmetric \( ^2 \Pi_g \) state, and its potential minimum lies about 8700 cm⁻¹ above the van der Waals minimum. They concluded that the \( A−X \) transition is fully allowed.

The present study is the first report on the Cl₃ absorption in the near-IR region. Time-resolved cavity ring-down spectroscopy26–29 (CRDS) was used to search for the electronic transition of Cl₃. We obtained theoretically the equilibrium constants for reactions (1a) and (1b) and experimentally the rate constants for reactions (1a), (1b), and (2).

EXPERIMENT

The CRDS apparatus used in the present study has been described in detail elsewhere.30,31 Cl atoms were generated by photodissociation of Cl₂ at 355 nm [Nd³⁺:YAG (yttrium aluminum garnet) laser, Spectra Physics, GCR-250]. A typical laser intensity was 80±5 mJ pulse⁻¹. The output from an optical parametric oscillation laser (Spectra-Physics, MOP-SL, 0.2 cm⁻¹ spectral resolution) was used to obtain the desired probe wavelengths in the near-IR region. A dye laser (Lambda Physik ScanMate pumped by the second harmonic output from a Nd³⁺:YAG laser, Quantel, Brilliant β) with coumarin dye (480 nm or 440 nm) was also used to probe Cl₃ in the visible region. Cavity ring-down mirrors (II-VI or Research Electro Optics, 7.8 mm diameter and 1 m curvature) had a specified maximum reflectivity of >0.999 and were mounted 1.04 m apart. Light leaking from the end mirror was detected by a photodiode (Thorlabs, PDA255) or a photomultiplier tube (Hamamatsu Photonics, R212UH) through a proper cutoff filter. The ring-down signal of the light intensity was sampled by a digitizing oscilloscope (Tektronix, TDS-7414L, 500 MHz, 8-bit resolution) and recorded in a personal computer (PC).

The decay of the leaked light intensity from the end mirror is represented by Eq. (3).
where $I_0$ and $I(t)$ are the light intensities at times 0 and $t$, respectively. $\tau_0$ is the cavity ring-down time without photolysis laser light (about 1.5 $\mu$s at 1300 nm and 1.5 $\mu$s at 440 nm), $L_R$ the length of the reaction region (0.40±0.01 m), $L$ the cavity length (1.04 m), $\tau$ the measured cavity ring-down time with photolysis laser light, and $c$ the velocity of light. $n$ and $\sigma$ are the concentration and absorption cross section of the species of interest, respectively. Each ring-down trace was digitized with a time resolution of 20 ns. The digitized traces were transferred to the PC and averaged over 32 or 64 runs to calculate the ring-down rate $\tau^{-1}$. The validity of using cavity ring-down spectroscopy for kinetic studies derives from the fact that the lifetimes of the products generated by photolysis are much longer than the associated cavity ring-down times.29

The reaction cell consisted of a Pyrex glass tube (21 mm inner diameter), which was evacuated by a combination of an oil rotary pump and a mechanical booster pump. The temperature of the gas flow region was controlled over the range 213–298 K by circulation of ethanol with a cooling circulator (Thomas, TRL 70 SLP). The difference between the temperature of the sample gas at the entrance and exit of the flow region was <1 K. Since the reaction region was located in the center 40 cm of the glass reactor, the temperature was uniform in the interaction region. The pressure in the cell was monitored by an absolute pressure gauge. Temperature ring-down times.29

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We also checked the possibility of formation of aerosols from photolysis of chlorine gas. A mixture of 4.5 \times 10^{16} \text{ molecule cm}^{-3} of Cl_2 and 100 Torr of N_2 was introduced into the reaction cell in batch system and photolysed at 355 nm (120 mJ pulse$^{-1}$, 10 Hz) for 15–30 s at 213 K. We could not find any difference between before and after photolysis in the ring-down signal. These results indicate that aerosols which survive for longer than seconds were not formed in our experimental conditions. Considering all of these results, we conclude that the absorption appearing in the Cl_2/N_2 mixture with 355 nm irradiation is attributed to the reaction product Cl_3.

We also attempted to detect transient photoabsorption at 430–450 and 460–500 nm. Chlorine concentration [Cl_2] was varied in the range from 9.0 to 11003 molecule cm$^{-3}$ for these experiments in 100 Torr total pressure of N_2 diluent at 213 K. Unfortunately, we could not obtain the quantitative experimental evidence of the absorption of Cl_3 at these wavelength regions because of the significant absorption of Cl_2 itself.

We tried to check whether the time profiles of the absorption intensity of Cl_3 will change or not when we added CH_4 to the reaction cell.
Cl$_3$ + CH$_4$ → products. \hspace{1cm} (4)

No decay change of Cl$_3$ was observed with \((2.0–5.3)\times10^{15}\) molecule cm$^{-3}$ of CH$_4$ at 219 K and 100 Torr total pressure of N$_2$ diluent as shown in Fig. 7. As described below, the decay is mostly governed by the diffusion rate of Cl$_3$ from the detection region and the equilibrium rates. Since there was no change in the Cl$_3$ decay, the reaction rate of Cl$_3$ with CH$_4$ is much smaller than the diffusion rate.

Theoretical calculations

All \textit{ab initio} calculations were carried out using the Gaussian 03 program package.\cite{4} The structures and harmonic vibrational frequencies of Cl$_3$ and Cl$_2$ were calculated at the MP4SDQ/6-311+G(d) level. Two structural forms of the Cl$_3$ radical, linear and bent forms, are obtained by the geometry optimization. The optimized parameters are given in Table II. The structural parameters of the linear form of Cl$_3$ radical are calculated to be \(r_1=2.0374\ \text{Å}, \ r_2=3.5988\ \text{Å}\), and \(\theta=180.0^\circ\), where \(r_1\) and \(r_2\) indicate short and long Cl–Cl bond lengths of the Cl$_3$ radical, respectively, and \(\theta\) means the angle of Cl–Cl–Cl. In the case of the bent form, the optimized parameters are \(r_1=2.0365\ \text{Å}, \ r_2=3.4962\ \text{Å}\), and \(\theta=94.7^\circ\). In both forms, one of the Cl–Cl distances of the Cl$_3$ radical (\(r_2\)) is significantly longer than the other (\(r_1\)), indicating that the Cl$_3$ radicals exist as a van der Waals complexes composed of a Cl$_2$ molecule and Cl atom, as predicted by Kaledin \textit{et al.}\cite{5} Harmonic vibrational frequencies of the Cl$_3$ radicals are given in Table III. The frequencies are calculated to be 528, 41, and 25 \text{cm}^{-1} for the linear form and 530, 50, and 22 \text{cm}^{-1} for the bent form. The zero-point energies (ZPEs) are 0.89 kcal/mol for the linear form and 0.86 kcal/mol for the bent form. All vibrational frequencies show positive values, meaning that the optimized structures of the Cl$_3$ radicals are located in local minima. The binding energy of the Cl atom to the Cl$_2$ molecule is calculated to be 350 \text{cm}^{-1} (without ZPE correction) and 300 \text{cm}^{-1} (including ZPE correction) for the linear form and 370 \text{cm}^{-1} (without ZPE correction) and 344 \text{cm}^{-1} (including ZPE correction) for the bent form.

The equilibrium constant of the Cl$_3$ formation reaction \([1a) \text{ and } (1b)]\) is estimated by

\[
K = \frac{Q(Cl_3)}{Q(Cl)_2} \times \exp\left(-\frac{\Delta U}{k_BT}\right),
\]

where \(Q's\) are the molecular partition functions and \(\Delta U\) is the formation energy of Cl$_3$ expressed by Eq. (5). The harmonic approximation is assumed in the calculation of vibrational frequencies. The total partition function \(Q\) is expressed on the product of vibrational, rotational, translational, and electronic partition functions. To estimate the rotational partition function, classical behavior for the rotation of Cl$_3$ is assumed. The equilibrium constants at 213 K for the linear form are calculated to be \(2.49 \times 10^{-20}\) cm$^3$ molecule$^{-1}$ at the MP4SDQ/6-311+G(d) level. The temperature dependence of \(K\) is given in Fig. 8. The equilibrium constant decreases with increasing temperature; at 298 K, \(K=1.38 \times 10^{-20}\) cm$^3$ molecule$^{-1}$. The equilibrium constant for the bent form is calculated to be \(K=1.12 \times 10^{-19}\) cm$^3$ molecule$^{-1}$ at 213 K, which is about four times larger than that of the linear form. Similar calculations were carried out at the MP2/6-311+ +G(d,p) level. The equilibrium constants for the linear and bent forms are calculated to be \(K=2.65 \times 10^{-20}\) and \(1.13 \times 10^{-19}\) cm$^3$ molecule$^{-1}$ at 213 K. Furthermore, the equilibrium constant at 213 K is calculated using anharmonic frequencies of the Cl$_3$ radical obtained at the MP2/6-311+ +G(d,p) level. The values for the linear and bent forms are calculated to be \(K(\text{anharmonic})=2.70 \times 10^{-20}\) and \(2.15 \times 10^{-19}\) cm$^3$ molecule$^{-1}$ at 213 K, respectively. Contribution of anharmonic effect increases the equilibrium constants for the bent form.

Hutton and Wright experimentally determined the lower limit value of the equilibrium constant, \(K>2.0 \times 10^{-22}\) cm$^3$ molecule$^{-1}\). Our present data are consistent with that of Hutton and Wright. Kaledin \textit{et al.} predicted that

\begin{table}[h]
\centering
\caption{Optimized parameters of Cl$_3$ calculated at the MP4SDQ/6-311+G(d) level. Bond lengths and angles are in angstroms and in degrees, respectively.}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & MP4SDQ/6-311+G(d) & & MR-SD-Cl$^a$ & & \\
 & Linear & Bent & Linear & Bent & \\
\hline
\(r_1\) & 2.0374 & 2.0365 & 2.0638 & 2.0638 & \\
\(r_2\) & 3.5988 & 3.4962 & 3.5720 & 3.4982 & \\
\(\theta\) & 180.0 & 94.7 & 180.0 & 95.8 & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Harmonic vibrational frequencies of Cl$_3$ (in cm$^{-1}$) and zero-point energies (ZPEs in kcal/mol) calculated at the MP4SDQ/6-311+G(d) level.}
\begin{tabular}{|c|c|c|}
\hline
Mode & Assignment & Cl$_3$ (linear) & Cl$_3$ (bent) \\
\hline
\(v_1\) & Cl–Cl stretching & 528$^a$ & 530$^a$ \\
\(v_2\) & Cl–Cl stretching & 41 & 50 \\
\(v_3\) & Bending & 25$^b$ & 22 \\
Zero-point energy & & 0.89 & 0.86 \\
\hline
$^a$The Cl–Cl stretching mode of free Cl$_2$ is calculated to be 529.0 \text{cm}^{-1} (ZPE=0.76 \text{kcal/mol}).
$^b$Doubly degenerated mode (\(\pi\)-bending mode).
\end{tabular}
\end{table}
the equilibrium constant at 295 K is $6.7 \times 10^{-23}$ cm$^3$ molecule$^{-1}$, which is significantly smaller than the experimental value. The difference may be caused by underestimation of $-\Delta U$ in their calculation because the Cl–Cl bond length of the Cl$_3$ radical was fixed in the geometry optimization. If we used the $K$ value reported by Kaledin et al., the concentration of Cl$_3$ should become too low to be detected experimentally.

**DISCUSSION**

**Phototransition**

Previous experimental observations of emission of Cl$_3$ were reported by two groups. Kawasaki et al. reported the excitation spectrum of Cl$_3$ at 415–427 nm with the use of laser induced fluorescence (LIF). Wright et al. also observed a broadband emission in the 370–440 nm regions at 400 Torr total pressure of N$_2$ diluent. These results support the existence of Cl$_3$. The present results show a new band at 1150–1350 nm.

Kaledin et al. reported that the low-lying doublet excited state is a bound linear symmetric $^1Σ^+_g$ state (an excited state complex), and its potential minimum lies about 8700 cm$^{-1}$ above the van der Waals minimum. The vertical electronic transition point is a further 9000 cm$^{-1}$ higher in energy than the potential minimum of the excited state complex. Namely, the vertical excitation energy of Cl$_3$ is calculated to be 17 700 cm$^{-1}$ from the van der Waals minimum. However, the van der Waals complex has a wide Franck-Condon region due to its structural flexibility, including the bent structure. Furthermore, the energy level of the excited state complex is significantly low (8700 cm$^{-1}$), while the relaxation energy from the vertical point to the excited state complex is large (9000 cm$^{-1}$). Therefore, absorption spectrum of Cl$_3$ would appear in the energy region 8700–17700 cm$^{-1}$. This excitation energy is consistent with that observed in the present experiment (7400–8710 cm$^{-1}$). Kaledin et al. also reported that the $A$-X transition is fully allowed. The absorption spectrum of Cl$_3$ observed in the present study could be assigned to be the $A$-$X$ transition from the wide Franck-Condon region of the van der Waals complex.

**Reaction mechanism of Cl$_3$ formation and decay**

As shown in Fig. 6, Cl$_3$ formation has a negative temperature dependence. These results are similar to that of ClOO formation, which is considered as a weak van der Waals complex with the bond dissociation energy of 1640 cm$^{-1}$. Assuming only the equilibrium reactions (1a) and (1b), the following equation is obtained:

$$[\text{Cl}_3]_{eq} = K[\text{Cl}_2][\text{Cl}]_0/(1 + K[\text{Cl}_2]).$$

(6)

The solid curve in Fig. 4 is a best-fit curve for Eq. (6), which well approximates the concentration dependence of Cl$_3$ on [Cl]. However, the reaction of Cl$_3$ with Cl should be included to determine the concentration of Cl$_3$ correctly. The rate constants of reactions (1a) and (2) were obtained only from the decay time profiles of the absorption intensity of Cl$_3$ and the buffer pressure dependence of the absorption intensity of Cl$_3$ in chemical simulations that were performed using the IBM chemical kinetics simulator software package and the reactions listed in Table IV. Simulation conditions were as follows: [Cl$_2$]$_0$=9.3$\times$10$^{16}$ molecule cm$^{-3}$, [Cl]$_0$ =1.0$\times$10$^{15}$ molecule cm$^{-3}$, photolysis laser intensity of 73 mJ pulse$^{-1}$, and 100 Torr total pressure of N$_2$ diluent at 213 K. [Cl]$_0$ was determined using the laser intensity and [Cl]$_0$. Using the theoretically obtained $K=2.7$ $\times$ 10$^{-20}$ molecule cm$^{-3}$ for the linear Cl$_3$, the best fit produces the values $k_{(1a)}=(1.5\pm0.6)\times10^{-14}$ cm$^3$ molecule$^{-1}$, $k_{(1b)}=(5.7\pm2.3)\times10^{-6}$ s$^{-1}$, $k_{(2)}=(2.5\pm4)\times10^{-10}$ cm$^{-1}$ molecule$^{-1}$ s$^{-1}$, and $k_d=2500$ s$^{-1}$ as shown in Fig. 2. The decay shapes of Cl$_3$ were mostly sensitive to $k_{(1a)}$, $k_{(1b)}$, and $k_d$. Since $k_{(2)}$ was not sensitive, $k_{(2)}$ was determined from the pressure dependence as follows. With $K=9.9\times10^{-20}$ molecule cm$^{-3}$ for the bent Cl$_3$, the simulated curve was essentially the same using the kinetic parameters of Table IV.

A simulation with $k_{(1a)}$, $k_{(1b)}$, $k_{(2)}$, and $k_d$ included was performed for the absorption intensity of Cl$_3$ as a function of Cl$_3$ concentration. As shown in Fig. 4, the results are essentially the same as approximated by a simple equilibrium Eq. (6).

Figure 5 shows the buffer pressure dependence of the absorption intensity of Cl$_3$. The production of Cl$_3$ increased experimentally with total pressure. A model calculation with reactions (1a), (1b), and (2) explains the tendency of this pressure dependence for both linear and bent structures of Cl$_3$. The present results show a new band at 370–440 nm regions at 400 Torr total pressure of N$_2$ diluent. Therefore, absorption spectrum of Cl$_3$ observed in the present study could be assigned to be the $A$-$X$ transition from the wide Franck-Condon region of the van der Waals complex.
Cl\textsubscript{3} as shown by the curves in Fig. 5. We used the chemical kinetic simulator software and the rate constants listed in Table IV. Hutton and Wright suggested the upper limit value of $k_{(2)}$ to be $2.8 \times 10^{-10}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at 298 K.\textsuperscript{3} Although the experimental data have large error bars, it is safe to say that $k_{(2)}$ is estimated to be in the order of the collisional cross section or $(2.5-4) \times 10^{-10}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}.

There is another possibility that Cl\textsubscript{3} is formed by the “radical-complex” mechanism that includes the reactions of Cl+M $\rightarrow$ ClM and ClM+Cl\textsubscript{2} $\rightarrow$ Cl\textsubscript{3}+M. This mechanism is similar to what was suggested by Troe for the O\textsubscript{2} and ClO\textsubscript{2} formation from corresponding atom and molecule under higher pressure experimental conditions up to 1000 bars.\textsuperscript{36} In the present work, we could not confirm the possibility of this radical-complex mechanism under the pressure range up to one quarter of a bar.

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