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# Negative Chemical Ionization Mass Spectrometric Study on the Dissociative Electron Attachment Process of Chlorofluorocarbons and Bromofluorocarbons

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The formation of a negative ion from chlorofluorocarbons($CCl_4$, $Cl_2FC-CClF_2$, $Cl_3C-CF_3$, $Cl_2FC-CCl_2F$, $Cl_3C-CClF_2$, $C_2Cl_5F$, $C_2Cl_6$, $C_2HCl_3$, $C_2Cl_4$) or bromofluorocarbons($Br_2FC-CF_3$, $BrF_2C-CBrF_2$, $Br_2FC-CBrF_2$, $CBr_3F$) was studied using negative chemical ionization mass spectrometry. The halide ion was mainly observed for all molecules. Among cholorofluoroethanes or bromofluoroethanes, a molecule with more chlorine or bromine atoms shows a higher intensity of $Cl^-$ or $Br^-$. For $C_2Cl_5F$, $C_2Cl_6$, $BrF_2C-CBrF_2$, $Br_2FC-CBrF_2$, and $CBr_3F$, the negative ions of the halogen molecule were also observed. Except for $CBr_3F$, the ion would be produced by dissociative electron attachment.

Halocarbons are known for their high electron affinity.[1] Many studies about electron attachment to halocarbons have been carried out in both theoretical and experimental aspects. Electron attachment is an important and fundamental reaction process in a gas and the condensed phase. For example, the electron swarm method (ES),[2] electron cyclotron resonance,[3] the flowing after glow Langmuir probe method (FALP),[4] threshold photoionization,[5] the high Rydberg atom beam method,[6] the pulse-radiolysis microwave cavity technique (PRMC)[7] and so on have been used to measure the attachment rate of a thermalized electron. Using an electron-capture detector (GC–ECD), Wentworth et al. studied the temperature dependence of electron attachment.[8] For these methods, using special instruments or changing the instruments' setting is necessary. Recently, Wentworth et al. have studied bound excited states of the anions of chloroethylene by negative chemical ionization mass spectrometry (NCIMS).[9,10] Only a quadrupole mass spectrometer with the negative chemical ionization method is necessary to study the electron-attachment reaction for the NCIMS method.

The main reaction of thermalized electrons toward halocarbons is to break carbon halogen bonds to give radicals and halide ions. For some halogenated molecules, $X_2^-$ (X is a halogen atom) is also observed. Especially, $Br_2^-$ has been detected in some studies. DeCorpo and Franklin found that $Br_2^-$ was produced from $CBr_4$ and $I_2^-$ from $Cl_4$ and $CHI_3$ when these molecules were irradiated with thermal electrons.[11] Alajajian et al. observed that $Br_2^-$ was produced from $CF_2Br_2$ using the krypton photoionization method.[12] Smith et al. found that $Br_2^-$ was produced from $CF_2Br_2$, $CBr_3F$, $BrF_2C-CBrF_2$, and $BrCH_2-CH_2Br$ using the FALP method.[13] Zook et al. observed that $Br_2^-$ was produced from dibrominated hydro- and fluoro- carbons by pulsed electron-beam high-pressure mass spectrometry with a buffer gas.[14] Compared with extensive studies of the formation of $Br_2^-$, there have been few reports concerning $Cl_2^-$ formation. The formation and dissociative mechanisms of molecular negative ions seem to be different depending on the kinds of molecules. It is necessary to study the negative-ion formation of chlorofluoroethanes and bromofluoroethanes, depending on the number of chlorine or bromine atoms.

In this paper, we discuss the formation of negative ions of $Cl_2FC-CClF_2$, $Cl_3C-CF_3$, $Cl_2FC-CCl_2F$, $Cl_3C-CClF_2$, $C_2Cl_5F$, $C_2Cl_6$, $Br_2FC-CF_3$, $BrF_2C-CBrF_2$, $Br_2FC-CBrF_2$, and $CBr_3F$ based on the NCIMS technique using isobutane for the reagent gas. We also consider the formation of negative ions of $CCl_4$, $C_2HCl_3$, and $C_2Cl_4$ for a comparison with Wentworth's result. Even though the instrument was constructed for analytical use, we could observe product negative ions and their temperature dependence. To explain the experimental results, we also calculated the atomic-charge distribution of anions.

## Experimental

$Cl_2FC-CClF_2$ (Tokyo-Kasei, purity > 99%), $Cl_3C-CF_3$ (Tokyo-Kasei, purity > 99%), $Cl_2FC-CCl_2F$ (Tokyo-Kasei, purity > 85%), $Cl_3C-CClF_2$ (Aldrich, purity 97%), $C_2Cl_5F$ (PCR incorporated, purity > 97%), $C_2Cl_6$ (Tokyo-Kasei, purity > 99%), $CCl_4$ (Tokyo-Kasei, purity > 99.5%), $BrF_2C-CBrF_2$ (Tokyo-Kasei, purity > 99%), $Br_2FC-CF_3$ (PCR incorporated, purity > 98%), $Br_2FC-CBrF_2$ (PCR incorporated, purity > 98%), $CBr_3F$ (Aldrich, purity 99%), $C_2HCl_3$ (Wako-Junyaku, purity > 98%), $C_2Cl_4$ (Wako-Junyaku, purity > 99%), and hexane (Wako-Junyaku, purity > 99%) were used as received.

Chemical ionization mass spectra were taken with a Shimadzu QP1100EX GC-MS equipped for negative chemical ionization. Negative chemical ionization has two steps. First, electrons provided from the filament are thermalized by collisions with the reagent gas. The next step has two cases. One case: Thermalized electrons are captured by the reagent gas to form an anion of reagent gas, which reacts with the sample gas. When the electron affinity of the sample gas is higher than that of the reagent gas, electrons transfer to the sample gas. Another case: Thermalized electrons are captured by the sample gas directly if there exists enough sample gas and its electron affinity is higher. Wentworth et al. used $CO_2$ for the reagent gas. The electron affinity of $CO_2$ is lower. In the latter case, direct electron capture occurs mainly. In this study, the reagent gas was isobutane. Isobutane has a high ability to thermalize electrons and its electron affinity is low. The latter case was also important in this study.

Figure 1 shows the ion-source apparatus. Samples are introduced from perpendicular to the paper (⊗ shows the position in Fig. 1) into the ion source through the capillary interface. Electrons, whose energy is 200 eV, are provided and then thermalized by collisions with isobutane. When electrons attach to the sample molecules, their energy distribution is not known. To confirm that most of the electrons are thermalized when they attach to a molecule, the intensity of the $Cl^-$ ion from $C_2Cl_4$, depending on the flux of isobutane, was observed. According to an electron-attachment spectra study, dissociative thermal electron attachment occurred for $C_2Cl_4$.[15] When the intensity of the dissociative $Cl^-$ ion from $C_2Cl_4$ is constantly changing with the flux of isobutane, the electrons seem to be thermalized. This result is shown in Fig. 2. Because we measured the ion intensity at the flux shown by the arrow in Fig. 2, most electrons were considered to be thermalized. The pressure under the mass analytical tube was monitored by an ion gauge at all times. The monitored pressure was $1—2\times10^{-6}$ and $2.5—3\times10^{-5}$ Torr (1 Torr = 133.322 Pa), with both the absence and presence of isobutane, respectively. The main gas in the reaction volume was isobutane, we could neglect the contribution of nitrogen or oxygen. The instrument was tuned using the NCIMS of tris(perfluorobutyl)-amine (TPFBA) at 523 K, and the condition remained unchanged throughout the measurements.

A gas chromatograph was operated in the split mode with a wide-bore capillary column to provide in-line purification of the samples. Helium was used for the carrier gas. Samples were diluted with hexane in 1/2000—1/50 mol% and 0.4—1.5 µl of them were injected. A single peak from the sample was observed in the chromatogram with no extraneous peaks or interferences. The temperature of the GC column was kept at 35 °C for $Cl_2FC–CClF_2$, $Cl_3C–CF_3$, $CCl_4$, $Cl_2FC–CCl_2F$, $Cl_3C–CClF_2$, and $C_2HCl_3$, 50 °C for $C_2Cl_4$, 60 °C for $C_2Cl_5F$, and 100 °C for $C_2Cl_6$. The peaks were observed at retention times of about 1.4, 1.4, 3.7, 5.0, 5.0, 5.9, 7.4, 9.0, and 9.2 min, respectively. Also, the temperature of the column was kept at 35 °C for $Br_2FC–CF_3$ and $BrF_2C–CBrF_2$, and 50 °C for $Br_2FC–CBrF_2$ and $CBr_3F$. The peaks were observed at about 2.2, 2.2, 4.3, and 5.2 min, respectively.

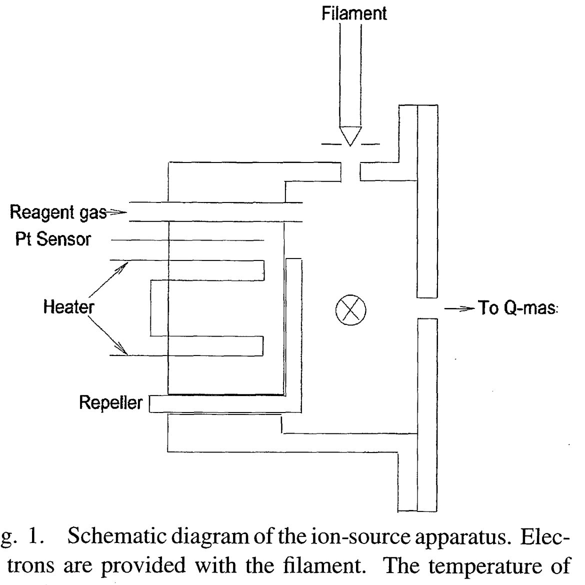

Fig. 1. Schematic diagram of the ion-source apparatus. Electrons are provided with the filament. The temperature of the ion source is measured with Pt sensor. Some electrons are corrected to the repeller to measure the concentration of electrons and the filament voltage is controlled to keep the concentration constant.

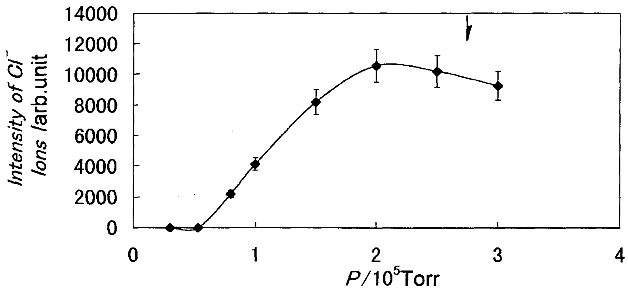

Fig. 2. The intensity of $Cl^-$ for $C_2Cl_4$ depending with pressure *P* of isobutane monitored by ion gauge. We have measured the intensity of all ions at the flux shown by the arrow.

The temperature of the ion source was controlled by computer. When the temperature was changed, the ion source was allowed to equilibrate for 30—60 min. The mass spectra were obtained via a personal computer. The ion abundance was obtained from the integrated sums of all isotopic masses of the ions.

The atomic charge distribution of anions was studied at the unrestricted Hartree–Fock (UHF) level of theory with the 6–31+G basis set for chlorofluoroethanes, and the 6–311+G basis set for bromofluoroethanes. The calculation was carried out using the Gaussian 94 program on a Silicon Graphics Indy with R4600PC.

## Results and Discussion

**Kinetics:** For a dissociative electron attachment to halocarbons, there are two cases. When a stable negative ion of the parent molecule exists, a parent molecule anion is produced ($k_1$). If the anion has sufficient energy to detach an electron, detachment will occur($k_{-1}$). If excess energy is sufficient to cleave the carbon–halogen bond, a halide ion will be produced through the precursor anion ($k_{1'}$). When the energy diagram of the parent molecule anion is repulsive, the lifetime of the parent molecule anion is too short for electron detachment and a dissociative reaction occurs immediately. It seems that a halide ion is produced directly ($k_{1*}$). Halocarbons RX (X = Cl,Br) will react with electrons as follows:

$$\mathrm{RX}+\mathrm{e}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RX}^{-*} \xrightarrow{k_{1'}} \mathrm{X}^- + \mathrm{R}, \tag{1}$$

or

$$\mathrm{RX}+\mathrm{e}^- \longrightarrow (\mathrm{RX}^{-*}) \xrightarrow{k_{1*}} \mathrm{X}^- + \mathrm{R}. \tag{1'}$$

$$\text{Negative ion } + \mathrm{P}^+ \xrightarrow{k_{\mathrm{N}'}} \text{Products}, \tag{2}$$

where $P^+$ is a positive ion.

The main observed ion was $Cl^-$ for RCl and $Br^-$ for RBr, respectively. $RX^-$ was not observed for any of the samples, except for $C_2Cl_4$. For some of the samples, $Cl_2{}^-$ or $Br_2{}^-$ was observed.

The sample gas diffuses evenly in the ion source from the capillary interface. Electrons are provided at a constant rate in the ion source at all times. We assumed a steady state treatment as for radiolysis in a cell. Reactions (1), (2) lead to the expression

$$[X^-] = \varkappa \frac{(k_1/k_{-1} \times k_1' + k_{1*})[RX][e^-]}{k_{N'}[P^+]} = \varkappa \frac{k[RX][e^-]}{k_N}, \quad (3)$$

where $k_1/k_{-1} \times k_{1'} + k_{1*} = k.$

When electrons whose energy is 200 eV are thermalized by collisions with isobutane, positive ions of isobutane are produced in high concentration. Because positive ions are provided during the measurement, we can assume that $[P^+]$ is constant and $k_{N'}[P^+] = k_N = a$ constant.

$\varkappa$ is constant, which includes the interaction volume, ion draw-out efficiency, ion lens and mass spectrometer transmission efficiencies and ion detection efficiency of the electron multiplier. The ion intensity of $X^-$ is proportional to the concentration of the sample. The proportional constant is $\varkappa k[e^-]/k_N$. If $\varkappa[e^-]/k_N$ is constant for all samples, $k$ can be estimated relatively. Because measurements are carried out with the same instrument settings, the ion lens and mass-spectrometer transmission efficiencies or ion detection efficiency could be same for all samples. However, the ion draw-out efficiency would be different for each sample, because high-energy ions would not be focused as well as low-energy ions.[12] By substituting the relationships

$$\begin{aligned}
k_1 &= A_1 T^{-1/2} \exp(-E_1/RT), \\
k_{-1} &= A_{-1} T \exp(-E_{-1}/RT), \\
k_{1'} &= A_{1'} T \exp(-E_{1'}/RT), \\
k_{1*} &= A_{1*} T^{-1/2} \exp(-E_{1*}/RT), \\
k &= \frac{A_1 T^{-1/2} \exp(-E_1/RT) \times A_{1'} T \exp(-E_{1'}/RT)}{A_{-1} T \exp(-E_{-1}/RT)} \\
&\quad + A_{1*} T^{-1/2} \exp(-E_{1*}/RT) \\
&= (A_1 \times A_{1'}/A_{-1}) T^{-1/2} \exp((-E_{-1} - E_{1'} + E_{-1})/RT) \\
&\quad + A_{1*} T^{-1/2} \exp(-E_{1*}/RT). \qquad (4)
\end{aligned}$$

If the electron concentration $[e^-]$ and ion draw-out efficiency are constant under the experimental condition, the Arrhenius parameters can be determined.

**Chlorofluorocarbons:** The concentration of the samples was 1/200 mol%, except for $C_2HCl_3$, $C_2Cl_5F$, and $C_2Cl_6$, whose concentrations were 1/40, 1/250, and 1/250 mol% respectively. The intensity of $Cl^-$ was proportional to the injection quantity of the sample (0.4—1.5 μl). The proportional constant was calculated by the least-squares method and converted to rate per $10^{-9}$ mol of the sample. The temperature was changed and the intensity of the ions was measured by the same method. Figure 3 shows an Arrhenius plot based on Eq. 4. It seems that for more chlorine atoms, the rate becomes faster. When the molecules have the same number of chlorine atoms, one of the molecules in which the chlorine atoms concentrate at one carbon atom gives a faster rate at higher temperature. At a lower temperature, the intensity of the ions produced from isomers become almost the same. It is shown that the intensity of the ions decreases slightly with increasing the temperature for chlorofluorocarbons, and the decreasing rate is smaller for the molecule in which chlorine atoms concentrate at one carbon atom. When electrons attach to a molecule and the bond length of R–Cl becomes larger than the crossing point of the potential energy surface for a neutral molecule and a negative ion, cleavage of the bond occurs. The probability for the existence of $RX^{-*}$ at the time when the bond length of R–Cl lengthens to the crossing point, that is the survival probability, is important for the production rate of dissociative ions. For some halogenated methane, the cross section for negative ion production increases with increasing temperature; this can be explained by the survival probability.[16] On the contrary, the rate for negative ion production decreases slightly with increasing temperature for $CCl_4$.[7c] This was observed in this study. For $CCl_4$ and a molecule which has many atoms, the survival probability is related to the rate of localization of excess electrons to the chlorine atom. In other words, when electrons attach to a molecule and an excess electron in $RX^{-*}$ localizes to one of the C–Cl bonds, cleavage of the bond occurs.[17] The rate of localization of excess electrons is related to the rate of formation of the halide ion. At higher temperature, excess electrons delocalize in $RX^{-*}$, which makes the rate of formation of the halide ion lower. For a molecule in which three chlorine atoms concentrate at one carbon atom, this effect seems to be smaller. In the case of $C_2Cl_4$, the parent negative ion was observed. Electron detachment occurs for $C_2Cl_4$. Compared with $C_2HCl_3$, the formation rate of the parent negative ion is greater for $C_2Cl_4$. These results are the same as Wentworth's.[9] The electron energy dependence of the cross section is different between $Cl_2FC–CClF_2$ and $Cl_3C–CF_3$, and is not observed for other chlorofluoroethanes. It is impossible to estimate the electron-attachment rate constants.

In the case of $C_2Cl_5F$ and $C_2Cl_6$, $Cl_2{}^-$ was also observed. There are two assumptions for $Cl_2{}^-$ or $Br_2{}^-$ formation:

$$RR'X_2 + X^- \xrightarrow{k_5} RR'X + X_2{}^-, \quad (5)$$

$$RR'X + X^- \xrightarrow{k_{5'}} RR' + X_2{}^-, \quad (5')$$

$$RR'X_2 + e^- \longrightarrow (RR'X_2^{-*}) \xrightarrow{k_6} RR' + X_2{}^-. \quad (6)$$

Equation 5 is an abstraction reaction of a halogen atom from the parent molecule, and occurs when the concentration of the sample is high. Equation 5′ is abstraction from a radical, which can be neglected because the concentration of the radical is the same as that of the halide ion. Equation 6 is the dissociative reaction of $X_2{}^-$. If a dissociative reaction would occur, the abundance of $Cl_2{}^-$ is proportional to the injection quantity of the parent molecule and the branching ratio of

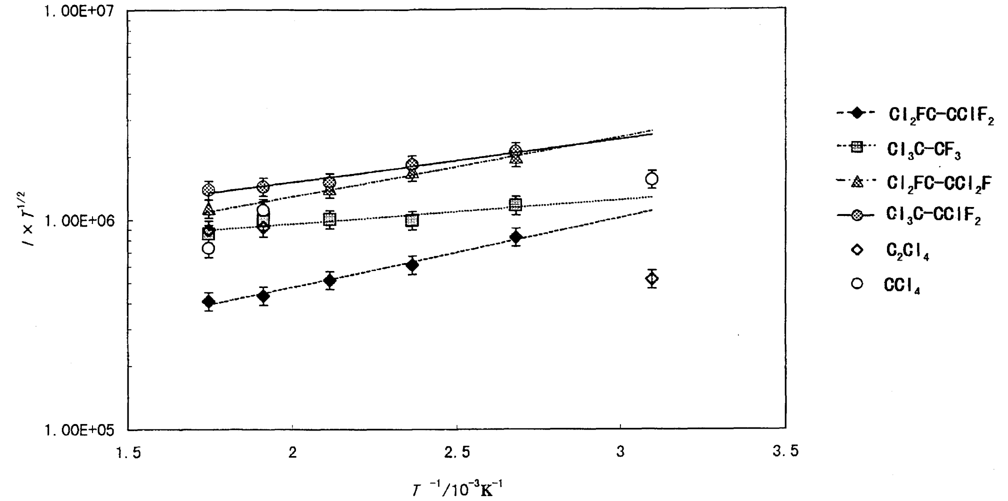

Fig. 3. Temperature dependence of dissociative $Cl^-$ formation rate for chlorofluorocarbons. *I* means ion intensity. The longitudinal axis is arbitrary unit.

$Cl_2^-$ is constant. For $C_2Cl_5F$ (1/100 mol%) and $C_2Cl_6$ (1/100 mol%), the branching ratio of $Cl_2^-$ is almost constant, 0.08 and 0.20, respectively. For the case of $Cl_2^-$, there have been few investigations about the dissociative reaction. In a $\gamma$-ray radiolysis study of $C_2Cl_6$, the formation of $C_2Cl_4$ was observed.[18] Though a decomposition study was carried out in the liquid phase, we can assume that $Cl_2^-$ formation in this work may occur through reaction 6. When a dissociative reaction occurs, the vibrational energy in $RR'X_2^{-*}$ must be distributed to a mode which will lead to the formation of $Cl_2^-$. For $C_2Cl_3F_3$ or $C_2Cl_4F_2$, this effect will be small. We discuss the case for the formation of $Br_2^-$ in the next section.

**Bromofluorocarbons:** The concentration of the samples was 1/500 mol% for $Br_2FC–CF_3$ and $BrF_2C–CBrF_2$, 1/1000 mol% for $BrF_2C–CBrF_2$ and $Br_2FC–CBrF_2$, and 1/2000 mol% for $Br_2FC–CBrF_2$. For $CBr_3F$, the concentration was 1/200, 1/100, and 1/50 mol%. The peak intensity of $Br^-$ was proportional to the injection quantity of the sample (0.4—1.5 μl). The proportional constant was calculated with the least-squares method and converted to the rate per $10^{-9}$ mol of the sample. The temperature was changed and the sample was measured by the same method. Figure 4 shows an Arrhenius plot. In bromofluoroethanes, it seems that for more bromine atoms, the rate becomes faster. For bromofluorocarbons, the rate of electron attachment also decreases slightly with increasing temperature. At lower temperature, the intensity of ions from $Br_2FC–CF_3$ and $BrF_2C–CBrF_2$ also becomes the same, though the decreasing rate with increasing temperature for $Br_2FC–CF_3$ is larger than that for $BrF_2C–CBrF_2$. The reason is the same as in the case of chlorofluorocarbons. The rate of localization of excess electrons in $BrF_2C–CBrF_2^{-*}$ seems to be faster than that in $Br_2FC–CF_3^{-*}$ at higher temperature.

For bromofluorocarbons, $Br_2^-$ was also observed, except for $Br_2FC–CF_3$. An abstraction or dissociative reaction would occur. If a dissociative reaction occurs, the abundance of $Br_2^-$ is proportional to the injection quantity of the parent molecule and the branching ratio of $Br_2^-$ is con-

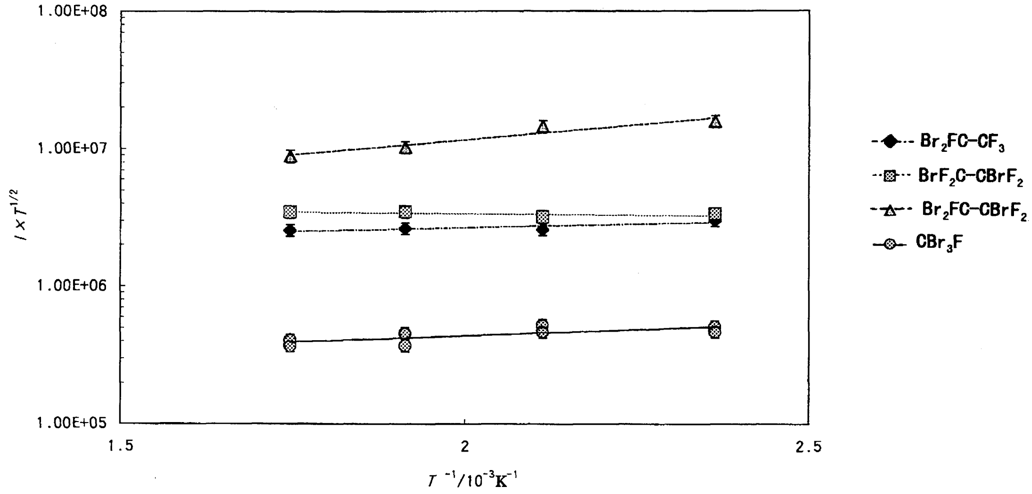

Fig. 4. Temperature dependence of dissociative $Br^-$ formation rate for bromofluorocarbons. *I* means ion intensity. The longitudinal axis is arbitrary unit.

stant, as in the cases of $C_2Cl_5F$ and $C_2Cl_6$. If abstraction would occur, the abundance of $Br_2^-$ would be proportional to square of the injection quantity of the parent molecule. When both abstraction and dissociative reactions occur, the branching ratio of $Br_2^-$ is the summation of the constant and the proportional part to the injection quantity of the parent molecule. The constant is equal to $k_6/(k+k_6)$. In Figs. 5 and 6, the abundance of $Br_2^-$ or the branching ratio of $Br_2^-$ is plotted versus the injection quantity of the parent molecule for $BrF_2C$–$CBrF_2$ (1/500 mol%) and $CBr_3F$ (1/50 mol%), respectively. For $BrF_2C$–$CBrF_2$, the abundance of $Br_2^-$ is proportional to the injection quantity of the parent molecule. On the other hand, the branching ratio of $Br_2^-$ of $CBr_3F$ is proportional to the injection quantity of the parent molecule. These facts mean that a dissociative reaction and abstraction would mainly occur for $BrF_2C$–$CBrF_2$ and $CBr_3F$, respectively.

In this work, the observed value of $k_6/(k+k_6)$ of $CBr_3F$ was 0.065 at 523 K. Smith et al. studied electron attachment for $CBr_3F$, and found that the branching ratio of $Br_2^-$ is 0.05 at 473 K and 0.08 at 373 K using the FALP method.[13] Our result is consistent with Smith's result. For $BrF_2C$–$CBrF_2$, $k_6/(k+k_6)$ was calculated to be 0.12 at 573 K, 0.15 at 523 K, 0.14 at 473 K, and 0.16 at 423 K in this study. Smith et

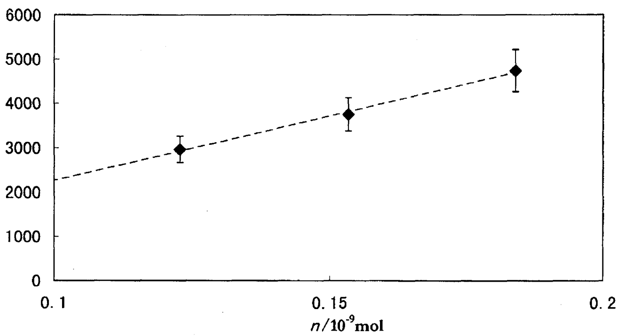

Fig. 5. The relation between $Br_2^-$ formation and injection quantity $n$ of $BrF_2C$–$CBrF_2$ (1/500 mol%) at 523 K. $I$ means ion intensity. The longitudinal axis is arbitrary unit. The abundance of $Br_2^-$ is proportional to the injection quantity of the sample.

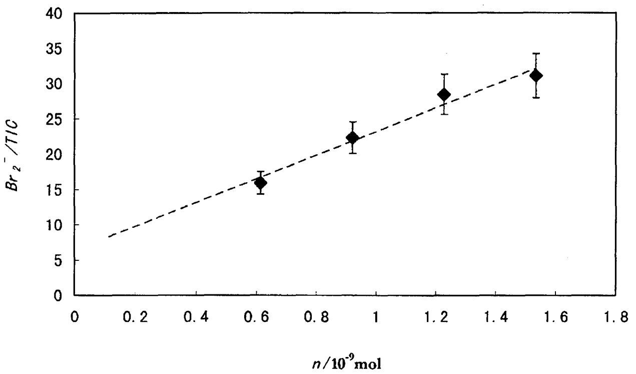

Fig. 6. The relation between $Br_2^-$ formation and injection quantity $n$ of $CBr_3F$ (1/50 mol%) at 523 K. The abundance of $Br_2^-$/TIC (Total Ion Chromate) is proportional to the injection quantity of the sample.

Table 1. Atomic Charge Distribution of Chlorofluorocarbons

| | | Atomic charge of $Cl^{a)}$ | | Atomic charge of $C^{a)}$ |
|---|---|---|---|---|
| $ClF_2C$–$CClF_2$ | $-0.1958^{b)}$ | — | — | $0.533^{b)}$ |
| $Cl_2FC$–$CF_3$ | $-0.2737^{c)}$ | $-0.2736^{c)}$ | — | $0.022^{c)}$ |
| $Cl_2FC$–$CClF_2$ | $-0.1277^{c)}$ | $0.0460^{c)}$ | — | $-0.444^{c)}$ |
| | $0.2283^{b)}$ | — | — | $-0.121^{b)}$ |
| $Cl_3C$–$CF_3$ | $-0.2021^{d)}$ | $-0.2021^{d)}$ | $-0.2021^{d)}$ | $-0.122^{d)}$ |
| $Cl_2FC$–$CCl_2F$ | $0.1240^{c)}$ | $0.1240^{c)}$ | — | $-0.623^{c)}$ |
| $Cl_3C$–$CClF_2$ | $-0.1717^{d)}$ | $-0.1717^{d)}$ | $-0.2369^{d)}$ | $0.022^{d)}$ |
| | $0.2302^{b)}$ | — | — | $-0.283^{b)}$ |
| $C_2Cl_5F$ | $-0.1953^{d)}$ | $-0.1953^{d)}$ | $-0.2292^{d)}$ | $0.028^{d)}$ |
| | $0.1504^{c)}$ | $0.1504^{c)}$ | — | $-0.578^{c)}$ |
| $C_2Cl_6$ | $-0.0612^{d)}$ | $-0.0612^{d)}$ | $-0.0612^{d)}$ | $-0.316^{d)}$ |

a) Calculated at the HF/6-31+G level of theory. b) Atomic charge in the $-CClF_2$ group. c) Atomic charge in the $-CCl_2F$ group. d) Atomic charge in the $-CCl_3$ group.

Table 2. Atomic Charge Distribution of Bromofluorocarbons

| | | Atomic charge of $Br^{a)}$ | | Atomic charge of $C^{a)}$ |
|---|---|---|---|---|
| $Br_2FC$–$CF_3$ | $-0.2037^{c)}$ | $-0.2037^{c)}$ | — | $-0.257^{c)}$ |
| $BrF_2C$–$CBrF_2$ | $-0.1314^{b)}$ | — | — | $-0.021^{b)}$ |
| $Br_2FC$–$CBrF_2$ | $-0.1703^{c)}$ | $-0.2162^{c)}$ | — | $-0.264^{c)}$ |
| | $0.1139^{b)}$ | — | — | $-0.169^{b)}$ |

a) Calculated at the HF/6-311+G level of theory. b) Atomic charge in the $-CBrF_2$ group. c) Atomic charge in the $-CBr_2F$ group.

al. obtained the branching ratio of $Br_2^-$ to be 0.10 at 473 K and 0.15 at 373 K, respectively. For the percentage of $Br_2^-$ relative to the total ion intensity, Zook et al. obtained 0.20 using isobutane as a reagent gas and 0.12 using helium at 423 K.[14] Therefore, the results would be in good agreement with the previous data for $BrF_2C$–$CBrF_2$ and $CBr_3F$. For $Br_2FC$–$CBrF_2$ (1/1000 mol%), the branching ratio of $Br_2^-$ is about 0.20, larger than $BrF_2C$–$CBrF_2$, at 523 K. The ratio becomes under 0.10 when the injection quantity of the parent molecule is smaller. Because the concentration of the sample is lower than $BrF_2C$–$CBrF_2$, an abstraction reaction would not occur.

**Comparison with Theoretical Results:** At a higher temperature, excess electron delocalizes in $RX^{-*}$, which makes the rate of formation of the halide ion lower. This effect is different for various kinds of molecules. To check whether it is easy for the localization of electrons in $RX^{-*}$ to occur, we calculated the atomic-charge distribution of the parent anion including with $C_2Cl_2F_4$. The structure of the neutral molecule was optimized by an ab initio Hartree–Fock calculation with the 3-21G basis sets. The energy of the anions was calculated with 6-31+G and 6-311+G basis sets for chlorofluorocarbons and bromofluorocarbons, respectively. The atomic charge of halogen atoms and the carbon atom of the $-CCl_xF_{3-x}$ group or the $-CBr_xF_{3-x}$ group are listed in Tables 1 and 2. For $Cl_3C$–$CF_3$, $Cl_3C$–$CClF_2$, and $C_2Cl_5F$, the atomic charge localizes at the $-CCl_3$ group, especially at chlorine atoms. It should be easy to cleave the C–Cl bond for these molecules. On the other hand, in the $-CCl_2F$ group, except for $Cl_2FC$–$CF_3$, the atomic charge localizes at the carbon atom, and does not localize at the chlorine atoms. This is the same for $C_2Cl_6$. For $Cl_2FC$–$CClF_2$, $Cl_2FC$–$CCl_2F$, and $C_2Cl_6$, motion which leads to the localization of charge to the chlorine atom is necessary. In the $-CBr_2F$ group, the atomic charge localizes not only at the carbon atom, but also at the bromine atoms. This would make the rate of formation of the bromide ion faster. For $BrF_2C$–$CBrF_2$, the atomic charge of the carbon atom is lower than at the bromine atom, which is the same as the $-CCl_3$ group. These results are consistent with the experimental ones. Because the atomic charge localizes at the chlorine atom, and not at the carbon atom for $C_2Cl_2F_4$, it should be easy to cleave the C–Cl bond, and the decreasing rate of formation of $Cl^-$ with increasing temperature will be small for them.

## References

1 R. E. Bühler, "The Chemistry of the Carbon–Halogen Bond," John Wiley & Sons, London (1973), Chap. 12.

2 a) A. A. Christodoulides and L. G. Christophorou, *J. Chem. Phys.*, **54**, 4691 (1971). b) D. L. McCorkle, I. Szamrej, and L. G. Christophorou, *J. Chem. Phys.*, **77**, 5542 (1982).

3 R. Schumacher, H. R. Sprunken, A. A. Christodoulides, and R. N. Schindler, *J. Phys. Chem.*, **82**, 2248 (1978).

4 a) D. Smith, N. G. Adams, and E. Alge, *J. Phys. B*, **17**, 461 (1984). b) E. Alge, N. G. Adams, and D. Smith, *J. Phys. B*, **17**, 3827 (1984).

5 a) A. Chutjian and S. H. Alajajian, *J. Phys. B*, **20**, 2117 (1987). b) S. H. Alajajian, M. T. Bernius, and A. Chutjian, *J. Phys. B*, **21**, 4021 (1988).

6 X. Ling, B. G. Lindsay, K. A. Smith, and F. B. Dunning, *Phys. Rev. A*, **45**, 242 (1992).

7 a) H. Shimamori, Y. Tatsumi, Y. Ogawa, and T. Sunagawa, *J. Chem. Phys.*, **97**, 6335 (1992). b) H. Shimamori, Y. Tatsumi, Y. Ogawa, and T. Sunagawa, *Chem. Phys. Lett.*, **194**, 223 (1992).

8 a) J. A. Ayala, W. E. Wentworth, and E. C. M. Chen, *J. Phys. Chem.*, **85**, 3989 (1981). b) W. E. Wentworth, T. Limero, and E. C. M. Chen, *J. Phys. Chem.*, **91**, 241 (1987). c) E. C. M. Chen, W. E. Wentworth, E. D. D'sa, and C. F. Batten, *J. Chromatogr.*, **399**, 121 (1987). d) E. D. D'sa, W. E. Wentworth, and E. C. M. Chen, *J. Phys. Chem.*, **92**, 285 (1988). e) E. C. M. Chen, K. Albyn, L. Dussack, and W. E. Wentworth, *J. Phys. Chem.*, **93**, 6827 (1989). f) E. C. M. Chen, E. S. Chen, M. S. Milligan, W. E. Wentworth, and J. R. Wiley, *J. Phys. Chem.*, **96**, 2385 (1992).

9 J. R. Wiley, E. C. M. Chen, and W. E. Wentworth, *J. Phys. Chem.*, **97**, 1256 (1993).

10 E. C. M. Chen, J. R. Wiley, C. F. Batten, and W. E. Wentworth, *J. Phys. Chem.*, **98**, 88 (1994).

11 J. J. DeCorpo and J. L. Franklin, *J. Chem. Phys.*, **54**, 1885 (1971).

12 S. H. Alajajian, M. T. Bernius, and A. Chutjian, *J. Phys. B*, **21**, 4021 (1988).

13 D. Smith, C. R. Herd, N. G. Adams, and J. F. Paulson, *Int. J. Mass Spectrom. Ion Processes*, **96**, 341 (1990).

14 D. R. Zook, W. B. Kington, and E. P. Grimsrud, *Int. J. Mass Spectrom. Ion Processes*, **104**, 63 (1991).

15 R. Kaufel, E. Illenberger, and H. Baumgartel, *Chem. Phys. Lett.*, **106**, 342 (1984).

16 D. Spence and G. J. Schulz, *J. Chem. Phys.*, **58**, 1800 (1973).

17 T. Sunagawa and H. Shimamori, *J. Chem. Phys.*, **107**, 7876 (1997).

18 T. Sawai, N. Ohara, and T. Shimokawa, *Bull. Chem. Soc. Jpn.*, **51**, 1300 (1978).