The branching ratio of anions in thermal electron attachment to chlorinated fluorobenzenes

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Abstract

The temperature dependences of the formation of negative ions from $C_6F_{6-x}Cl_x$, $CF_3C_6F_{5-x}Cl_x$, and $NC_5F_{5-x}Cl_x (x = 1,2)$ were studied using negative chemical ionization mass spectrometry. Cl^- and the parent negative ion were produced. The $(M - Cl)^-$ (M: parent molecule) was also observed for $CF_3C_6F_{5-x}Cl_x$ and $NC_5F_{5-x}Cl_x$. The temperature dependence of the relative intensity, $(M - Cl)^-/Cl^-$, suggested that the electron affinity of the fragment radicals decreases in the order, $CF_3C_6F_4 > C_5F_4N > C_6F_5$. On the other hand, the relative intensity, Cl^-/M^-, suggested that the electron affinity of the parent molecules decreases in the order, $CF_3C_6F_{5-x}Cl_x \gg NC_5F_{5-x}Cl_x > C_6F_{6-x}Cl_x$. Geometries of the parent anions were also calculated using with B3LYP/6-31+G method. The parent anions have an out-of-plane deformed structure and the extent of the deformation corresponds to that of the electron affinity for the parent molecule.
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1. Introduction

Electron attachment to halo-carbons is an important and fundamental reaction process in the gas and condensed phases in radiation chemistry because halogen atoms or halogenated compounds have high electron affinities [1]. Fragment anions or parent anions are produced from the electron attachment process. For the fluorinated benzene derivatives, such as C_6F_6, $CF_3C_6F_5$, $C_6F_5C_6F_5$, C_6F_5CN, C_5F_5N, etc. only parent anions were produced by the thermal electron attachment [2]. On the other hand, for the molecules present in chlorine or bromine atoms, X, substituted for one or two of the fluorine atoms on the fluorinated benzene derivatives, fragment anions: X^- or $(M - X)^-$ (M: parent molecule), were also observed. For example, there have been some studies of the electron attachment to C_6F_5X, i.e., time-of-flight mass spectrometry (TOF) [3], the flowing afterglow Langmuir probe method (FALP) [4], the electron swarm method (ES) [5], the electron capture detector (ECD) [6], the pulse radiolysis microwave cavity

method (PRMC) [7], or negative chemical ionization mass spectrometry (NCIMS) [8]. Based on the TOF, FALP and NCIMS results, it was shown that the electron attachment to C_6F_5X produces X^-, $C_6F_5^-$, and $C_6F_5X^-$ and the production rate of these negative ions is different depending on the halogen atom X, the pressure of the ambient gas and the temperature [3,4,8].

We have studied the temperature dependence (373–573 K) of the intensity of anions produced from electron attachment to $C_6F_4X_2$ (X: Cl,Br,I) and XC_6F_4Br (X: Cl, CF_3, BrC_6F_4, CN) with NCIMS [8]. The relative intensity, $(M - Br)^-/Br^-$, at the high-temperature limit decreases in the order $BrC_6F_4CN > BrCF_3C_6F_4 > BrC_6F_4C_6F_4Br > BrC_5F_4N > BrC_6F_4Cl > 1,4-C_6F_4 Br_2 > C_6F_5Br$. This means that the electron affinity of $M - Br$ decreases in the order $C_6F_4CN > CF_3C_6F_4 > C_6F_4C_6F_4Br > C_5F_4N > C_6F_4Cl > C_6F_4Br > C_6F_5$. This will be the same for the chlorinated fluorocarbons. To check this effect regarding chlorine substitution, we studied the temperature dependence (373–573 K) of the negative ion formation of $C_6F_{6-x}Cl_x$, $CF_3C_6F_{5-x}Cl_x$, and $NC_5F_{5-x}Cl_x$ ($x = 1,2$) by NCIMS. We have also studied the molecular orbital calculation in order to optimize the structure of the parent anions.

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2. Experimental

C$_6$F$_5$Cl, 3-CF$_3$C$_6$F$_4$Cl, 3,5-CF$_3$C$_6$F$_3$Cl$_2$, 3-NC$_5$F$_4$Cl, and 3,5-NC$_5$F$_3$Cl$_2$ were supplied by Tokyo-Kasei and 1,3-C$_6$F$_4$Cl$_2$ was supplied by Aldrich. Hexane used as the solvent was purchased by Wako-Junyaku. All were used as received.

Our experimental apparatus has been previously described in detail [8,9]. Electrons, whose energy is 200 eV, are provided from the filament and thermalized by collision with the reagent gas. The reagent gas was isobutane [9]. To confirm that electrons are thermalized at the incident temperature, the intensity of the Cl$^-$ ion produced from C$_2$Cl$_4$ was measured by changing the flux of isobutane. It is known that the thermal electron attachment for C$_2$Cl$_4$ led to the Cl$^-$ formation. The pressure of the mass analytical tube was monitored by an ion gauge and increased with the flux of isobutane. The intensity of the Cl$^-$ ion from C$_2$Cl$_4$ was almost constant when the pressure monitored at the analytical tube was greater than 3.3×10^{-3} Pa. Because we measured the ion intensity at the pressure of 4.0×10^{-3} Pa, most of the electrons should be thermalized [9]. The monitored pressure was $(1.3–2.6) \times 10^{-4}$ Pa and $(3.3–4.6) \times 10^{-3}$ Pa, with and without isobutane, respectively. The main gas in the reaction volume was isobutane, therefore, we could neglect the contribution of nitrogen or oxygen. The produced anions were mass selected by the quadruple pole mass filter and detected by the electron multiplier. Chemical ionization spectra were taken using a Shimadzu QP1100EX GC-MS equipped for negative chemical ionization. No anions of isobutane were observed under the experimental conditions. The observed anions were produced from the attachment of electrons thermalized by collisions with isobutane and not from the electron transfer from the isobutane anion. The instrument was tuned using the NCI mass spectra of tris(perfluorobutyl)amine (TPFBA) at 523 K and the conditions remained constant throughout the measurements.

The gas chromatograph was operated in the split mode using a wide-bore capillary column to provide in-line purification of the samples. The carrier gas was helium which was pumped in at the capillary interface. Samples were diluted with hexane in 1 mol% for C$_6$F$_5$Cl, 1,3-C$_6$F$_4$Cl$_2$, 3-NC$_5$F$_4$Cl, and 3,5-NC$_5$F$_3$Cl$_2$ and 1/10 to 1/100 mol% for 3-CF$_3$C$_6$F$_4$Cl and 3,5-CF$_3$C$_6$F$_3$Cl$_2$, 0.4–1.5 μl sample was then injected. The samples were separated from hexane through the capillary column. A single peak due to electron attachment to the sample gas was observed in the chromatogram with no extraneous peaks or interference. The temperature of the GC column was kept at 353 K for C$_6$F$_5$Cl, 3-NC$_5$F$_4$Cl and 3-CF$_3$C$_6$F$_4$Cl, at 373 K for 3,5-CF$_3$C$_6$F$_3$Cl$_2$, and at 393 K for 1,3-C$_6$F$_4$Cl$_2$ and 3,5-NC$_5$F$_3$Cl$_2$. The peaks were observed at the retention times of 2.7, 2.6, 3.3, 4.9, 2.8, and 2.5 min, respectively.

The temperature of the reaction volume was controlled by a computer. When the temperature was changed, the ion source was allowed to equilibrate for 30–60 min. The mass spectra were obtained using a personal computer. The ion abundance was obtained from the integrated sums of all the isotopic masses of the ions. Ab initio MO calculations using the B3LYP method have been carried out with the 6-31+G basis set using the Gaussian 98 programs [10].

3. Results and discussion

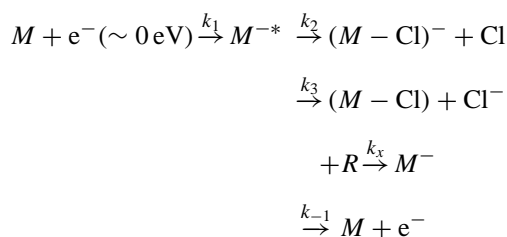### 3.1. The temperature dependence of the formation of negative ions

The intensity of the ion was summed around the peak area and was proportional to the injection quantity of the sample (0.4–1.5 μl) for 3-CF$_3$C$_6$F$_4$Cl and 3,5-CF$_3$C$_6$F$_3$Cl$_2$. The intensity of each ion per 10^{-7} mol of the sample was calculated by the least-squares method. For other samples, the ion intensities of a 1.0 μl injection were measured several times and averaged. The branching ratio was obtained as the relative intensity of the ions. The temperature of the ion source chamber was changed and the intensity of the ions was measured by the same method.
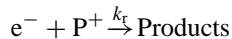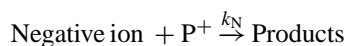
To check whether the temperature of the sample molecule was the same as that of the electrons, the temperature of the capillary interface was changed. The temperature of the interface was maintained at 100 K lower than that of the ion source. If the sample gas passed through the interface at a lower temperature and was not heated enough in the ion source chamber, the intensity and the relative ratio of the ions should be influenced. The intensity and the relative ratio of the ions did not change, indicating that the temperature of the electrons should be almost the same as that of the sample molecules in the reaction chamber.

For all samples, Cl$^-$ and the parent anion were observed. $(M - \mathrm{Cl})^-$ (M = parent molecule) was also observed for CF$_3$C$_6$F$_{5-x}$Cl$_x$ and NC$_5$F$_{5-x}$Cl$_x$. The intensity of the parent anion decreased with the increasing temperature, while that of Cl$^-$ increased. The intensity of $(M - \mathrm{Cl})^-$ was unchanged with the temperature.

3.2. Kinetics and dynamics

Because the intensity of the parent anions dramatically increases at low temperatures, electron detachment from the parent anion should occur at high temperatures. The reaction mechanism is as follows:

$$M + \mathrm{e}^- (\sim 0\,\mathrm{eV}) \xrightarrow{k_1} M^{-*} \xrightarrow{k_2} (M - \mathrm{Cl})^- + \mathrm{Cl}$$

$$\xrightarrow{k_3} (M - \mathrm{Cl}) + \mathrm{Cl}^-$$

$$+ R \xrightarrow{k_x} M^-$$

$$\xrightarrow{k_{-1}} M + \mathrm{e}^-$$

Negative ion $+ P^+ \overset{k_N}{\rightarrow}$ Products

$e^- + P^+ \overset{k_r}{\rightarrow}$ Products

where P^+, M^{-*}, and R represent a positive ion, a vibrationally excited parent anion, and the reagent gas, respectively.

The sample gas should be spread over the ion source chamber when they were ejected from the capillary interface. Electrons were constantly provided from the filament. We can assume a steady state condition of electrons supplied by the ion source just like radiolysis in a cell. When electrons whose energy was 200 eV were thermalized several times by collisions with isobutane, positive ions of isobutane were produced and electrons were simultaneously ejected for a high concentration of isobutane. The monitoring pressure at the mass analytical tube did not increase by the introduction of the sample molecules, indicating that the concentration of the sample should be less than that of isobutane. Therefore, the concentration of electrons and positive ions of isobutane should be much greater than that of the negative ions produced from the sample. The concentration of positive ions and electrons would maintain constant during the measurement. These assumptions lead to the results that $k_{N'}[P^+] = k_N =$ constant and that the rate (k_r) of the electron–ion recombination reaction should be maintained constant during the measurement. The electron–ion recombination and the ion–ion recombination are competitive. The rate constant of k_N is different among the anions because of the size and the charge distribution. It is assumed that the rate constant will be greater for the larger size of the anion and the localization of the charge in the anion. Therefore, the value will be smaller for Cl^- and larger for the parent anions.

The instrument constant includes the interaction volume, ion draw-out efficiency, ion lens and mass spectrometer transmission efficiencies and ion detection efficiency of the electron multiplier. If measurements are carried out with the same instrument settings, the ion lens and mass spectrometer

transmission efficiencies or ion detection efficiency should be the same for all the samples. However, the ion draw-out efficiency would be different for the ion and sample. When ions with a higher translation energy are produced, they could not be focused as well as the same type ions with a low energy [11]. Because we discussed that the branching ratio of ions and the production mechanism of each ion would not significantly differ among the samples, the relative difference in the ion draw-out efficiency and the instrumental constants should be regarded as almost the same for all the compounds studied. The reaction rate constant could be described as $k = A \exp(-E/RT)$, where A is a pre-exponential factor and E is the apparent activation energy. Therefore, the branching ratio of the fragment ions, $[(M-Cl)^-]/[Cl^-]$, can be expressed as,

$$\frac{[(M-Cl)^-]}{[Cl^-]} \propto \frac{k_2}{k_3} = \frac{A_2}{A_3} \exp\left(\frac{-(E_2 - E_3)}{RT}\right). \tag{1}$$

We can assume that reactions k_2, k_3, and k_x will occur following k_1 and $[M^{-*}] = 0$ at a steady state. The relative ratio between the chloride ion and the parent anion is described as,

$$\frac{[Cl^-]}{[M-]} \propto \frac{k_3}{k_x} + \frac{k_3 k_{-1}}{(k_x k_N)}. \tag{2}$$

Though the ion draw-out efficiency would be different among M^-, $(M - Cl)^-$ and Cl^-, the comparison of the branching ratios $[(M - Cl)^-]/[Cl^-]$ and $[Cl^-]/[M^-]$ will represent the relative character.

The temperature dependences of the branching ratios, $(M - Cl)^-/Cl^-$ and Cl^-/M^- are plotted in Figs. 1 and 2, respectively. For C_6F_5Cl and $1,3-C_6F_4Cl_2$, the values were almost the same as previously obtained [8]. Table 1 shows the difference between the activation energy of the production of $(M - Cl)^-$ and that of Cl^-, $(E_2 - E_3)$ and the ratio of the Arrhenius parameter for the formation of $(M - Cl)^-$ and Cl^-, A_2/A_3, obtained from Eq. (1). Because $(M - Cl)^-$ was not observed for C_6F_5Cl and $1,3-C_6F_4Cl_2$, the value of A_2/A_3 was estimated to be smaller than 10^{-5}. The relative
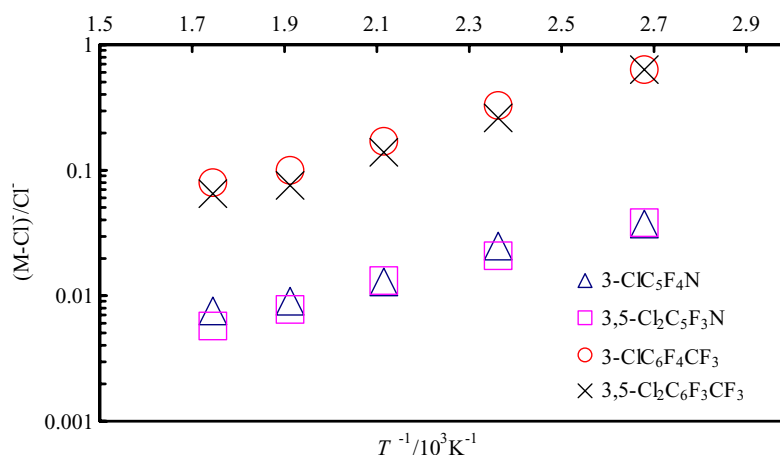

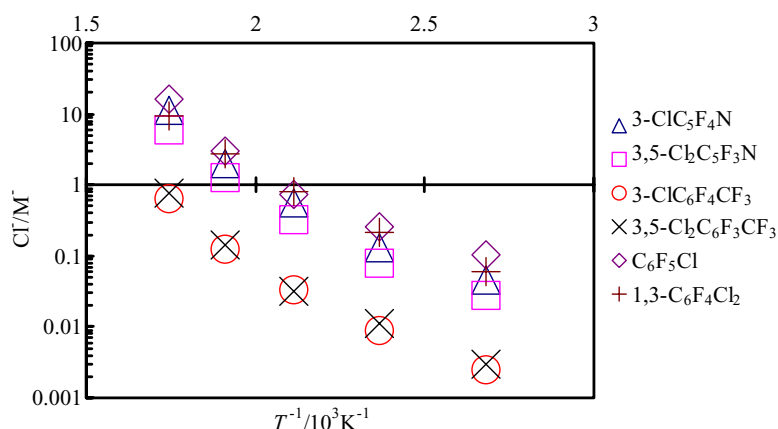Fig. 1. The temperature dependence of the relative branching ratio $(M - Cl)^-/Cl^-$.

Fig. 2. The temperature dependence of the relative branching ratio Cl^-/M^-.

intensity, $(M-Cl)^-/Cl^-$, increases with the decreasing temperature. This is different from the result obtained for the bromine substitution [8]. The intensity of Cl^- increased with the increasing temperature, though that of $(M-Cl)^-$ was unchanged. Therefore, the temperature dependence of the relative intensity reflects that of the intensity of Cl^-. The activation energy of the formation of Cl^- is on the order of the value of $-(E_2-E_3)$. Between the mono- and di-chlorinated compounds, the differences between the activation energy, the values of (E_2-E_3), are almost the same, revealing that the fragmentation mechanisms should be the same. The ratio of the A-factor reflects the branching ratio of $M-Cl+Cl^-$ and that of $(M-Cl)^- +Cl$ at the high-temperature limit. The branching ratio of $(M-Cl)^- +Cl$ at the high-temperature limit is smaller than that of $M-Cl+Cl^-$ for all compounds and becomes smaller in the order $CF_3C_6F_4^- +Cl >$ $NC_5F_4^- +Cl > C_6F_5^- +Cl$. The heat of formation of the anion $+$ radical produced from the same parent anion is represented as the difference between the electron affinity of the anion and the bonding energy. Because the cleavage of the C–Cl bond occurs for both $(M-Cl) + Cl^-$ and $(M-Cl)^- +Cl$, the bonding energy is the same and the heat of formation of Cl^- and $(M-Cl)^-$ should be

Table 1
The difference between the activated energy of the production of $(M-Cl)^-$ and Cl^-, (E_2-E_3) and the ratio of the arrhenius parameter, A_2/A_3

	E_2-E_3[a] (eV)	A_2/A_3[b]
3-ClC$_6$F$_5$	–	<1.0e-5[c]
3,5-ClC$_6$F$_4$	–	<1.0e-5[c]
3-ClC$_5$F$_4$N	−0.155	3.0e-4
3,5-Cl$_2$C$_6$F$_3$N	−0.177	2.0e-4
3-ClC$_6$F$_4$CF$_3$	−0.202	1.2e-3
3,5-Cl$_2$C$_6$F$_3$CF$_3$	−0.218	7.0e-4

[a] The difference between the activated energy of the production of $(M-Cl)^-$ and Cl^-.
[b] The ratio of the Arrhenius parameter for $(M-Cl)^-$ formation and for Cl^- formation.
[c] $(M-Cl)^-$ was not observed.

related to the difference between the electron affinity of Cl and $M-Cl$. The higher the electron affinity of $M-Cl$ becomes, the higher the value of A_2/A_3. The trend in the value of A_2/A_3 indicates that the electron affinity of the $M-Cl$ radical increases in the order $EA(C_6F_5) < EA(C_5F_4N) < EA(CF_3C_6F_4)$. This is the expected result from the bromine substitution one.

For all compounds, the relative ion intensity, Cl^-/M^- and its slope increased with the increasing temperature. At lower temperatures, the production rate of fragment anions, that is, the former term of Eq. (2) dominates the branching ratio of anions. On the other hand, electron detachment (k_{-1}) from the parent anion cannot be neglected at the higher temperatures. Therefore, the relative ratio of the parent anion decreases. Because the bonding energy of C–Cl should be almost the same among these molecules, the heat of formation of Cl^- should be similar. Therefore, the greater the electron affinity of the parent molecule becomes, the greater the relative ratio of M. The trend in the branching ratio of the parent anion indicates that the electron affinity of the parent molecule increases in the order $EA(ClC_6F_5) < EA(ClC_5F_4N) < EA(ClCF_3C_6F_4)$. This is the same trend as the $M-Cl$ radical.

To compare the character of the parent anions, the geometry of the parent anion has been optimized. The optimized structures are shown in Fig. 3. Only the dissociative C–Cl bond is out-of-plane and the bond length is longer for $C_6F_{6-x}Cl_x$. The second substituted Cl in 1,3-$C_6F_4Cl_2$ is in the plane and behaves like F atoms. The para site C–F bond against the Nitrogen in $NC_5F_{5-x}Cl_x$ is projected out and the meta site C–F or C–Cl ones becomes hollow, indicating that partial out-of-plane deformation occurs. The –CF$_3$ base in $CF_3C_6F_{5-x}Cl_x$ and the para site C–F bond against –CF$_3$ is projected out and the meta and the ortho site C–F or C–Cl ones becomes hollow, indicating that full out-of-plane deformation occurs. The full out-of-plane deformation is the same as the fluorinated benzene derivatives [12]. The extent of the out-of-plane deformations increases in the order $C_6F_{6-x}Cl_x < NC_5F_{5-x}Cl_x < CF_3C_6F_{5-x}Cl_x$.
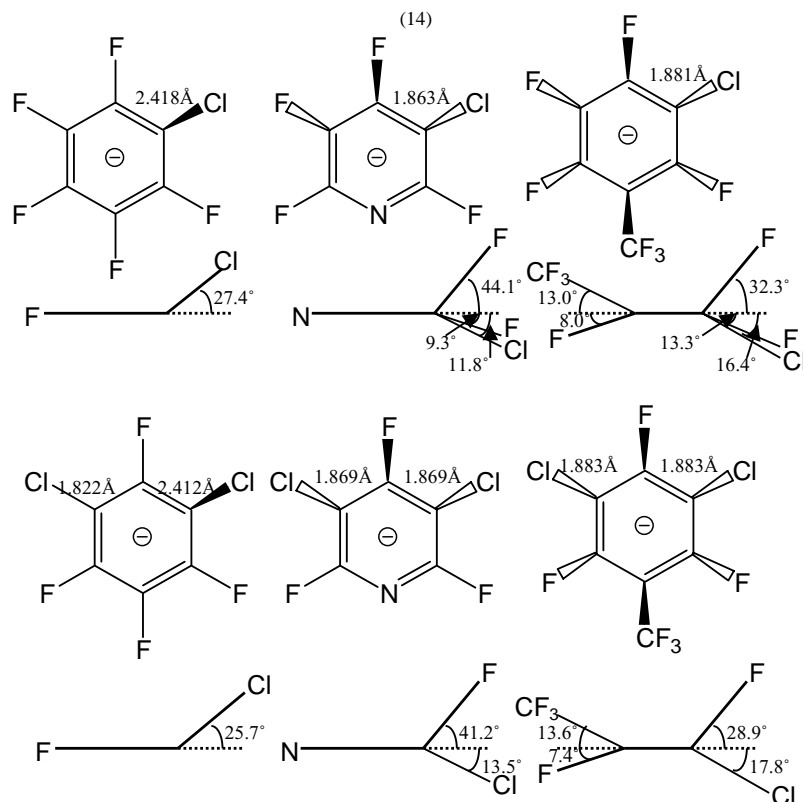
Fig. 3. The optimized structure of parent anions calculated with B3LYP/6-31+G method. Numbers given in Å and degree refer to the C–Cl bond lengths and the deformed angle, respectively.

This corresponds to the trend in electron affinity of the parent molecule. The out-of-plane projecting angle increases in the order $C_6F_{6-x}Cl_x < CF_3C_6F_{5-x}Cl_x < NC_5F_{5-x}Cl_x$. This is also the same trend as the fluorinated benzene derivatives [12]. These results suggest that the second substituted Cl in the fluorinated benzene derivatives works almost the same as the F atoms and the cleavage of the C–Cl bond in the parent anion is difficult, especially for the molecule with a higher electron affinity.

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