© 2000 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 73, 1973—1978 (2000)* 1973

Production of Negative Ions from Fluorocarbons and Reaction Mechanism

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(Received March 2, 2000)

The temperature dependence of the formation of negative ions from C_6F_6, C_5F_5N, C_6F_5CN, $C_6F_5CF_3$, and $C_6F_5C_6F_5$ was studied by using negative chemical ionization mass spectrometry. Parent negative ion and fragment ions: F^- and $(M-F)^-$ (M = Parent Molecule) were observed. Secondary product ions: $C_5F_4^-$ and $C_5F_2^-$ for C_6F_6 and $C_5F_6N^-$ and C_4FN^- for C_5F_5N were also observed at temperatures higher than 523 K. A cluster of the parent molecule and F^- is produced for C_6F_6 and C_5F_5N. The intensity of parent negative ions increases, while that of fragment ions and secondary ions decreases with decreasing temperature. Such results show that electron detachment from the parent anions will occur. Geometry of parent negative ions and cluster anions of C_6F_6, C_5F_5N, C_6F_5CN, and $C_6F_5CF_3$ were also calculated using the Hartree–Fock method. The structure and the distribution of the spin density are almost the same for all these molecules. This similarity means that the production of negative ions from them and the reaction mechanisms are almost the same.

Electron attachment is an important fundamental chemical reaction. Especially, it is known that halocarbons have high electron affinity.[1] Some theoretical and experimental studies about electron attachment to C_6F_6 or C_6F_5X (X is a halogen atom) have been carried out. For C_6F_5X, time-of-flight mass spectrometry (TOF),[2] flowing afterglow Langmuir probe method(FALP),[3,4] electron swarm method (ES),[5] electron capture detector (ECD),[6] atmospheric pressure ionization mass spectrometry (APIMS),[7] or pulse radiolysis microwave cavity method (PRMC)[8] have been used to study electron attachment. The electron attachment rate was obtained by FALP, electron swarm method, PRMC, and high Rydberg atom beam method. The results of TOF and FALP showed that the electron attachment to C_6F_5X produces X^-, $C_6F_5{}^-$, and $C_6F_5X^-$ and the production rates of these negative ions depend on the halogen atom X, the pressure of ambient gas and the temperature.[2,3] Significantly, the thermal electron attachment to C_6F_6 produces $C_6F_6{}^-$, and the rate decreases dramatically with increasing temperature.[3a,5—7] The temperature dependence of electron attachment rate was observed by ECD, APIMS, and high pressure mass spectrometry,[9a] and the electron affinity of C_6F_6 was determined.[6,7,9—11]

C_5F_5N and C_6F_5X (X = CN, CF_3, and C_6F_5) have structures similar to C_6F_6. It is interesting to study the reactivity of these compounds with electrons and the reaction mechanism of their anions compared with the case of C_6F_6. For C_5F_5N, Kebarle et al. determined the electron affinity to be 0.68 eV, which is only 0.16 eV larger than C_6F_6[12]. They have also determined electron affinities of C_6F_5CN, $C_6F_5CF_3$, and $C_6F_5C_6F_5$ to be 1.105, 0.86, and 0.82 eV, respectively.[12] Fenzlaff and Illenberger have studied the formation of negative ions from $C_6F_5CF_3$ by measuring electron attachment spectra and observed the parent anion, F^-, $C_6F_4CF_3{}^-$, $CF_3{}^-$, and $C_6F_5{}^-$.[13] But there are no reports about the production of negative ions from C_5F_5N, C_6F_5CN, and $C_6F_5C_6F_5$. Compared with C_6F_6, there is little information about the reaction mechanism of their anions.

In this research, we have studied the product ions from electron attachment to C_6F_6, C_5F_5N, C_6F_5CN, $C_6F_5CF_3$, and $C_6F_5C_6F_5$ using negative chemical ionization mass spectrometry (NCIMS). Even though the instrument is constructed for analytical use, we can observe produced negative ions from them and can determine the electron affinity of C_6F_6, C_5F_5N, and $C_6F_5C_6F_5$. We have also made a simple calculation of molecular orbitals to estimate the production and reaction mechanism of negative ions.

Experimental

C_6F_6 (Tokyo-Kasei, purity $>$ 98%), C_5F_5N (Tokyo-Kasei, purity $>$ 98%), C_6F_5CN (Tokyo-Kasei, purity $>$ 99%), $C_6F_5CF_3$ (Tokyo-Kasei, purity $>$ 98%), $C_6F_5C_6F_5$ (Tokyo-Kasei, purity $>$ 98%), hexane (Wako-Junyaku, purity $>$ 99%), and cyclohexane (Wako-Junyaku, purity $>$ 99%) were used as received.

Our experimental apparatus has been described in detail elsewhere.[14] Electrons whose energy is 200 eV are provided from the filament and thermalized by collision with reagent gas. Samples are introduced into the ion source through the capillary interface under the collision region, and thermal electrons attach to the sample gas. Chemical ionization spectra were taken with a Shimadzu QP1100EX GC-MS equipped for negative chemical ionization. The reagent gas was isobutane. Anions of isobutane were not observed under our experimental conditions. The observed anions were produced from the attachment of electrons thermalized by collision with isobutane, not from an electron transfer from the anion of isobutane. The instrument was tuned using the NCl mass spectra of tris(perfluorobutyl)amine (TPFBA) at 523 K and conditions were kept constant 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 and pumped in at the capillary interface. Samples were diluted with hexane or cyclohexane. The retention time of hexane is just below that of C_6F_6, though cyclohexane appears beyond C_6F_6. We used cyclohexane as a solvent at 523 K to check that hexane did not affect the production of fragment negative ions. The ratio of the production of anions was similar when cyclohexane was used as a solvent. Hexane was used throughout the measurements. Samples were diluted in 1/1000—1 mol%, 1 mol%, 1/100—1/2000 mol%, 1/100 mol%, and 1/10—1/200 mol% for C_6F_6, C_5F_5N, $C_6F_5CF_3$, C_6F_5CN, and $C_6F_5C_6F_5$, respectively, and 0.4—1.5 μl of them was injected. A single peak from the sample was observed in the chromatogram with no extraneous peaks or interference. The temperature of the GC column was kept at 50 °C for C_6F_6, 35 °C for C_5F_5N and $C_6F_5CF_3$, 100 °C for C_6F_5CN, and 150 °C for $C_6F_5C_6F_5$. The peaks were observed at the retention times of about 2.0, 2.6, 3.6, 3.0, and 2.8 minutes for C_6F_6, C_5F_5N, $C_6F_5CF_3$, C_6F_5CN, and $C_6F_5C_6F_5$, respectively.

The temperature of the ion source was controlled by computer. When the temperature was changed, the setting was finished in 30—60 minutes. The mass spectra were obtained via personal computer. The ion abundance was obtained from the integrated sums of all isotopic masses of the ions. Hartree–Fock molecular orbital calculations were carried out with the 6-31+G basis set using the Gaussian 94 program.

Results and Discussion

Kinetics. For dissociative electron attachment of C_6F_6, F^-, and $C_6F_5{}^-$ ions were reported to appear at electron energies of 4.5 eV and 8.7 eV, and the yield of F^- was several times larger than that of $C_6F_5{}^-$.[13,15,16] For thermal electron attachment, a nondissociative reaction will mainly occur when the amount of the ambient gas is enough to deexcite the excited parent ion.[2] Frazier et al. have measured the electron transmission spectra of C_6F_6 and have observed electron absorption peaks at 0.42 eV (degenerate $1e_{2u}$ (π^*) MO) and 4.5 eV ($1b_{2g}$ MO).[5d] Fenzlaff and Illenberger have concluded that the ground state of a parent negative ion produced by nondissociative thermal electron attachment is characterized as a state in which the excess electron occupies one of the degenerate electronic orbitals. They have considered that the state is subject to a Jahn–Teller distortion, with the potential minimum corresponding with the symmetrical formation of $1e_{2u}$ (π^*) MO. They have also mentioned that the excited states of parent anions produced by dissociative attachment of electrons whose energies are 4.5 and 8.7 eV can be characterized as the states in which the attached electron occupies $1b_{2g}$ MO and core excited orbital, respectively.[13,16] However, MO calculations have suggested the ground state of $C_6F_6{}^-$ is produced by an electron occupying σ^*-type orbital[17,18] or π^*–σ^* combination orbital[19] with respect to ESR coupling constants. By theoretical study, the first excited state of $C_6F_6{}^-$ is $A_{1g}(\sigma^*)$ MO.[18] Christophorou et al. have measured the photodetachment cross section of $C_6F_6^-$. The observed peaks at 2.31 eV and 3.03 eV, which were not observed with electron attachment spectra and electron absorption spectra, were assigned as σ^*–σ^* transition of $C_6F_6{}^-$.[20] Fenzlaff and Illenberger have studied the formation of negative ions from $C_6F_5CF_3$ by the electron impact technique.[13] They have observed the parent anion, F^-, $C_6F_4CF_3{}^-$, $CF_3{}^-$, and $C_6F_5{}^-$. As in the case of C_6F_6, non-dissociative reaction will occur mainly for the thermal electron attachment to $C_6F_5CF_3$. The fragment ions from $C_6F_5CF_3$ were produced by attachment of electrons whose energy is higher.

The main observed ions from C_6F_6 and C_5F_5N in this study are listed in Tables 1 and 2, respectively. Not only $C_6F_5^-$, F^-, and parent ions, but also $C_5F_4^-$, $C_5F_3^-$, and $C_5F_2^-$, were observed for C_6F_6 in measurements at higher concentration, and the yield of F^- is much smaller than that of $C_6F_5^-$ and $C_5F_4^-$. C_6F_6 is very stable against thermal decomposition up to a temperature of 800 K. Because the highest temperature used in our experiment was 573 K, C_6F_6 was not decomposed thermally. Fenzlaff and Illenberger have suggested that, when an electron whose energy is larger than 8.7 eV attaches to C_6F_6, the internal excess energy for the neutral system (Parent Molecule−F) is high enough to make further fragmentation reactions possible. If $C_5F_4^-$, $C_5F_3^-$, and $C_5F_2^-$ are produced by electron attachment to fragments, the abundance of F^- will be much larger, because F^- and the precursor of fragments are produced simultaneously. As mentioned previously, hexane used as solvent does not affect the dissociative electron attachment reaction. The most probable path for production of $C_5F_4^-$ is detachment of the CF_3 radical from $C_6F_7^-$, which will be produced as a cluster of C_6F_6 and F^-. Hiraoka et al. have observed $C_6F_7^-$ using a pulsed electron beam mass spectrometer.[21] We observed $C_6F_7^-$ when the concentration of the sample was 1% at 373 K. The yield of F^- is much smaller than that of $C_5F_4{}^-$, if $C_6F_7^-$ will be produced. $C_5F_3^-$ and $C_5F_2^-$ could be produced by a secondary reaction like decomposition of $C_5F_4^-$. To check the dependence of the concentration of the sample, ion intensities obtained from the sample whose concentration was 1% were measured at 373 K. Not only the parent anion, but also F^-, $C_6F_5{}^-$, $C_5F_4{}^-$, $C_5F_2{}^-$, and $C_6F_7{}^-$ were observed. The intensities of these anions relative to that of the parent anion were lower than 1/200, 1/150, 1/50, 1/200, and 1/100, respectively. The intensity of the parent anion relative to the total intensity was larger than 95% and the intensity was almost 200 times larger than that obtained from the sample whose concentration was 0.5%. This will show that the parent anions were produced from thermal electron attachment, while fragment ions were produced by attachment of electrons whose energy is higher than thermal. For $C_6F_5CF_3$, the main observed ion was the parent negative ion. Though the fragment ions, $C_6F_5{}^-$ and $C_6F_4CF_3{}^-$ were observed at 523 K under conditions of higher concentration, the intensities of these ions were too low to determine the rate.

Because electron attachment spectra or electron transmission spectra have not been observed for C_5F_5N, C_6F_5CN, and $C_6F_5C_6F_5$, there is no information about energies of the negative ionic state. Not only the parent anion, but also F^-, $C_5F_4N^-$, $C_5F_3N^-$, $C_5F_6N^-$, and C_4FN^- were observed for C_5F_5N. It seems that $C_5F_6N^-$ is a cluster produced from the reaction between the parent molecule and F^-. The reaction mechanism is similar to C_6F_6, that is, F^- and $C_5F_4N^-$ are produced from an excited state of the parent anion, and a cluster anion of C_5F_5N and F^- is observed. For C_6F_6, only the anion produced by the detachment of the CF_3 radical from the cluster, not the cluster itself, was observed at higher temperature. On the other hand, the cluster anion was observed for C_5F_5N even at 523 K. $C_4F_3N^-$, whose production path is a detachment of the CF_3 radical from $C_5F_6N^-$, was not observed at all. It seems that $C_5F_6N^-$ is much more stable than $C_6F_7^-$. If C_5F_4N has enough internal excess energy to cause fragmentation, it is possible that C_4FN^- is produced from electron attachment to the fragments. Because $C_5F_6N^-$ is produced from the reaction between F^- and the parent molecule, the primary abundance of F^- and C_5F_4N, which will be the precursor of the fragments, is related to the summation of the intensity of F^- and that of $C_5F_6N^-$. If C_4FN^- will be produced from electron attachment to the fragments, the relative intensity, $C_4FN^-/(F^-+C_5F_6N^-)$, becomes larger with increasing temperature. The abundance of C_4FN^- is larger than the summation of the intensity of F^- and that of $C_5F_6N^-$ only at 473 K. This means that C_4FN^- is not produced from electron attachment to the fragment of C_5F_4N. Decomposition of $C_4F_3N^-$, which is produced by the detachment of the CF_3 radical from $C_5F_6N^-$, is the main production path of C_4FN^-. This is similar to the mechanism for the production of $C_5F_2^-$. It seems that $C_4F_3N^-$ is less stable than C_4FN^-. This is the reason that $C_4F_3N^-$ was not observed at all. For C_6F_5CN and $C_6F_5C_6F_5$, only the parent negative ion was observed.

For C_6F_6, C_5F_5N, C_6F_5CN, $C_6F_5CF_3$, and $C_6F_5C_6F_5$, thermal electron attachment reaction will produce parent negative ions and fragment ions will be produced when electrons, whose energy is equal to the first excited state of the parent anion, attach to the molecule. As shown in Tables 1 and 2, fragment ions were observed when the concentration of the sample was larger than 0.1 mol%. When the concentration of the sample is lower than 0.1 mol%, the attachment process of electrons whose energy is higher than thermal and the sequent reactions can be negligible. The reaction mechanism will be:

$$\mathrm{M} + \mathrm{e}^- \ (\approx 0\,\mathrm{eV})\,(+\mathrm{R}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M}^-$$

$$\mathrm{M} + \mathrm{e}^- \ (> 0\,\mathrm{eV}) \underset{k_{-1*}}{\overset{k_{1*}}{\rightleftharpoons}} \mathrm{M}^{-*} \xrightarrow{k_{2*}} (\mathrm{M{-}F})^- + \mathrm{F}$$

$$\xrightarrow{k_{3*}} \mathrm{M{-}F} + \mathrm{F}^-$$

$$C_6F_6 + F^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_6F_7^{-}{}^*$$

$$C_6F_7^{-}{}^* \xrightarrow{k_5} C_5F_4^- + CF_3$$

$$C_5F_4^- \xrightarrow{k_6} C_5F_2^-,\ \text{etc.}$$

$$C_5F_5N + F^- \underset{k_{-4'}}{\overset{k_{4'}}{\rightleftharpoons}} C_5F_6N^{-*}$$

$$C_5F_6N^{-*} \xrightarrow{k_{5'}} C_4F_3N^- + CF_3$$

$$C_4F_3N^- \xrightarrow{k_{6'}} C_4FN^-,\ \text{etc.}$$

$$\text{Negative ion} + \mathrm{P}^+ \xrightarrow{k_\mathrm{N}} \text{Products}$$

where M is the parent molecule, R is the reagent gas, and P^+ is a positive ion.

Sample gas diffuses evenly in the ion source from capillary interface. Electrons are provided at a constant rate in the ion source all the time. We assumed steady state treatment as for radiolysis in a cell. These reactions lead to the expression:

$$[\mathrm{M}^-] = \varkappa \frac{k_1}{k_{-1} + k_\mathrm{N}} [\mathrm{M}][\mathrm{e}^-], \tag{1}$$

Table 1. The Temperature Dependence of the Intensity of the Product Negative Ions from Electron Attachment to C_6F_6

Temperature/K	Concn/%	$C_5F_2^-$	$C_5F_4^-$	$C_6F_5^-$	$C_6F_6^-$
573	1.0	3.00×10^3	6.55×10^3	3.25×10^3	2.60×10^3
523	0.5	3.60×10^3	7.60×10^3	3.80×10^3	8.80×10^3
473	0.2	—	1.50×10^4	—	3.70×10^4
423	0.1	—	—	—	1.53×10^5
373	1/200	—	—	—	2.52×10^6
323	1/1000	—	—	—	2.30×10^7

The intensity of ion per nmol of the sample is arbitrary unit.

Table 2. The Temperature Dependence of the Intensity of the Product Negative Ions from Electron Attachment to C_5F_5N

Temperature/K	C_4FN^-	F^-	$C_5F_4N^-$	$C_5F_6N^-$	$C_5F_5N^-$
573	0.54×10^3	0.75×10^3	0.86×10^3	—	3.44×10^3
523	0.13×10^3	0.74×10^3	0.47×10^3	0.25×10^3	1.19×10^4
473	0.61×10^3	—	0.85×10^3	0.55×10^3	6.84×10^4
423	—	0.84×10^3	0.96×10^3	2.59×10^3	3.035×10^5
373	—	0.35×10^3	—	2.38×10^3	5.65×10^5

Ions were observed when 1.0 μl of 1.0 mol% of the sample was injected.

$$[(\mathrm{M{-}F})^-] = \varkappa \frac{k_{1*}k_{2*}}{k_{-1*}+k_{2*}+k_{3*}+k_\mathrm{N}} \times \frac{[\mathrm{M}][\mathrm{e}^-]}{k_\mathrm{N}}, \tag{2}$$

$$[\mathrm{F}^-]+[\mathrm{C_5F_2^-}]+[\mathrm{C_5F_4^-}] = \varkappa \frac{k_{1*}k_{3*}}{k_{-1*}+k_{2*}+k_{3*}+k_\mathrm{N}} \times \frac{[\mathrm{C_6F_6}][\mathrm{e}^-]}{k_\mathrm{N}}, \tag{3}$$

$$[\mathrm{F}^-]+[\mathrm{C_4FN}^-]+[\mathrm{C_5F_6N}^-] = \varkappa \frac{k_{1*}k_{3*}}{k_{-1*}+k_{2*}+k_{3*}+k_\mathrm{N}} \times \frac{[\mathrm{C_5F_5N}][\mathrm{e}^-]}{k_\mathrm{N}}. \tag{4}$$

When electrons whose energy is 200 eV are thermalized by collision with isobutane, positive ions of isobutane are produced with high concentration. As the concentration of positive ions is much larger than that of negative ions, we can assume $[\mathrm{P}^+]$ constant during the measurement and $k_{\mathrm{N}'}[\mathrm{P}^+] = k_\mathrm{N}$ = a constant.

$\varkappa$ is a 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. If measurements are carried out with the same instrument settings, ion lens and mass spectrometer transmission efficiencies or ion detection efficiency will be same for all samples. But ion draw out efficiency would be different for each ion and sample; when ions which have high translation energy would be produced, they would not be focused as well as low energy ions.[22] Because the mass of the main ions produced in this study is larger than 150, that is, parent anion or so on, the difference of the translation energy of ions would not be so large. So ion draw out efficiency and $\varkappa$ are assumed to be same for all ions.

The right side of Eqs. 1, 2, 3, and 4 can be written as $\varkappa k[\mathrm{M}][\mathrm{e}^-]$ (k is rate constant for production of each negative ion). By substituting the relationships, $k_1 = \mathrm{A_1T^{-1/2}exp}\ (-\mathrm{E_1/RT})$, $k_{-1} = \mathrm{A_{-1}T\,exp}(-\mathrm{E_{-1}/RT})$, $k_{1*} = \mathrm{A_{1*}T^{-1/2}exp}\ (-E_{-1*}/RT)$, $k_{-1*} = A_{-1*}T\exp\ (-E_{-1*}/RT)$, $k_{2*} = A_{2*}T\exp\ (-E_{2*}/RT)$, $k_{3*} = A_{3*}T\exp\ (-E_{3*}/RT)$, $k_\mathrm{N} = A_\mathrm{N}$ = const, temperature dependences of the intensity of ions are described as follows:

$$k([\mathrm{M}^-]) = A_1T^{-1/2}\exp(-E_1/RT)/(TA_{-1}\exp(-E_1/RT)+A_\mathrm{N}), \tag{5}$$

$$k([\mathrm{M{-}F}^-]) = A^*A_{2*}\exp(-E_{2*}/RT)/A_\mathrm{N}/T^{1/2}, \tag{6}$$

$$k([\mathrm{F}^-]+[\mathrm{C_5F_2^-}]+[\mathrm{C_5F_4^-}]) = A^*A_{3*}\exp(-E_{3*}/RT)/A_\mathrm{N}/T^{1/2}, \tag{7}$$

$$k([\mathrm{F}^-]+[\mathrm{C_4FN}^-]+[\mathrm{C_5F_6N}^-]) = A^*A_{3*}\exp(-E_{3*}/RT)/A_\mathrm{N}/T^{1/2}, \tag{8}$$

$$A^* = A_{1*}\exp(-E_{1*}/RT)/\Big(A_{-1*}\exp(-E_{-1*}/RT) + A_{2*}\exp(-E_{2*}/RT)+A_{3*}T\exp(-E_{3*}/RT)+A_\mathrm{N}\Big).$$

If the electron concentration $[\mathrm{e}^-]$ is constant over the experimental region, Arrhenius parameters can be determined from Eq. 5.

Temperature Dependence of the Ratio of Produced Negative Ions from Fluorocarbons. Except for $\mathrm{C_5F_5N}$, the concentration of the sample was prepared so the peak intensity of the ion was proportional to the injection quantity of the sample (0.4—1.5 μl). The proportional constant was calculated with the least-squares fitting method and converted to the rate per 10^{-9} mol of the sample. For $\mathrm{C_5F_5N}$, the converted rate per 10^{-9} mol of the sample decreases during measurements, especially at lower temperatures. It seems that $\mathrm{C_5F_5N}$ is adsorbed on the wall of the ion source. Only 1.0 μl of the sample was injected for $\mathrm{C_5F_5N}$. The temperature was changed and the intensity of ions was measured by the same method. The converted relative rates of the product ions from $\mathrm{C_6F_6}$ and $\mathrm{C_5F_5N}$ are listed in Tables 1 and 2, respectively. Figure 1 shows the temperature dependence of the intensity of product anions, which is related to the rate constant for the production of anions, $k([\mathrm{M}^-])$.

Christophorou and Datskos have measured the temperature dependence of the rate of electron detachment from $\mathrm{C_6F_6^-}$ using ES method.[23] The rate of electron detachment increases with increasing the temperature, increasing the energy of the attaching electron, and decreasing with the pressure of the ambient gas. It means that the rate increases as the internal energy of $\mathrm{C_6F_6}^-$ increases. Adams et al., Spyrou and Christophorou, and Wentworth et al. have studied temperature dependence of thermal electron attachment to $\mathrm{C_6F_6}$ using FALP method,[3] ES method,[5a] and ECD[6] or APIMS method,[7] respectively. They have reported that, in higher temperature regions, an apparent decrease of attachment rate has been observed. The temperature at which the decreasing appears is 474, 423, and 300 K for ECD, ES method, and FALP, respectively. The difference is related to the experimental conditions. When electrons attach to the molecule, the parent molecule is excited into higher vibrational levels in a negative-ion state with increasing the temperature. In the case of ECD, the total pressure is 1 atm, which is sufficient for the ambient gas to collide with parent anions, leading to complete vibrational relaxation. The distribution of the internal energy of the parent anions is not related to the temperature. On the other hand, for FALP, the pressure of the ambient gas is 0.4—1.2 Torr (1 Torr = 133.322 Pa). If the pressure of the ambient gas is not sufficient for deexcitation of parent anions, electron detachment from the parent

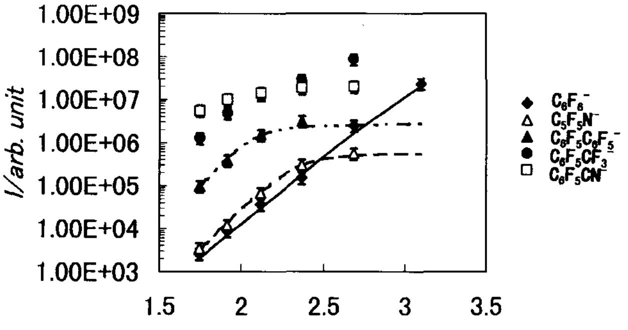

Fig. 1. Temperature dependence of the intensity of parent negative ions. I means ion intensity per 10^{-7} mol. The longitudinal axis is arbitrary unit.

Table 3. Estimated Arrhenius Parameters

	$E_{-1}{}^{a)}$/eV	$E_{-1}{}^{d)}$/eV	A_{-1}/A_N	A_1/A_N
C_6F_6	0.52 $0.86^{b)}$ $0.83^{c)}$	0.55 ± 0.03	3.0×10^6	1.0×10^9
C_5F_5N	0.68	0.68 ± 0.03	3.5×10^5	1.0×10^7
$C_6F_5C_6F_5$	0.82	0.80 ± 0.05	6.5×10^5	5.0×10^7
$C_6F_5CF_3$	0.86	—	—	1.0×10^9
C_6F_5CN	1.105	—	—	3.5×10^8

a) Ref. 12. b) Ref. 6. c) Ref. 7. d) This work.

anions with vibrational excited energy will occur. Because pressure out of the ion source is about 3×10^{-5} Torr in our system, deexcitation of the parent anions with vibrational excited energy does not occur sufficiently. The distribution of the internal energy of the parent anions is related with the temperature.

The intensity of parent anions decreases with increasing the temperature. This will be caused by electron detachment and recombination with positive ions. At lower temperature, the production of parent anions is inhibited mainly by recombination with positive ions. From the electron attachment spectra of C_6F_6 and $C_6F_5CF_3$, parent ions are produced from thermal electron attachment. For other fluorocarbons, thermal electron attachment will occur. We can assume that $E_1 = 0$. Assuming that k_N is larger than k_{-1} and k_{-1} can be neglected at lower temperature, we can determine the ratio, A_1/A_N. With the value of A_1/A_N, we can estimate A_{-1}/A_N and E_{-1} from Eq. 5, when the sets of the temperature and the intensity of ions are given. For $C_6F_5CF_3$ and C_6F_5CN, electron affinity is large and the production of parent anions is mainly inhibited by recombination with positive ions, even at higher temperatures. We cannot obtain Arrhenius-type plots and estimate the value of electron affinity for these molecules. The estimated values are listed in Table 3. Electron affinities of these molecules obtained from the thermal charge transfer reaction using high pressure mass spectrometry are also presented. The values obtained in this work concur with these. The electron affinity of C_6F_6 is determined with some experiments. With ECD[6] and APIMS[7] method, the obtained values are 0.86 and 0.83 eV. In these experiments, the pressure of the ambient gas is high enough to deexcite the parent anion, which has vibrational excited energy. This will decrease the rate for electron detachment. Higher pressure of the ambient gas will change the distribution of the internal energy of the anion. That will lead to a larger value of electron affinity.

Structures of Parent Negative Ion and Cluster. Shchegoleva suggested the structure of the ground state of $C_6F_6{}^-$ is bending and the SOMO occupied by the attached electron is π^*–σ^* combination orbital.[19] Hiraoka et al. have shown the same out-of-plane deformation of $C_6F_6^-$[24] as Shchegoleva. They have also studied the structure of $C_6F_7^-$.[21] To compare reactions of $C_6F_6^-$, $C_5F_5N^-$, $C_6F_5CF_3^-$, and $C_6F_5CN^-$, the geometry of the parent negative ion and the cluster anion have been optimized.

As with $C_6F_6^-$, out-of-plane deformation, the para C–F bond being upside the plane and the ortho and meta C–F ones being downside, occurs in $C_5F_5N^-$, $C_6F_5CF_3^-$, and $C_6F_5CN^-$. The out-of-plane angle becomes larger for $C_6F_6^-$ (37.2°) < $C_6F_5CN^-$ (42.5°) < $C_6F_5CF_3^-$ (47.2°) < $C_5F_5N^-$ (50.8°). Because the structure is the same among the four anions, the shape of SOMO will be almost the same around the para-site carbon and reactivity of anions will be also the same. The structures of the cluster anion produced from the parent molecule and F^-, and that of the (parent molecule$-$F)$^-$ anion are also optimized. For C_5F_5N, $C_6F_5CF_3$, and C_6F_5CN, three types of anions are produced. The one which is produced by the F atom attaching or detaching to the para-site carbon has the lowest energy among the three. For $C_5F_5N^-$, more than half (0.51) of the excess electrons exist in the nitrogen atom and rest exist almost evenly on five fluorine atoms. Electron distribution of the para-site carbon is about 0.0 and the spin concentrates to that carbon (1.06). This means that there exists an unpaired electron at the para-site carbon. Because the spin density values of the para-site carbon of $C_6F_5CF_3^-$ and $C_6F_5CN^-$ are 0.94 and 0.87, reactivity of the para-site carbon is also high. These are the reasons that the anion which is produced by the F atom attaching or detaching to the para-site carbon has the lowest energy among the three types of anions. The higher spin density of the para-site carbon will cause larger out-of-plane deformation. The structure of the cluster anion in $C_5F_6N^-$, $C_6F_6CF_3^-$, and $C_6F_6CN^-$ is the same as that in $C_6F_7^-$. This means that the reaction mechanisms of $C_5F_6N^-$, $C_6F_6CF_3^-$, and $C_6F_6CN^-$ are nearly the same as that of $C_6F_7^-$. The difference of enthalpy between the cluster anion and the parent molecule + F^- is calculated with the HF/6-31+G method. ΔH becomes larger $C_6F_5CN < C_6F_5CF_3 < C_5F_5N < C_6F_6$. It seems that $C_5F_6N^-$ is easier to produce than $C_6F_7^-$, and exists in a more stable state. This is coincident with the experimental results. It will be possible to produce $C_6F_6CN^-$ and $C_6F_6CF_3^-$ from the parent molecule and F^-. Because little F^- is produced by electron attachment to C_6F_5CN and $C_6F_5CF_3$, $C_6F_6CN^-$ and $C_6F_6CF_3^-$ or products from them were not observed with NCIMS method. The results of ab intio calculation with the HF/6-31+G method show that the mechanism of the production and reaction of $C_5F_6N^-$ is the same as that of $C_6F_7^-$.

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