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# Negative Chemical Ionization Mass Spectrometric Study on the Electron-Attachment Process of Nitric Carbons

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The formation of negative ions from halogenated acetonitriles $XCH_2CN$ (X = F, Cl, Br, I) and $C_6F_4(CN)_2$ was studied using negative chemical ionization mass spectrometry. The halide ion was observed for $XCH_2CN$ (X = Cl, Br, I). While the intensity of the ion increased with increasing temperature for $ICH_2CN$, the temperature dependence for the production of ions was only slightly observed over the temperature range of 393–537 K for $ClCH_2CN$ and $BrCH_2CN$. The parent anions were observed for $C_6F_4(CN)_2$. The intensity of the parent anions increased in the order $1,3\text{-}C_6F_4(CN)_2^- < 1,2\text{-}C_6F_4(CN)_2^- < 1,4\text{-}C_6F_4(CN)_2^-$. A temperature dependence for the parent anions was not observed. The difference in the intensity can be explained by a recombination reaction with the positive ions.

Electron attachment is an important and fundamental reaction process for radiation chemistry, plasma chemistry, space chemistry or so on. Though it is known that the CN radical has a high electron affinity as well as halogen atoms, the chemistry of nitric compounds differs from that of the halogenated compounds. This difference is caused by the presence of a π orbital in the CN group. For halogenated methanes, the excess electron occupies the $\sigma^*_{\text{c-x}}$ (X = halogen atom) molecular orbital (MO) when thermal electrons attach to the molecule and dissociation of the halide ion directly occurs.[1] On the other hand, cleavage of the C-C bond occurs for $CH_3CN$ when electrons with energy near to 3 eV occupy the $\pi^*_{\text{CN}}$ MO.[2]

Though it is important to study the electron-attachment process in molecules with halogen atoms and the CN group, there is little information about electron attachment to these kinds of compounds. Hacaloglu et al. studied the electron-attachment spectra of $FCH_2CN$ and $ClCH_2CN$.[3] They showed that fragment ions ($F^-$, $CN^-$, $CFCN^-$, $CHCN^-$, and $CHFCN^-$) are produced when electrons with energy near to 0.8 eV are attached to $FCH_2CN$. Thermal-electron attachment occurs for $ClCH_2CN$ and $Cl^-$ is produced. Other fragment ions are produced at higher energy resonances. Doren et al. measured the rate of thermal-electron attachment to $XCH_2CN$ (X = F, Cl, Br) using the flowing-afterglow Langmuir-probe method (FALP).[4] No attachment was observed for $FCH_2CN$. Only halide ions were produced when electrons were attached to $ClCH_2CN$ and $BrCH_2CN$. Though the rate of electron attachment to $ClCH_2CN$ increases with increasing temperature at a rate which is characterized by an activation energy of 50±15 meV, the electron-attachment rate for $BrCH_2CN$ is almost constant over the temperature range of 295–556 K. Sunagawa et al. measured the electron-attachment cross sections for $XCH_2CN$ (X = Cl, Br, I) at room temperature using the pulse-radiolysis microwave cavity technique (PRMC) and observed that the thermal electron-attachment rate increases in the order $ICH_2CN < ClCH_2CN < BrCH_2CN$.[5] However, there has been no study about ions produced from electron attachment to $ICH_2CN$ and their temperature dependence.

Using negative chemical ionization mass spectrometry (NCIMS), we studied the production of negative ions from electron attachment to $C_6F_5CN$ and $BrC_6F_4CN$ compared with $C_6F_6$, $C_6F_5Br$ and $C_6F_4Br_2$.[6–7] Only the parent anions were observed for $C_6F_5CN$.[6] For $BrC_6F_4CN$, $C_6F_4CN^-$ was observed, while $Br^-$, (parent molecule – Br)$^-$, and the parent anion were observed for the bromofluorobenzenes.[7] The C–CN bond also does not cleave in this case. Compared with $C_6F_5CN$ and the bromofluorobenzenes, it is worth studying electron attachment to $C_6F_4(CN)_2$. There have been no reports about electron attachment to $C_6F_4(CN)_2$.

In this paper, we consider the temperature dependence of the formation of negative ions from electron attachment to $XCH_2CN$ (X = F, Cl, Br, I) and $C_6F_4(CN)_2$ based on the NCI-MS technique and compare it with previous data.

## Experimental

$FCH_2CN$ (Aldrich, purity 98%), $ClCH_2CN$ (Tokyo-Kasei, purity > 98%), $BrCH_2CN$ (Tokyo-Kasei, purity > 95%), $ICH_2CN$ (Tokyo-Kasei), $1,2\text{-}C_6F_4(CN)_2$ (Aldrich, purity 95%), $1,3\text{-}C_6F_4(CN)_2$ (Aldrich, purity 98%), $1,4\text{-}C_6F_4(CN)_2$ (Aldrich, purity 99%), and $C_2H_5CN$ (Tokyo-Kasei, purity > 99%) were used as received.

Our experimental apparatus has been described in detail elsewhere.[9] Electrons with energy of 200 eV were provided from the filament and thermalized by collisions with the reagent gas. Samples were introduced into the ion source through a capillary interface under the collision region, and thermal electrons attached to the sample gas. The chemical ionization spectra were taken with a

Shimadzu QP1100EX GC-MS equipped for negative chemical ionization. The reagent gas was isobutane. The instrument was tuned using the NCI spectra of tris(perfluorobutyl)amine (TPFBA) at 523 K, and the conditions were kept constant throughout the measurements.

A gas chromatograph was operated in the splitless mode with a wide-bore capillary column to provide in-line purification of the samples. Samples were diluted with $C_2H_5CN$ in 1.0 mol% for $FCN_2CN$, 7/1000 mol% for $ClCH_2CN$, 1/500 mol% for $BrCH_2CN$ and $ICH_2CN$, 1/1000 mol% for 1,2-$C_6F_4(CN)_2$, 1/200 mol% for 1,3-$C_6F_4(CN)_2$, and 1/2000 mol% for 1,4-$C_6F_4(CN)_2$. 0.4–1.5 µL of the solution was injected. The temperature of the GC column was kept at 35 °C for $FCH_2CN$, 80 °C for $ClCH_2CN$, 100 °C for $BrCH_2CN$, 120 °C for $ICH_2CN$, and 135 °C for $C_6F_4(CN)_2$. The peaks were observed at retention times of about 1.1, 2.1, 2.3, and 5.0 minutes for $XCH_2CN$ (X = F, Cl, Br, I) respectively. The retention time were 3.6, 3.4, and 2.9 minutes for 1,2-, 1,3-, and 1,4-$C_6F_4(CN)_2$, respectively. For all samples, helium was used for the carrier gas. A single peak from the sample was observed in the chromatogram with no extraneous peaks or interference.

The temperature of the ion source was controlled by computer. The temperature was measured by a Pt sensor, besides the reaction volume. When the temperature was changed, the setting was completed with 30–60 minutes. 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.

## Results and Discussion

**Halogenated Acetonitriles.** Fragment ions: $F^-$, $CHCN^-$, $CHFCN^-$, and $CFCN^-$ were observed at a higher temperature for 1.0 mol% $FCH_2CN$. The temperature dependencies of the intensities of the produced ions are listed in Table 1. At lower temperature, $CFCN^-$ was not observed, and the intensity of $CHFCN^-$ was greater than that of $CHCN^-$. From the electron-attachment spectra,[3] the main ions were found to be $CHCN^-$ and $F^-$. The intensity of $CHCN^-$ was four-times greater than that of $F^-$ and several hundred times greater than that of $CHFCN^-$. The relative intensity, $F^-/(CHCN^-+CHFCN^-)$, was 0.28 at 333 K in this study. $CHFCN^-$ was produced from an abstraction reaction of the F atom from the parent molecule by $CHCN^-$. This is the same process as that for the production of $C_6F_7^-$ from $C_6F_6$. No anions were observed for 0.1 mol% $FCH_2CN$. Fragment ions were produced from the attachment of electrons whose energy was larger than thermal.[3] The attachment of electrons whose energy was not thermal was ignored when the concentration of the sample was less than 0.1 mol%.

Only halide ions were observed for $XCH_2CN$ (X = Cl, Br, I). This corresponds with the result of a previous study.[4] For $ClCH_2CN$, $Cl^-$ is produced from a thermal electron-attachment process.[3] Though the electron attachment spectra have not been studied for $BrCH_2CN$ and $ICH_2CN$, the same process as that for $ClCH_2CN$ is assumed. The electron-attachment process for $XCH_2CN$ (X = Cl, Br, I) is direct dissociation, as follows:

$$XCH_2CN + e^-(+R) \xrightarrow{k_1} (XCH_2CN^{-*}) \rightarrow X^- + CH_2CN.$$

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

where $P^+$ is a positive ion and R is the reagent gas. We can assume a steady state treatment as for radiolysis in a cell. When electrons whose energy is 200 eV are thermalized by collisions with isobutane, positive ions of isobutane are produced in a high concentration. Because positive ions are provided during the measurement, we can assume $k_{N'}[P^+] = A_N = \alpha$ constant. The rate of the production of the halide ions, $k$, is expressed by substituting the relationship $k_1 = A_1T^{-1/2}\exp(-E_1/RT)$, obtained from the absolute reaction rate theory,

$$k = A_1/A_N \times T^{-1/2}\exp(-E_1/RT). \qquad (1)$$

The intensity of the produced anions increased proportionally with the quantity of the sample injection. The proportional constant was calculated by the least-squares method and converted to rate per $10^{-9}$ mol of the sample. Because $ClCH_2CN$ and $BrCH_2CN$ were adsorbed by the wall in the ion source, the measurement was repeated until the proportional constant became constant. The temperature was changed and the intensity of the ions was measured by the same method. Figure 1 shows an Arrhenius plot based on Eq. 1. The intensity of the ions increased with increasing temperature for $ICH_2CN$, and the activation energy was 0.2±0.03 eV. On the other hand, the temperature dependence of the production of ions was only slightly observed over the temperature range studied in $ClCH_2CN$ and $BrCH_2CN$. Under 423 K, it seems that the intensity of the ions became greater. At higher temperatures, the translation energy of the ions became larger. Ions with higher energy will not be focused as efficiently as those with lower energy and the ion draw-out efficiency for the former becomes lower.[10] The effect is larger for lighter ions. Based on a FALP measurement, the rate constant of electron attachment to $ClCH_2CN$ increases with increasing temperature, while that to $BrCH_2CN$ is almost constant.[4] The temperature dependence for $ClCH_2CN$ is different from the FALP result.

The ratio of the intensity of the halide ions from $BrCH_2CN$ and $ICH_2CN$ relative to that from $ClCH_2CN$, and its tempera-

Table 1. Temperature Dependence of the Intensity of Produced Ions from $FCH_2CN$ of 1.0 mol%

| T/K | $F^-$ | $CHCN^-$ | $CFCN^-$ | $CHFCN^-$ | $F^-/CHCN^-+CHFCN^-$ |
|---|---|---|---|---|---|
| 573 | $6.27 \times 10^3$ | $6.62 \times 10^3$ | $3.40 \times 10^3$ | $7.46 \times 10^3$ | 0.45 |
| 523 | $6.09 \times 10^3$ | $5.33 \times 10^3$ | $2.15 \times 10^3$ | $7.84 \times 10^3$ | 0.46 |
| 473 | $5.17 \times 10^3$ | $4.00 \times 10^3$ | $3.00 \times 10^3$ | $7.84 \times 10^3$ | 0.44 |
| 423 | $4.34 \times 10^3$ | $3.09 \times 10^3$ | $1.65 \times 10^3$ | $8.19 \times 10^3$ | 0.38 |
| 373 | $3.00 \times 10^3$ | $2.04 \times 10^3$ | — | $7.03 \times 10^3$ | 0.33 |
| 333 | $2.23 \times 10^3$ | $3.76 \times 10^3$ | — | $4.07 \times 10^3$ | 0.28 |

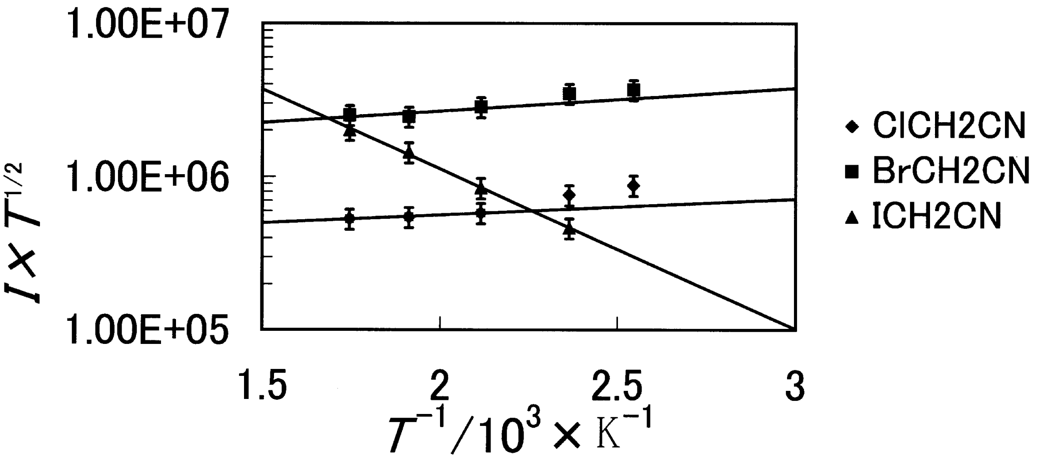

Fig. 1. The temperature dependence of the formation of halide ions for halogenated acetonitriles. I means ion intensity per $10^{-9}$ mol of the sample. The longitudinal axis is arbitrary unit.

ture dependence, are listed in Table 2 along with the values obtained by the previous date for a comparison. The values at 295 K were extrapolated from Fig. 1. Because the ion draw-out efficiency seems to become larger for $Cl^-$ and $Br^-$ at temperatures lower than 423 K, the values obtained at temperatures higher than 473 K were used for the extrapolation. Because the extrapolated value is slightly smaller than the previous data, increasing the ion draw-out efficiency with decreasing temperature is effective for $Cl^-$. The relative ratio for $BrCH_2CN$ decreases with increasing temperature in the FALP. On the contrary, in this study, the ratio is almost constant at 4.56 for temperatures higher than 423 K. This value is near to the relative ratio at room temperature in the FARP and the PRMC. In the case of FALP, the increase in the electron attachment rate constant with increasing temperature would be caused by an increase in the internal energy of $ClCH_2CN$. This would increase the overlap in the Franck–Condon region between $ClCH_2CN$ and the dissociating state of $ClCH_2CN^-$ at higher temperature as well as for the electron-scattering study of $CF_3Cl$.[11] In this study, the energy distribution of electrons is mainly reflected from the pressure of the reagent gas, and would be slightly different from that at the temperature. That would cause an overlap effect smaller than for the case of FALP.

Doren et al. extrapolated the enthalpy for the dissociative electron attachment to halogenated acetonitriles and considered that $I^-$ would be produced from attachment to $ICH_2CN$ at the collisional rate.[4] They have also mentioned that the Klots theory for s-wave electron attachment cross-section gives a larger value of the attachment rate constant for $ICH_2CN$ than for $BrCH_2CN$ and $ClCH_2CN$. It appears that the kind of fragment ion is correct. However, a temperature dependence is observed and the attachment is not collisional for $ICN_2CN$. The intensity of $I^-$ is smaller than that of $Br^-$, even at higher temperatures at which the attachment rate constant of $BrCH_2CN$ would reach the collisional. At lower temperatures, the intensity of $I^-$ becomes even smaller than that of $Cl^-$. This result corresponds with that of PRMC.[5] As mentioned by Sunagawa et al.,[5] this behavior can be interpreted in terms of the relative location of the potential-energy curves between a neutral molecule and the dissociating negative-ion similar to the series of brominated methanes.[12] The position of the dissociating negative-ion potential relative to that of the neutral one is determined by the bond dissociation energy (BD) and the electron affinity (EA) of the halogen atom, X. The value of EA(X)-BD is related to the exothermicity of the thermal electron attachment, and determines the overlap in the Franck–Condon region. The enthalpy for dissociative electron attachment to $ClCH_2CN$, $BrCH_2CN$, and $ICH_2CN$ is extrapolated to be –0.7, 0.3–0.5, and 1.3 eV, respectively.[4] The relative potential-energy curve of the dissociating negative-ion becomes lower with subtitution for the

Table 2. The Ratio of the Intensity of Halide Ions from $BrCH_2CN$ and $ICH_2CN$ Relative to That from $ClCH_2CN$

| | $BrCH_2CN/ClCH_2CN$ | | | $BrCH_2CN/ClCH_2CN$ | $ICH_2CN/ClCH_2CN$ |
|---|---|---|---|---|---|
| T/K | FALP | PRMC | T/K | This work | This work |
| 295 | 4.87 | 5.00(0.5$^{a)}$) | | 4.11$^{b)}$ | 0.19$^{b)}$ |
| 368–386 | 4.79 | | 393 | 4.19 | — |
| | | | 423 | 4.55 | 0.61 |
| 468–476 | 3.69 | | 473 | 4.88 | 1.45 |
| | | | 523 | 4.47 | 2.62 |
| 556 | 2.47 | | | | |
| | | | 573 | 4.71 | 3.77 |

a) The ratio of the rate constant for $ICH_2CN/ClCH_2CN$. b) The value is extrapolated from Fig. 1.

heavier halogen atom. When the halogen atom changes from Cl to Br, the negative-ion state becomes lower and crosses near to the equilibrium position of the neutral potential curve; that is, the overlap in the Franck–Condon region increases. This would cause an increase in the survival probability of the negative-ion against the autodetachment of an electron. This is the reason why the value of the dissociative electron attachment rate for $BrCH_2CN$ is greater than that for $ClCH_2CN$. On the other hand, when the halogen atom is I, the negative-ion state becomes lower and crosses at a shorter internuclear distance than the equilibrium distance of the neutral. This would cause the probability of the transition from the neutral to the negative-ion state to become lower. The activation energy of $ICH_2CN$ is regarded as being the vertical energy at the crossing point.

**Fluorinated Phthalonitriles.** The parent anions were mainly observed for $C_6F_4(CN)_2$. This is the same for $C_6F_5CN$. Only for 1,2-$C_6F_4(CN)_2$, $C_6F_3(CN)_2^-$ was also observed a little. Thermal electron attachment would occur just as for $C_6F_5CN$, and the reaction process would be expressed as follows:

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

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

$$\text{Negative ion} + \mathrm{P}^+ \overset{k_\mathrm{N}}{\rightarrow} \text{Products},$$

where M is the parent molecule, R is the reagent gas, and $P^+$ is a positive ion. The production rate of the parent anions, $k$, can be expressed by substituting the relationships $k_1 = A_1T^{-1/2} \exp(-E_1/RT)$ and $k_{-1} = A_{-1}T \exp(-E_{-1}/RT)$, which are obtained when the absolute reaction rate theory is applied to the two-molecules reaction and the uni-molecular reaction, respectively:

$$k = A_1T^{-1/2}\exp(-E_1RT)/(A_{-1}T\ \exp(-E_{-1}/RT) + A_N). \qquad (2)$$

The intensity of the produced anions increased proportionally with the quantity of the injection of the sample. 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 2 shows an Arrhenius plot based on Eq. 2. The temperature dependence of the production of anions is small under the condition in this study. The electron affinity of $C_6F_4(CN)_2$ is so large that electron detachment from the parent anions can be negligible. The intensity of the parent anion increases in the order 1,3-$C_6F_4(CN)_2^-$ < 1,2-$C_6F_4(CN)_2^-$ < 1,4-$C_6F_4(CN)_2^-$. Because electron detachment ($k_{-1}$) would not occur, the difference would be caused by the rate of the recombination reaction with positive ions ($k_N$). This means that the rate of the recombination reaction would increase in the order 1,4-$C_6F_4(CN)_2^-$< 1,2-$C_6F_4(CN)_2^-$< 1,3-$C_6F_4(CN)^-$. To consider the reactivity with positive ions, we made a Hartree-Fock calculation of $C_6F_4(CN)_2^-$. The 6-31+G basic set was used for the calculation. Ritchie has proposed that the rate of recombination of the nucleophile, $X^-$, with the cation in a given solvent is empirically related with the nucleophilic parameter of $X^-$.[13] Because the nucleophility would be reflected to the charge distribution, we have considered the atomic charge distribution of the anions listed in Table 3. The value of the atomic charge of the C–F for the ortho-site against the C–CN is large, especially at the C–F for the inner ortho-site in 1,3-$C_6F_4(CN)_2^-$. On the other hand, the value is equal for all of the C–Fs in 1,4-$C_6F_4(CN)_2^-$. The atomic charge of the C–F for the ortho-site against the C–CN becomes larger, 1,4-$C_6F_4(CN)_2^-$ (−0.895) < 1,2-$C_6F_4(CN)_2^-$ (−1.085) < 1,3-$C_6F_4(CN)_2^-$ (−2.24). The larger value of the atomic charge means that the excess electron localizes to the atoms. The localization of electrons would cause easy electron transfer, and the rate of recombination with positive ions would become large. This result is coincident with the experimental one.

$C_6F_3(CN)_2^-$ was observed only for 1,2-$C_6F_4(CN)_2$. For detecting this difference, the same calculation for $C_6F_3(CN)_2^-$ was carried out. Two or three kings of $C_6F_3(CN)_2^-$ ions exist for 1,2-

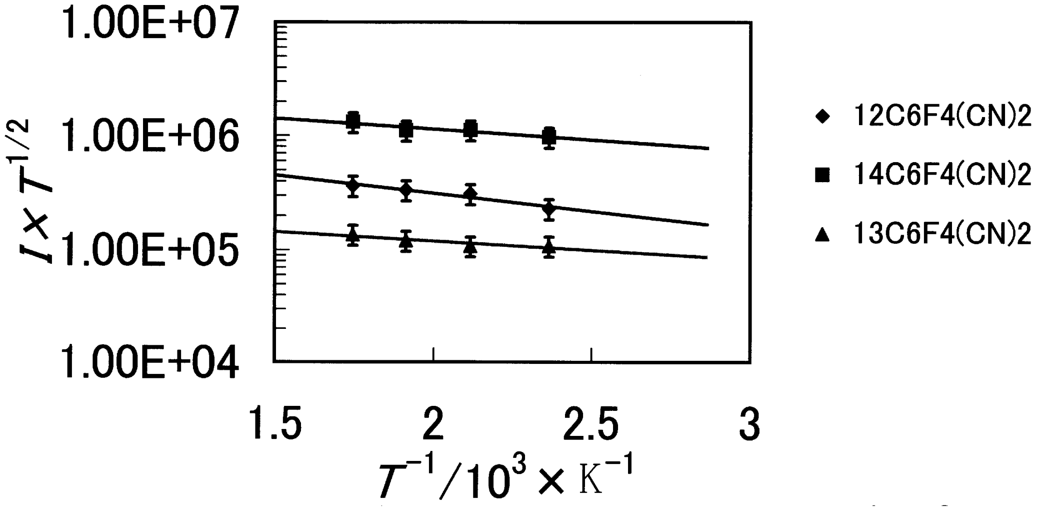

Fig. 2. The temperature dependence of the formation of parent anions for $C_6F_4(CN)_2$. I means ion intensity per $10^{-9}$ mol of the sample. The longitudinal axis is arbitrary unit.

Table 3. Atomic Charge Distribution of $C_6F_4(CN)_2^-$

| | $1,2\text{-}C_6F_4(CN)_2^-$ | | $1,3\text{-}C_6F_4(CN)_2^-$ | | $1,4\text{-}C_6F_4(CN)_2^-$ | |
|---|---|---|---|---|---|---|
| 1C–X[a)] | C: 0.97 | CN:−0.43 | C: 1.60 | CN:−0.07 | C: 1.49 | CN:−0.20 |
| 2C–X[a)] | C: 0.97 | CN:−0.43 | C:−1.88 | F: −0.36 | C:−0.525 | F: −0.37 |
| 3C–X[a)] | C:−0.72 | F: −0.365 | C: 1.60 | CN:−0.07 | C:−0.525 | F: −0.37 |
| 4C–X[a)] | C: 0.43 | F: −0.385 | C:−0.51 | F: −0.38 | C: 1.49 | CN:−0.20 |
| 5C–X[a)] | C: 0.43 | F: −0.385 | C: 0.34 | F: −0.38 | C:−0.525 | F: −0.37 |
| 6C–X[a)] | C:−0.72 | F: −0.365 | C:−0.51 | F: −0.38 | C:−0.525 | F: −0.37 |

a) X = F or CN group

$C_6F_4(CN)_2$ and 1,3-$C_6F_4(CN)_2$, respectively. The structure and atomic charge distribution of all the $C_6F_3(CN)_2^-$ ions were calculated. The atomic charge of the carbon without a fluorine atom was –0.46 and –0.11 for the *ortho*-site and *meta*-site against the C–CN bonds in 1,2-$C_6F_3(CN)_2^-$, –0.69, 0.09, and –1.44 for the outer *ortho*-site, *meta*-site, and inner *ortho*-site against the C–CN bonds in 1,3-$C_6F_3(CN)_2^-$, and –0.71 for 1,4-$C_6F_3(CN)_2^-$, respectively. When the atomic charge of the carbon without a fluorine atom is near 0.0, electron detachment would be difficult and the anion could be detected. 1,2-$C_6F_3(CN)_2^-$ observed in this study would be produced from the cleavage of the C–F bond, which is the *meta*-site against the C–CN bonds. Though $C_6F_3(CN)_2^-$ produced from the cleavage at the *meta*-site could also be produced for 1,3-$C_6F_4(CN)_2$, the anion was not observed. The atomic charge of the carbon at the inner *ortho*-site against the C–CN bonds was –2.36, and as same as 1,3-$C_6F_4(CN)_2^-$, recombination reaction would make it difficult to detect 1,3-$C_6F_3(CN)_2^-$. The results of the HF/6-31+G calculation could explain the reactivity of the anions.

## Conclusion

The temperature dependence for the production of negative ions from $XCH_2CN$ and $C_6F_4(CN)_2$ was studied. Fragment ions were observed at higher temperatures from 1.0 mol% $FCH_2CN$. Only halide ions were produced from the other halogenated acetonitriles. A temperature dependence was observed only for $ICH_2CN$. At 423 K, the intensity of halide ions increased in the order $I^- < Cl^- < Br^-$. These results can be explained by the model of the relative position of the potential curve. The parent anion was mainly observed for $C_6F_4(CN)_2$. The intensity of the parent ions increased in the order 1,3-$C_6F_4(CN)_2^-$ < 1,2-$C_6F_4(CN)_2^-$ < 1,4-$C_6F_4(CN)_2^-$. The difference can be explained by a recombination reaction with positive ions. A simple molecular orbital calculation can explain the reactivity of the anions.

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