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Isomer Effect of the Production of Negative Ions from C_6H_4XY and $C_6H_{10}X_2$ (X, Y = Halogen)

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The temperature dependence of the formation of negative ions from C_6H_4XY (X, Y = Cl, Br, I) and *cyclo*-$C_6H_{10}X_2$ (X = Cl, Br) was studied using negative chemical ionization mass spectrometry. The heavier halide ion was mainly observed for C_6H_4XY. The production rate of halide ions became greater in the order $C_6H_4ClBr \ll C_6H_4ClI < C_6H_4BrI$. The relative production rate of the major ions between isomers is related to the character of the substituted halogen atom in the system. The main observed ion was X^- for $C_6H_{10}X_2$. The production rate of halide ions increased in the order *cyclo-cis*-1,4-$C_6H_{10}Cl_2$ < *cyclo-trans*-1,4-$C_6H_{10}Cl_2$ ~ *cyclo-trans*-1,2-$C_6H_{10}Cl_2$ ≪ *cyclo-trans*-1,2-$C_6H_{10}Br_2$. For *cyclo-trans*-1,2-$C_6H_{10}Br_2$, not only Br^-, but also Br_2^-, was observed. Four-center elimination with rotation of the C–Br bond seemed to occur when Br_2^- was produced from *cyclo-trans*-1,2-$C_6H_{10}Br_2$.

Electron attachment is an important fundamental chemical reaction. Halocarbons have a high electron affinity[1] and some theoretical and experimental studies about electron attachment to C_6H_5X, C_6F_5X, and $C_6H_4X_2$ (X is a halogen atom) have been carried out. For example, time-of-flight mass spectrometry (TOF),[2] the flowing afterglow Langmuir probe method (FALP),[3–4] the electron swarm method (ES),[5] electron capture detector (ECD),[6] atmospheric pressure ionization mass spectrometry (APIMS),[7] the pulse radiolysis microwave cavity method (PRMC),[8] and negative chemical ionization mass spectrometry (NCIMS)[9] have been used to study electron attachment. 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 the ambient gas and the temperature.[2–3] The trend is almost the same for para-$C_6F_4X_2$, though the branching ratio of halide ions is greater for *ortho*-$C_6F_4X_2$.[9] On the other hand, only halide ions were produced from electron attachment to C_6H_5X and *para*-$C_6H_4X_2$.[10] For molecules with heavier halogen atoms, the resonance energy of attachment electrons decreases. This is related to the electron attachment rate constant. The resonance energy also decreases with an increase in the number of halogen atoms. However, there is little information about C_6H_4XY in which two kinds of halogen atoms are substituted.

cyclo-Hexanes have a ring-shaped structure like that of benzenes. Though there have been some studies about the halogenated benzenes mentioned above, there is no report about $C_6H_{10}X_2$ (X is a halogen atom). In this research, we studied the product ions from electron attachment to C_6H_4XY (X, Y = Cl, Br, I) and $C_6H_{10}X_2$ (X = Cl, Br) using NCIMS and analyzed the isomer effect.

Experimental

C_6H_4BrCl (Tokyo-Kasei, purity > 99%), *ortho*-C_6H_4ClI (Tokyo-Kasei, purity > 98%), *meta*-C_6H_4ClI (Tokyo-Kasei, purity > 97%), *para*-C_6H_4ClI (Tokyo-Kasei, purity > 99%), *ortho*-C_6H_4BrI (Tokyo-Kasei, purity > 95%), *meta*-C_6H_4BrI (Tokyo-Kasei, purity > 97%), *para*-C_6H_4BrI (Tokyo-Kasei, purity > 98%), *cyclo*-1,4-$C_6H_{10}Cl_2$ (Tokyo-Kasei, purity > 99%), *cyclo-trans*-1,2-$C_6H_{10}Cl_2$ (Tokyo-Kasei, purity > 96%), *cyclo-trans*-1,2-$C_6H_{10}Br_2$ (Tokyo-Kasei, purity > 96%), and hexane (Wako-Junyaku, purity > 99%) were used as received.

Our experimental apparatus has been described in detail elsewhere.[11] Electrons whose energy is 200 eV are provided from the filament and thermalized by collisions with the reagent gas. Samples are introduced into the ion source through the capillary interface under the collision region where electrons are thermalized, 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 collisions with isobutane, and were not due to an electron transfer from the anion of isobutane. The instrument was tuned using the NCI mass spectra of tris(perfluorobutyl)amine (TPFBA) at 523 K, and the operating 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 as the carrier gas and pumped in at the capillary interface. Samples were diluted with hexane at 1/1000 mol%, 1/5000 mol%, 1/5000 mol%, 1 mol%, 1/10 mol%, and 1/100 mol% for C_6H_4BrCl, C_6H_4ClI, C_6H_4BrI, *cyclo*-1,4-$C_6H_{10}Cl_2$, *cyclo-trans*-1,2-$C_6H_{10}Cl_2$, and *cyclo-trans*-1,2-$C_6H_{10}Br_2$, respectively, and 0.4–1.5 µL of them was injected. A single peak from the sample was observed in a chromatogram with no extraneous peaks or interference. The temperature of the GC column was kept at 423 K for C_6H_4BrCl, 443 K for C_6H_4ClI, and 453 K for C_6H_4BrI and $C_6H_{10}X_2$. The peaks were observed at retention times of about 3.34, 2.92, 2.94, 5.65, 3.01, 3.04, 3.89, 3.46, 3.49, 1.75, 2.0, 1.6, and 2.75 minutes for *ortho*-C_6H_4BrCl, *meta*-C_6H_4BrCl, *para*-C_6H_4BrCl, *ortho*-C_6H_4ClI, *meta*-C_6H_4ClI, *para*-C_6H_4ClI, *ortho*-C_6H_4BrI, *meta*-C_6H_4BrI, *para*-C_6H_4BrI, *cyclo-trans*-1,4-$C_6H_{10}Cl_2$, *cyclo-cis*-1,4-$C_6H_{10}Cl_2$, *cyclo-trans*-1,2-$C_6H_{10}Cl_2$ and *cyclo-trans*-1,2-$C_6H_{10}Br_2$, 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 a personal computer. The ion abundance was obtained from the integrated sums of all the isotopic masses of the ions.

Results and Discussion

C_6H_4XY: For C_6H_4XY, the produced ions were halide ions, X^- and Y^-. The main halide ion was the heavier one. The relative intensities of the ions, X^-/Y^- for each C_6H_4XY, are listed in Table 1. The differences between the exothermicity for the production of anions are also presented. Because the bond-dissociation energies for C_6H_4XY (X, Y = Cl, Br, I) cannot be obtained, those for C_6H_5X (X = Cl, Br, I) were used. The relative ion intensity, Cl^-/I^-, for every C_6H_4ClI is smaller than Cl^-/Br^- and Br^-/I^-, because the difference in the exothermicity of C_6H_4ClI is the largest. Among C_6H_4XI (X = Cl, Br) isomers, X^-/I^- of the *para*-C_6H_4XI is the largest. On the other hand, Cl^-/Br^- of the *meta*-C_6H_4ClBr is the largest among C_6H_4ClBr isomers. The trend concering the electron affinity of the parent anions seems to be different between C_6H_4XI and C_6H_4ClBr.

For dissociative electron attachment to halocarbons, the reaction scheme is written as

$$\mathrm{M} + \mathrm{e}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{M}^{-*} \xrightarrow{k_2} (\mathrm{M}-\mathrm{X}) + \mathrm{X}^- \tag{1}$$

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

where X is a halogen atom and P^+ is a positive ion. We assumed a steady-state treatment for radiolysis in a cell. The concentration of halide ions was presented as

$$[\mathrm{X}^-] = \kappa(k_1 \times k_2/k_{-1})[\mathrm{M}][\mathrm{e}^-]/k_{\mathrm{N'}}/[\mathrm{P}^+] = \kappa k[\mathrm{M}][\mathrm{e}^-]/k_{\mathrm{N'}}\,, \tag{3}$$

where $k_1 \times k_2/k_{-1} = k$ and $k_{\mathrm{N'}}[\mathrm{P}^+] = k_{\mathrm{N}}$. Because the positive ions are provided during the measurement, we can assume that $[\mathrm{P}^+]$ and k_{N} are constant.

By substituting the relationships $k_1 = A_1T^{-1/2}\exp(-E_1/RT)$, $k_{-1} = A_{-1}T\exp(-E_{-1}/RT)$, and $k_2 = A_2T\exp(-E_2/RT)$, the rate is described as follows:

$$k = (A_1A_2/A_{-1})T^{-1/2}\exp\{-(E_1 + E_2 - E_{-1})/RT\}, \tag{4}$$

where κ, depending on the instrument, can be a constant for the same ions produced from the same molecule. Because we can assume that the concentration of electrons is constant during the experimental condition, the Arrehnius parameters can be determined.

The intensity of halide ions was proportional to the injection quantity 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 1 shows an Arrhenius plot based on eq.4 for the main ions produced from *ortho*-C_6H_4XY (X, Y = Cl, Br, I). The production rate of the halide ions became greater in the order $C_6H_4ClBr \ll C_6H_4ClI < C_6H_4BrI$. Thermal electron attachment occurs for C_6H_5I and *para*-$C_6H_4I_2$, though the resonance energy of electrons is larger than thermal for C_6H_5X and *para*-$C_6H_4X_2$ (X = Cl, Br).[10] It is appropriate that thermal electron attachment occurs for C_6H_4XI (X = Cl, Br). This is the reason why the production rate of ions from C_6H_4XI (X = Cl, Br) is greater than that from C_6H_4ClBr. The production rate increases with decreasing temperature. This is explained by the fact that the survival probability of the parent anion[4] and the ion draw-out efficiency of the produced ions change with temperature,[11]

Table 1. The Relative Ion Intensity and the Difference between the Exothermicity for the Production of Anions

			X^-/Y^-	$d(\Delta H)$[a)]/eV	R.I.[b)]
	ortho-		0.029		1.0
C_6H_4ClBr	*meta-*	Cl^-/Br^-	0.050	0.40	0.95
	para-		0.042		0.66
	ortho-		< 0.001		1.0
C_6H_4ClI	*mata-*	Cl^-/I^-	< 0.001	0.78	1.09
	para-		0.001		0.87
	ortho-		0.046		1.0
C_6H_4BrI	*meta-*	Br^-/I^-	0.039	0.38	0.905
	para-		0.067		1.22

a) The difference between the exothermicity for the production of ions. The bond-dissociating energy was used for C_6H_5X except for C_6H_4XY, because the latter were not obtained.

b) The intensity of the major ion of *meta-* or *para*-C_6H_4XY relative to that of *ortho*-C_6H_4XY.

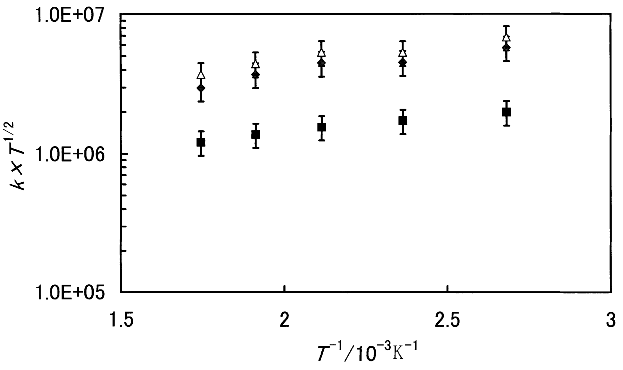

Fig. 1. The temperature dependence of the production rate of the main halide ions from *ortho*-C_6H_4XY (X, Y = Cl, Br, I). The longitudinal axis is arbitrary unit. ■: Br^- produced from *ortho*-C_6H_4ClBr; △ : I^- produced from *ortho*-C_6H_4BrI; ◆: I^- produced from *ortho*-C_6H_4ClI.

similar to fluoro-chloroethanes. The former means that the attached electron delocalizes in the parent anion at higher temperature, which makes it difficult to cleave the carbon–halogen bond. The latter means that ions with high translation energy are not focused as well as those with low energy, and that the translation energy of the ions becomes larger at higher temperature between the same ions produced from the same molecule.

The production rate of the major ions of *meta*- or *para*-C_6H_4XY relative to *ortho*-C_6H_4XY is obtained and presented in the right-hand column of Table 1. For C_6H_4ClX (X = Br, I), the production rate of X^- of *para*-C_6H_4ClX is the least among the three isomers. On the other hand, the production rate of I^- of *meta*-C_6H_4BrI is the least for C_6H_4BrI. The isomer effect between C_6H_4Cl-X (X = Br, I) and C_6H_4Br-I seems to be different. To check the character of the substituted halogen atoms in the system, the Mulliken atomic charge distribution of isomers for C_6H_4Cl and C_6H_4Br radicals produced from dissociative electron attachment was calculated using the B3LYP/6-311+G method. The atomic charge on the isolated carbon atom whose bond with the halogen atom was cleaved, and that on the remaining halogen are listed in Table 2. The fact that the atomic charge on the isolated carbon atom is positive means that the acceptability of the electrons is high. In this case, it is not easy to cleave the carbon-halogen bond. For *para*-C_6H_4Cl and *meta*-C_6H_4Br, this is the case. This corresponds to the experimental results listed in Table 1; that is, the value of R.I. for *para*-C_6H_4ClBr, *para*-C_6H_4ClI, and *meta*-C_6H_4BrI is the smallest among each of the three isomers. It seems that the effect becomes smaller for the cleavage of iodine than bromine by comparing C_6H_4ClBr with C_6H_4ClI. When the electron affinity of the release halogen is lower, the effect of the acceptability of the electrons on the isolated carbon becomes smaller, and the efficiency of the cleavage of the carbon–halogen bond is not so different between the isomers. Comparing halogen atoms, the atomic charge of Cl in C_6H_4Cl is positive, like the H atoms, though that of Br in C_6H_4Br is almost neutral. It seems that chlorine in C_6H_4Cl has a character like the hydrogen atoms.

Table 2. The Mulliken Atomic Charge Distribution of C_6H_4Cl and C_6H_4Br Radicals

		Isolated carbon	Remained halogen
	ortho-	-0.48	0.49
C_6H_4Cl	*meta-*	-0.06	0.49
	para-	0.14	0.64
	ortho-	-0.26	0.06
C_6H_4Br	*mata-*	0.42	0.05
	para-	0.02	0.04

$C_6H_{10}X_2$: Halide ions were produced from electron attachment to $C_6H_{10}X_2$. The production rate of halide ions became greater in the order *cyclo*-*cis*-1,4-$C_6H_{10}Cl_2$ < *cyclo*-*trans*-1,4-$C_6H_{10}Cl_2$ ~ *cyclo*-*trans*-1,2-$C_6H_{10}Cl_2$ ≪ *cyclo*-*trans*-1,2-$C_6H_{10}Br_2$. Figure 2 shows the temperature dependence of the production rate of halide ions. The production rate of halide ions increases with increasing temperature. Br_2^- was also observed for *cyclo*-*trans*-1,2-$C_6H_{10}Br_2$. The formation process of Br_2^- is a dissociative reaction because the intensity of the ion increases with increasing quantity of the sample. The reaction scheme is described as

$$\mathrm{M} + \mathrm{e}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{M}^{-*} \xrightarrow{k_3} (\mathrm{M} - \mathrm{X}_2) + \mathrm{X}_2^- \tag{5}$$

The relative rate of the production of ions is written as

$$\mathrm{k}[\mathrm{Br}_2^-]/k[\mathrm{Br}^-] = A_3/A_2 \exp\{-(E_3-E_2)/RT\}. \tag{6}$$

The relative ion intensity, Br_2^-/Br^-, is plotted in Fig. 3. The branching ratio of Br_2^- increases with decreasing temperature. This is the same trend as that for bromoethylenes. Similar to bromoethylenes[12] and bromochloroetanes,[13] four-center elimination seems to occur for the production of Br_2^-. The fact that the ring of $C_6H_{10}X_2$ is constructed not by the benzene type, but by single bonds, makes the reaction mechanism similar to that of haloalkanes and haloalkenes. The difference between the activation energy for the production of Br^- and that of Br_2^-, (E_3-E_2), is 0.07 eV. The ratio of the Arrhenius parameter for

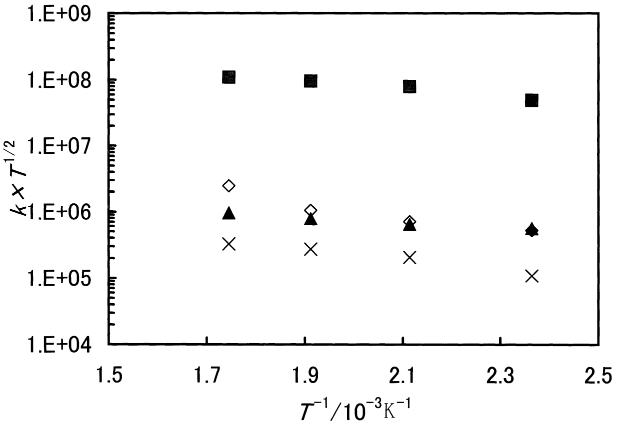

Fig. 2. The temperature dependence of the production rate of the halide ions from *cyclo*-$C_6H_{10}X_2$ (X = Cl, Br). The longitudinal axis is arbitrary unit. ◇: *cyclo*-*trans*-1,2-$C_6H_{10}Cl_2$; ■: *cyclo*-*trans*-1,2-$C_6H_{10}Br_2$; ▲: *cyclo*-*trans*-1,4-$C_6H_{10}Cl_2$; ×: *cyclo*-*cis*-1,4-$C_6H_{10}Cl_2$.

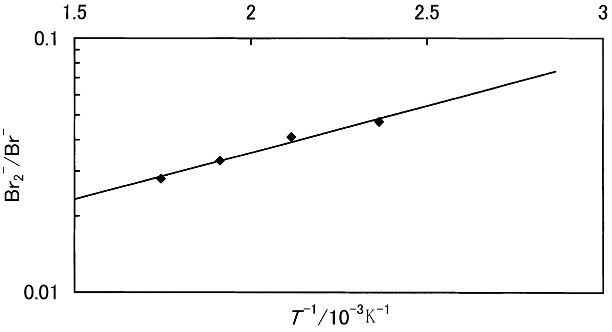

Fig. 3. The temperature dependence of the ratio Br_2^-/Br^- for *cyclo-trans*-1,2-$C_6H_{10}Br_2$.

the formation of Br_2^- and Br^-, A_3/A_2, is 0.0065. Though the activation energy for the formation of Br_2^- is lower than that of Br^-, the ratio of the production of Br_2^- is much lower than that for bromoethylenes[12] at the high-temperature limit. Rotating the C-Br bonds is necessary for *cyclo-trans*-1,2-$C_6H_{10}Br_2$ before the four-center elimination occurs. This is the reason for the lower branching ratio.

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