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Negative Chemical Ionization Mass Spectrometric Studies on Dissociative Electron Attachment Processes of Chloroethylenes and Bromoethylenes

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The temperature dependence of the formation of negative ions from chloroethylenes (*cis*-1,2-$C_2H_2Cl_2$, *trans*-1,2-$C_2H_2Cl_2$, C_2HCl_3, C_2Cl_3F, C_2Cl_4) and bromoethylenes (*cis*-1,2-$C_2H_2Br_2$, *trans*-1,2-$C_2H_2Br_2$, C_2HBr_3, 1,1-$C_2Br_2F_2$) was studied using negative chemical ionization mass spectrometry. The halide ion was observed for all samples. Other fragment anions, $(M-X)^-$ (parent molecule, M, less one halogen atom, X)$^-$ and X_2^- were produced for some samples. The former was observed for *trans*-1,2-$C_2H_2X_2$ and C_2HBr_3, and the latter for 1,2-$C_2H_2Cl_2$, *cis*-1,2-$C_2H_2Br_2$, and C_2HBr_3. The branching ratio of X_2^- and $(M-X)^-$ decreases with increasing the temperature. The branching ratio of X_2^- is considerably different for chloroethylenes and for bromoethylenes.

Electron attachment is an important process of fundamental chemical reactions. Because halocarbons have high electron affinity,[1] it is necessary to study electron attachment reactions of halocarbons. To measure the rate constants of thermal electron attachment reaction to halomethanes and haloethanes, there have been many studies. For example, the electron swarm method (ES),[2] the flowing afterglow Langmuir probe method (FALP),[3] and the pulse-radiolysis microwave cavity technique (PRMC)[4] have been used. The halide ions are produced mainly when thermal electrons attach to these molecules. For brominated hydro- and fluoro-methanes or ethanes, Br_2^- was also observed using the krypton photoionization method,[5] the FALP,[6] and the pulsed electron-beam high-pressure mass spectrometry.[7] Along with the characterization of halomethanes and haloethanes, there are some studies about electron attachment reactions to haloethylenes.

For haloethylenes, electron-transmission spectra,[8] electron-attachment spectra,[8b—10] the electron capture detector (ECD),[11] and the negative chemical ionization mass spectrometry (NCIMS)[12,13] have been used to study electron attachment. From the results of electron-transmission spectra and the electron impact technique, it was found that for fluoroethylenes, the vertical electron attachment energy increases with fluorination.[14] In contrast to fluorination, it was observed that the vertical electron attachment energy to chloroethylenes decreases with chlorination; electron-transmission spectra or electron-attachment spectra were used.[8—10] The temperature dependence of the electron attachment rate to chloroethylenes and $C_2H_2Br_2$ was studied using ECD.[11] From the Arrhenius parameters for the rate constants of electron attachment, one can conclude that electron detachment from the parent negative ion and dissociative reactions will occur. The electron affinities of C_2Cl_4 and C_2HCl_3 have been determined by the temperature dependence of NCIMS.[12,13] However, the temperature dependence of the production ratio relative to the halide ion of other fragment ions has not been studied well. Especially there is little information on bromoethylenes. Why the ratio of the fragment ions produced from dissociative reactions varies from one molecule to another is not explained well.

In this research, we have studied the ions produced from electron attachment of chloroethylenes or bromoethylenes using the NCIMS method at 323—573 K. Even though the instrument is constructed for analytical use, we can measure the intensity of ions produced from chloroethylenes or bromoethylenes and their temperature dependence. We have also tried to explain the differences of the branching ratio of the fragment ions with the results of simple calculations of molecular orbitals.

Experimental

Cis-1,2-$C_2H_2Cl_2$ (Tokyo-Kasei, purity > 99%), *trans*-1,2-$C_2H_2Cl_2$ (Tokyo-Kasei, purity > 99%), C_2HCl_3 (Wako-Junyaku, purity > 98%), C_2Cl_4 (Wako-Junyaku, purity > 99%), 1,2-$C_2H_2Br_2$ (mixture of *cis*-1,2- and *trans*-1,2-, Tokyo-Kasei, purity > 98%), C_2HBr_3 (Tokyo-Kasei, purity > 97%), 1,1-$C_2Br_2F_2$ (PCR incorporated, purity > 97%), C_2Cl_3F (PCR incorporated, purity > 97%), and hexane (Wako-Junyaku, purity > 99%) were used as received.

Our experimental apparatus has been described in detail elsewhere.[15] 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. The instrument was tuned using the NCI 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. Samples were diluted with hexane in 1/500—1/10 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 interference. The temperature of the GC column was kept at 50 °C for *cis*-1,2-$C_2H_2Cl_2$, *trans*-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_3F, and at 80 °C for C_2Cl_4. The peaks were observed at the retention times of about 2.0, 1.6, 4.3, 2.3, and 4.0 min, respectively. Also, the temperature of the column was kept at 50 °C for *cis*-1,2-$C_2H_2Br_2$, *trans*-1,2-$C_2H_2Br_2$, and 1,1-$C_2Br_2F_2$, and at 100 °C for C_2HBr_3. The peaks were observed at about 6.7, 4.7, 2.3, and 5.0 min, respectively.

The temperature of the ion source was controlled by computer. When the temperature was changed, the setting was finished in 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.

Results and Discussion

Kinetics: In all cases, the halide ion was observed mainly. Along with the halide ion, the negative ion of halogen molecule X_2^-, $(M–X)^-$ (parent molecule, M, less one halogen atom, X)$^-$, and the parent negative ion M^- have been observed for some molecules. Christophorou et al. studied electron-attachment spectra of chloroethylenes (*cis*-1,2-$C_2H_2Cl_2$, *trans*-1,2-$C_2H_2Cl_2$, 1,1-$C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4) under low energy (0—10 eV) electron impact with a time-of-flight mass spectrometer.[9] For 1,2-$C_2H_2Cl_2$, most of the fragment ions are produced when the energy of electrons is near 1 eV. On the other hand, both the parent negative ions and the fragment ions are produced by thermal electron attachment for other chloroethylenes. Wentworth et al. have shown that the resonant state of the parent anion is the excited repulsive state for 1,2-$C_2H_2Cl_2$ and the bound state for other chloroethylenes.[11] When electrons attach to the molecule, the excited repulsive state or the vibrationally excited state of the parent negative ion, M^{-*}, is produced and the subsequent dissociation occurs. Wentworth et al. have determined that the electron affinity of C_2HCl_3 and C_2Cl_4 are 0.3 and 0.5 eV, respectively.[12] Because the electron affinity of the parent molecule and M–X will be smaller than that of halogen atom or halogen molecule, electron detachment will occur from the parent molecule anions and $(M–X)^-$. The intensity of Cl^- produced from electron attachment to C_2Cl_4 is more than ten times larger than that from electron attachment to 1,2-$C_2H_2Cl_2$. Electron-attachment spectra of 1,2-$C_2H_2Cl_2$ have shown that the intensity of Cl^- at which electron's energy is near thermal is about ten times smaller than the maximum intensity of Cl^-.[9,10] If the integral of the intensity of Cl^- against the overall electron energy is almost the same for chloroethylenes, the ratio between the intensity at which electron's energy is near thermal and the maximum intensity will reflect the relative intensity of ions produced from thermal electron attachment. The energy of the attaching electrons seems to be almost thermal. Though electron-attachment spectra or electronic absorption spectra have not been obtained for bromoethylenes, the peak energy of electrons that attach to bromoethylenes will be lower than the case of chloroethylenes. By the results in this study and the electron attachment study, haloethylenes will react with electrons as follows:

$$\mathrm{M} + \mathrm{e}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M}^{-*} \xrightarrow{k_2} \mathrm{X}^- + \mathrm{M{-}X}$$

$$\xrightarrow{k_3} \mathrm{X_2}^- + \mathrm{M{-}X_2}$$

$$\xrightarrow{k_4} \mathrm{X} + (\mathrm{M{-}X})^-$$

$$(\mathrm{M{-}X})^- \xrightarrow{k_5} \mathrm{M{-}X} + \mathrm{e}^-$$

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

where P^+ is a positive ion.

The sample gas diffuses evenly in the ion source from the capillary interface. Electrons are provided at a constant rate in the ion source all the time. We assumed a steady state treatment as for radiolysis in a cell. The above reaction schemes lead to the following expressions:

$$[\mathrm{M}^{-*}] = \varkappa \frac{k_1}{k_{-1} + k_2 + k_3 + k_4 + k_N} [\mathrm{M}][\mathrm{e}^-] \tag{1}$$

$$[\mathrm{X}^-] = \varkappa \frac{k_1 k_2}{k_{-1} + k_2 + k_3 + k_4 + k_N} \times \frac{[\mathrm{M}][\mathrm{e}^-]}{k_N} \tag{2}$$

$$[\mathrm{X_2}^-] = \varkappa \frac{k_1 k_3}{k_{-1} + k_2 + k_3 + k_4 + k_N} \times \frac{[\mathrm{M}][\mathrm{e}^-]}{k_N} \tag{3}$$

$$[(\mathrm{M{-}X})^-] = \varkappa \frac{k_1 k_4}{k_{-1} + k_2 + k_3 + k_4 + k_N} \times \frac{[\mathrm{M}][\mathrm{e}^-]}{k_5 + k_N} \tag{4}$$

When electrons whose energy is 200 eV are thermalized by collision with isobutane, positive ions of isobutane are produced in high concentration. Because the concentration of positive ions is much larger than that of negative ions, we can assume $[P^+]$ constant during the measurement and $k_{N'}[P^+] = k_N = A_N$ = a constant. Though $k_{N'}$ will be different for each anion, k_N values are assumed to be of almost the same order because of higher concentration of positive ions. $\varkappa$ 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. If measurements are carried out with the same instrument settings, the ion lens and mass spectrometer transmission efficiencies, or ion detection efficiency will be the same for all samples. But the ion draw-out efficiency would be different for the ion and sample, when high-energy ions would be produced and they would not be focused as well as low-energy ions.[5,15]

From the results of Christophorou's study, the branching ratio of Cl_2^- and $(M–Cl)^-$ are 0.16 and 0.03 for *cis*-1,2-$C_2H_2Cl_2$, 0.14 and 0.07 for *trans*-1,2-$C_2H_2Cl_2$, 0.002 and 0.001 for 1,1-$C_2H_2Cl_2$, and 0.0095 and 0.0014 for C_2HCl_3. For C_2Cl_4, $C_2Cl_3^-$ was not observed, but the parent ion $C_2Cl_4^-$ was detected. The branching ratios of Cl_2^- and

$C_2Cl_4^-$ are 0.0042 and 0.041, respectively. If we can neglect the production of ions whose branching ratio is smaller than 0.01, $k_3 = k_4 = 0$ for 1,1-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4. From the results of the electron attachment study, the parent negative ions are produced by thermal electron attachment and the fragment negative ions, Cl^- and Cl_2^- are observed at which electron energy is nearly thermal for 1,1-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4.[9,10] Wentworth et al. have shown that the ground state of the anion is the bound state.[11] These results mean that both dissociative reaction and detachment reaction occur from the parent anion. We can assume $k_3 = k_4 = 0$ and $k_2 + k_{-1} > k_N$ for 1,1-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4. On the other hand, Cl^-, Cl_2^-, and $(M\text{–}Cl)^-$ are observed when electrons whose energy is near 1 eV attach to *cis*-1,2-$C_2H_2Cl_2$ and *trans*-1,2-$C_2H_2Cl_2$.[9,10] The direct dissociation, that is, where the resonant state is the excited repulsive state, will occur for them.[11] We can assume $k_2 + k_3 + k_4 > k_N$ for *cis*-$C_2H_2Cl_2$ and *trans*-1,2-$C_2H_2Cl_2$. The right side of equations. 1—4 can be written as $\varkappa k[M][e^-]$ (k is the rate constant for the production of each negative ion). For bromoethylenes, thermal electron attachment reactions will occur in the same way as for chloroethylenes. By substituting the relationships $k_1 = A_1T^{-1/2}\exp(-E_1/RT)$, $k_{-1} = A_{-1}T\exp(-E_{-1}/RT)$, $k_2 = A_2T\exp(-E_2/RT)$, $k_3 = A_3T\exp(-E_3/RT)$, $k_4 = A_4T\exp(-E_4/RT)$, $k_5 = A_5T\exp(-E_5/RT)$, and with those assumptions, the rates will be described as follows in this study:

C_2HCl_3 and C_2Cl_4 :

$$k([M^-]) = A_1/A \times T^{-3/2}\exp(-E_1/RT) \qquad (5)$$

$$k([Cl^-]) = A_1A_2/A/A_N \times T^{-1/2}\exp(-(E_1+E_2)/RT) \qquad (6)$$

$$A = A_{-1}\exp(-E_{-1}/RT) + A_2\exp(-E_2/RT)$$

1,2-$C_2H_2Cl_2$ and Bromoethylenes :

$$k([X^-]) = A_1A_2/\Sigma\{A_x\exp(-E_x/RT)\} \\ /A_N \times T^{-1/2}\exp(-(E_1+E_2)/RT)$$

$$k([X_2^-]) = A_1A_3/\Sigma\{A_x\exp(-E_x/RT)\} \\ /A_N \times T^{-1/2}\exp(-(E_1+E_3)/RT)$$

$$k([(M\text{–}X)^-]) = A_1A_4/\Sigma\{A_x\exp(-E_x/RT)\} \\ /\{A_5T\exp(-E_5/RT)+A_N\} \times T^{-1/2}\exp(-(E_1+E_4)/RT)$$

$$x = 2 \text{ for } X^-,\ x = 3 \text{ for } X_2^-,\ \text{and } x = 4 \text{ for } (M\text{–}X)^- \qquad (7)$$

$$k([X^-])/k([X_2^-]) = A_2/A_3\exp(-(E_2-E_3)/RT) \qquad (8)$$

Chloroethylenes: The concentration of the samples was 1/10 mol% for *cis*-1,2-$C_2H_2Cl_2$ and *trans*-1,2-$C_2H_2Cl_2$, 1/100 mol% for C_2HCl_3 and C_2Cl_3F, and 1/400 mol% for C_2Cl_4. 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 by the least-squares method and converted to the rate per 10^{-9} mol of the sample. The temperature was changed and the intensity of the produced ion was measured by the same method. The converted relative rates are listed in Table 1.

The abundant ion was Cl^-. The molecular negative ions for *cis*-1,2-$C_2H_2Cl_2$ and *trans*-1,2-$C_2H_2Cl_2$ were observed. $(M\text{–}Cl)^-$ for *trans*-1,2-$C_2H_2Cl_2$ under 373 K, and the parent negative ion for C_2Cl_4 at 323 K were also observed. These results show good agreement with Christophorou's,[9] though we could not observe $(M\text{–}Cl)^-$ for *cis*-1,2-$C_2H_2Cl_2$. The parent negative ions were observed for C_2Cl_4, not for C_2HCl_3 or C_2Cl_3F in this work, though Wentworth et al. have observed both $C_2HCl_3^-$ and $C_2Cl_4^-$ using NCIMS.[11] When electrons attach to the molecule, the distribution of the vibrational energy of the negative-state of the parent molecule is related with the temperature. If the pressure of the ambient gas is high enough for gas molecules to collide with the parent anions which have vibrational excited energy, the internal energy of the parent anions will become lower and the parent anions can survive without electron detachment. If the pressure of the ambient gas is not sufficient for deexcitation of parent anions, electron detachment from the parent anions which have vibrational excited energy will occur. In this study, the pressure of the ambient gas was about 3×10^{-5}

Table 1. The Temperature Dependence of the Negative Ion Formation Ratio for Chloroethylenes

		C_2Cl_4		C_2HCl_3		C_2Cl_3F	c-1,2-$C_2H_2Cl_2$		t-1,2-$C_2H_2Cl_2$	
		Int.[a)]	R[b)]	Int.[a)]	R[b)]	Int.[a)]	Int.[a)]	R[b)]	Int.[a)]	R[b)]
573 K	Cl^-	4.64e6		1.72e6		1.95e6	1.33e5		1.42e5	
	Cl_2^-						>0.90e4	<14.8	1.00e4	14.2
523 K	Cl^-	5.44e6		1.92e6		1.92e6	1.66e5		1.72e5	
	Cl_2^-						1.33e4	12.5	1.37e4	12.5
473 K	Cl^-	5.96e6		2.05e6		2.04e6	1.84e5		1.75e5	
	Cl_2^-						1.84e4	10.0	1.58e4	11.1
423 K	Cl^-	6.95e6		2.07e6		2.08e6	2.23e5		1.95e5	
	Cl_2^-						2.25e4	9.9	1.90e4	10.3
373 K	Cl^-	6.94e6		2.22e6		2.24e6	3.04e5		2.25e5	
	Cl_2^-						3.30e4	9.2	2.25e4	10.0
323 K	Cl^-	7.02e6		2.26e6			3.70e5		2.20e5	
	Cl_2^-	2.95e4[c)]	238[c)]	2.15e4[c)]	105[c)]		3.70e4	10.0	2.20e4	10.0

a) Int. is the intensity of the produced ion per 10^{-9} mol of the sample. The intensity is arbitrary unit. b) R is the ratio of Cl^-/Cl_2^-.
c) This is estimated by using the data of Ref. 4.

Torr (1 Torr = 133.322 Pa) and not high enough to cool down the vibrationally excited parent ions. On the other hand, Wentworth et al. studied at the case in which the pressure of the reagent gas was 0.85 Torr which was sufficient to thermalize the excited parent anions. This is one difference between this work and Wentworth's study. The electron detachment rate, k_{-1}, is too large to detect the parent negative ion of C_2HCl_3 in our condition.

The abundance of Cl^- shows a little decrease with increasing the temperature. Especially for *cis*-1,2-$C_2H_2Cl_2$, the decreasing rate is larger. Sunagawa et al. suggested a model: in the $CHBr_3$ molecule, the initial electron attachment occurs in the negative-ion state in which the CBr_3 deformation mode is vibrationally excited, and the subsequent dissociation occurs in the C–Br stretching mode.[17] Although the CBr_3 deformation mode in the negative-ion of the $CHBr_3$ molecule and the deformation mode of the negative ion of chloroethylenes may not be the same, the latter will behave like the former. When electrons attach to the molecule, the excess electron in the deformation mode of M^{-*} localizes to one of the C–Cl bonds and the cleavage of the bond occurs. Sunagawa et al. suggested that, in the electron attachment to $CHCl_3$, the attachment to the local CCl_3 group in the virationally excited state is enhanced at an elevated temperature.[17] At higher temperatures, the excess electron localizes in the deformation mode. This will cause the transition rate of the deformation mode of M^{-*} to the antibonding C–Cl orbital to become smaller, and the rate of formation of the halide ions to become lower. For *cis*-1,2-$C_2H_2Cl_2$, this effect is larger. There is no difference between C_2HCl_3 and C_2Cl_3F for the kind of produced ions and the intensity of ions. In this case, there is no effect of fluorination.

There are two processes for the production of the molecular negative ion. One is that the halide ion abstracts a halogen atom from the parent molecule or radical and another is a dissociative reaction of the negative parent ion. When the concentration of the parent molecule is high enough for occurrence of ion-molecule reactions, the molecular negative ion will be produced from an abstraction reaction. As written in another paper,[15] if a dissociative reaction occurs, the abundance of Cl_2^- is proportional to the injection quantity of the parent molecule and the branching ratio of Cl_2^- is constant. On the contrary, if abstraction occurs, the abundance of Cl_2^- is proportional to the square of the injection quantity of the parent molecule. In the cases of *cis*-1,2-$C_2H_2Cl_2$ and *trans*-1,2-$C_2H_2Cl_2$, the abundance of Cl_2^- is proportional to the injection quantity of the parent molecule and as shown in Table 1, the ratio Cl^-/Cl_2^- can be determined at each temperature. For chloroethylenes, Cl_2^- is produced from dissociative electron attachment.

Though the branching ratio of Cl_2^- for C_2HCl_3 and C_2Cl_4 is small, the intensity of Cl^- for them is many times larger than that for 1,2-$C_2H_2Cl_2$. Because Christophorou et al. have shown the relative intensity Cl_2^-/Cl^- at 333 K,[9] we can estimate the intensity of Cl_2^- for C_2HCl_3 and C_2Cl_4 at 323 K. The estimated result is also shown in Table 1. The intensity of Cl_2^- for all chloroethylenes is nearly the same. Figure 1 shows the temperature dependence of the relative ratio of the production of Cl^- and Cl_2^- for 1,2-$C_2H_2Cl_2$. For both *cis*- and *trans*-1,2-$C_2H_2Cl_2$, the relative ratio Cl^-/Cl_2^- is almost the same for the temperature variations. The difference of the activation energy for the production of Cl^- and that of Cl_2^-, (E_2-E_3) is 0.02 eV and the Arrhenius parameter for the formation of Cl^- is twenty times larger than that of Cl_2^-. Because the *A*-factor represents the ratio of the partition function of the transition state and the reactant, A_2/A_3 means the ratio of the partition function of the transition state of Cl^- production and that of Cl_2^- production. These will show that the mechanism of production of Cl_2^- would be almost the same for both *cis*- and *trans*-1,2-$C_2H_2Cl_2$.

Bromoethylenes: The concentration of the samples was 1/100 mol% for *cis*-1,2-$C_2H_2Br_2$ and *trans*-1,2-$C_2H_2Br_2$, 1/400 mol% for 1,1-$C_2Br_2F_2$, and 1/500 mol% for C_2HBr_3. 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 method and converted to the rate per 10^{-9} mol of the sample. The temperature was changed and the intensity of the produced ion was measured by the same method. The converted relative rates are listed in Table 2. *Cis*-1,2-$C_2H_2Br_2$ and *trans*-

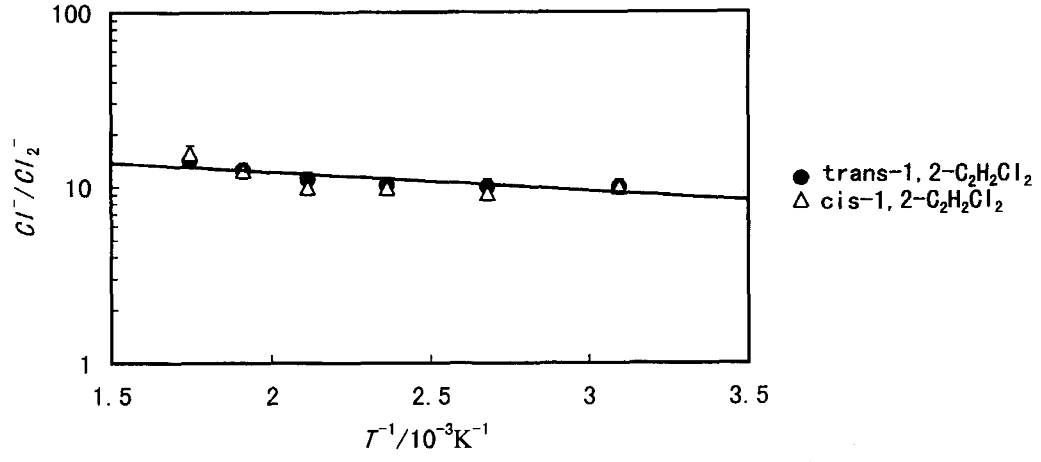

Fig. 1. The temperature dependence of the ratio Cl^-/Cl_2^- for 1,2-$C_2H_2Cl_2$.

Table 2. The Temperature Dependence of the Negative Ion Formation Ratio for Bromoethylenes

		C_2HBr_3		c-1,2-$C_2H_2Br_2$		t-1,2-$C_2H_2Br_2$		1,1-$C_2Br_2F_2$	
		Int.[a)]	B.R.[b)]	Int.[a)]	B.R.[b)]	Int.[a)]	B.R.[b)]	Int.[a)]	B.R.[b)]
573 K	Br^-	5.10e6	0.55	6.58e5	0.42	1.32e6	1.00	7.59e6	1.00
	Br_2^-	4.20e6	0.45	9.23e5	0.58	—		—	
523 K	Br^-	5.58e6	0.53	7.02e5	0.394	1.62e6	1.00	9.41e6	1.00
	Br_2^-	4.98e6	0.47	1.08e6	0.606	—		—	
473 K	Br^-	6.30e6	0.504	6.70e5	0.374	1.67e6	1.00	1.00e7	1.00
	Br_2^-	6.20e6	0.496	1.12e6	0.636	—		—	
423 K	Br^-	8.30e6	0.45	7.20e5	0.365	2.17e6	0.95	1.44e7	1.00
	Br_2^-	9.36e6	0.50	1.25e6	0.635	—		—	
	$(M–Br)^-$	9.00e4	0.05	—		1.00e5	0.05	—	
373 K	Br^-	8.26e6	0.42	7.20e5	0.365	2.21e6	0.89	1.97e7	1.00
	Br_2^-	1.02e7	0.52	1.25e6	0.635	—		—	
	$(M–Br)^-$	1.20e5	0.06	—		2.66e5	0.11	—	
323 K	Br^-			7.10e5	0.33	2.66e6	0.86		
	Br_2^-			1.42e6	0.67	—			
	$(M–Br)^-$			—		4.30e5	0.14		

a) Int. is the intensity of the produced ion per 10^{-9} mol of the sample. The intensity is arbitrary unit. b) B.R. is the branching ratio of the negative ions.

1,2-$C_2H_2Br_2$ were a mixed sample. Using the gas chromatograph, we could differentiate from *cis*-1,2-$C_2H_2Br_2$ and *trans*-1,2-$C_2H_2Br_2$. Because the peak intensity cannot reflect the mixed ratio correctly, we have no idea of the ratio. For all samples, Br^- was observed. The molecular negative ions for *cis*-1,2-$C_2H_2Br_2$ and C_2HBr_3, $(M–Br)^-$ for *trans*-1,2-$C_2H_2Br_2$ and C_2HBr_3 under 423 K were also observed. The abundance of Br^- and Br_2^- shows a little decrease with increasing the temperature, except for Br^- of *cis*-1,2-$C_2H_2Br_2$. Compared with *cis*- and *trans*-1,2-$C_2H_2X_2$, $(M–X)^-$ was observed only for *trans*-1,2-$C_2H_2X_2$. The fact that hydrogen atoms are away from each other will be effective for the production of $(M–X)^-$. For trihaloethylenes, $(M–X)^-$ was produced for C_2HBr_3 but not for C_2HCl_3. The difference of the branching ratio of $(M–X)^-$ will be caused by the difference of electron affinity of the M–X radical. The intensity of $(M–X)^-$ decreases with increasing the temperature. Electron detachment from $(M–X)^-$ will occur.

The process for the production of Br_2^- is a dissociative reaction for the same reason as explained for chloroethylenes. The rate of the formation of Br_2^- increases with decreasing the temperature. Figure 2 shows the temperature dependence of the relative ratio of the production of Br^- and Br_2^- for *cis*-1,2-$C_2H_2Br_2$ and C_2HBr_3. Around room temperature, the ratio for *cis*-1,2-$C_2H_2Br_2$ is the same as that for C_2HBr_3, and the yield of Br_2^- is twice that of Br^-. The difference between the activation energy of the production of Br^- and that of Br_2^-, (E_2-E_3), is 0.01 eV and 0.036 eV for *cis*-1,2-$C_2H_2Br_2$ and C_2HBr_3, respectively. The ratio of the Arrhenius parameter for the formation of Br^- and Br_2^-, A_2/A_3, is 0.92 and 1.97 for *cis*-1,2-$C_2H_2Br_2$ and C_2HBr_3, respectively. From the ratio of the *A*-factor for *cis*-1,2-$C_2H_2Br_2$, the partition function of the transition state of the production of Br_2^- is larger than that of Br^-.

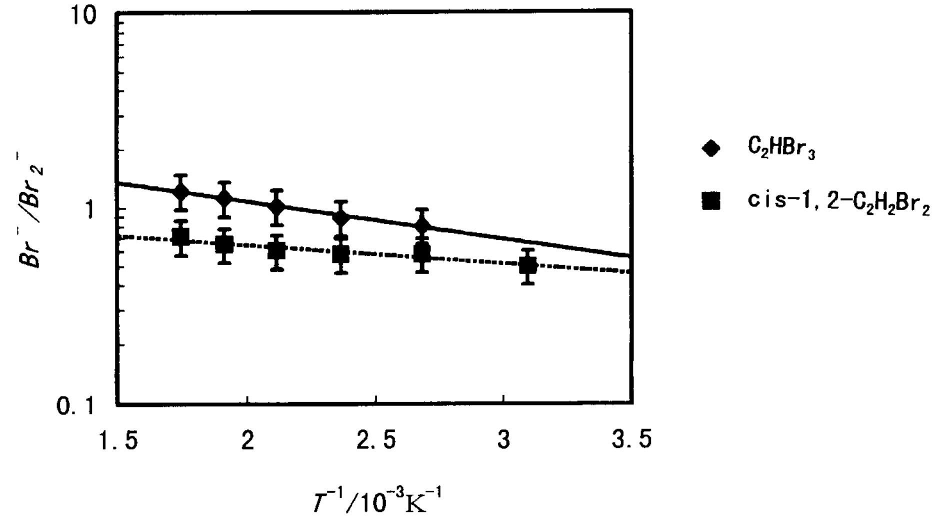

Fig. 2. The temperature dependence of the ratio Br^-/Br_2^- for *cis*-1,2-$C_2H_2Br_2$ and C_2HBr_3.

This is different from chloroethylenes. Another difference between chloroethylenes and bromoethylenes lies in the fact that the molecular negative ions were produced for *trans*-1,2-$C_2H_2Cl_2$ and C_2HBr_3 but not for *trans*-1,2-$C_2H_2Br_2$ and C_2HCl_3. These results suggest that the reaction mechanism of the formation of $X_2{}^-$ is different for chloroethylenes and for bromoethylenes. When the excess vibrational energy of the parent anion is provided to the transition state, leading to the formation of the molecular negative ion, $X_2{}^-$ will be produced. Because the activation energy of the formation of $X_2{}^-$ is lower than that of X^-, the excess energy necessary to produce the transition state leading to the formation of $X_2{}^-$ is low, especially for C_2HBr_3. With increasing the temperature, the excess energy will be distributed in a wide range of vibrational states. That will make it difficult to produce the transition state and this is the reason why the production of $X_2{}^-$ decreases with increasing the temperature. The difference between chloroethylenes and bromoethylenes will be caused by the difference of the transition states.

Molecular Orbital Calculation: To confirm the difference of the branching ratio of $(M–X)^-$, the atomic charge distribution of $(M–X)^-$ is calculated on 1,2-$C_2H_2X_2$, C_2HX_3, and C_2Cl_4 at the Hartree–Fock (HF) level of the theory. The 6-31+G(d,p) and 6-311+G(d,p) basis sets were used for chloroethylenes and bromoethylenes, respectively. The calculation was carried out using the Gaussian 94 program on Silicon Graphics Indy with R4600PC. The calculated atomic charge distribution in $(M–X)^-$ is listed in Table 3. Because there are three types of $(M–X)^-$ for trihaloethylenes, the atomic charge of all of them is shown. The atomic charge of the halogen atom at the *trans*-site of the cleaved bond is larger than that of the halogen atom at the *cis*-site. When the excess electron localizes at the farther site of the cleaved bond, it will be difficult to remove. The localization of the excess electron at the halogen atom at the *trans*-site of the cleaved bond makes electron detachment from $(M–X)^-$ difficult. This causes the branching ratio of $(M–X)^-$ to be larger and gives a higher value of electron affinity of the M–X radical. The branching ratio of $(M–X)^-$ is larger when the atomic charge of the halogen atom relative to that of the isolated carbon is larger. These results correspond with the experimental ones.

From the results of ab initio calculation study of unimolecular dissociative HCl elimination reaction of di- and trichloroethylene, there exist three types of paths: the three- and the four-center eliminations and the elimination through the isomers produced from the H or Cl migration reactions.[18] We can also assume the same types of paths for $X_2{}^-$ elimination from the parent anion. For 1,2-$C_2H_2X_2$, the three-center elimination cannot occur and the four-center elimination is available only for *cis*-1,2-$C_2H_2X_2$. The only path for $X_2{}^-$ elimination from *trans*-1,2-$C_2H_2X_2$ is through the isomer produced from the H or halogen atom migration. The H atom migration leads to the 1,2-dihaloethylidene anion and the four-center-like elimination will occur. The halogen atom migration leads to the 2,2-dihaloethylidene anion and the three-center-like elimination will occur. We have tried to optimize the structure of the intermediates, the 1,2-dihaloethylidene anion and the 2,2-dihaloethylidene anion at the Moller–Plesset second order perturbation method (MP2) level of the theory, with the same basis sets as used before. For the 2,2-dibromoethylidene anion, there were no optimized structures. Only *cis*-type 1,2-dibromoethylidene anion could be optimized. It seems to be difficult to eliminate $Br_2{}^-$ from *trans*-1,2-$C_2H_2Br_2{}^-$. This is the reason why $Br_2{}^-$ is not observed from *trans*-1,2-$C_2H_2Br_2{}^-$. On the other hand, not only *cis*-type 1,2-dichloroethylidene anion but also *trans*-type 2,2-dichloroethylidene anion could be optimized and the 2,2-dichloroethylidene anion has the lower energy. This means that, for *trans*-1,2-$C_2H_2Cl_2{}^-$, the elimination through 2,2-dichloroethylidene anions will occur. For *cis*-1,2-$C_2H_2Cl_2$, the Cl atom migration and the rotation around C–C axis would occur simultaneously. Because the Cl atom migration means the cleavage of the carbon–halogen bond,

Table 3. The Atomic Charge Distribution and the Branching Ratio of $(M–X)^-$

	Atomic charge distribution[a]			B.R.[b]
	X	C[c]	X/C	
cis-1,2-C_2H_2Cl	−0.095[d]	−0.597	0.159	0.03[f]
trans-1,2-C_2H_2Cl	−0.381[e]	−0.630	0.605	0.07[f]
C_2HCl_2 *trans*-	−0.144[d]	−0.898	0.160	0.0014[f]
$Cl_2C{=}CH$	−0.214[e], 0.022[d]	−0.790	0.271, −0.028	
cis-	−0.287[e]	−0.669	0.429	
C_2Cl_3	−0.155[e], 0.019[d]	−1.023	0.152, −0.019	—
cis-1,2-C_2H_2Br	−0.298[d]	−0.514	0.580	—
trans-1,2-C_2H_2Br	−0.460[e]	−0.408	1.127	0.107[g]
C_2HBr_2 *trans*-	−0.255[d]	−0.182	1.401	0.061[g]
$Br_2C{=}CH$	−0.370[e], −0.250[d]	−0.360	1.028, 0.694	
cis-	−0.378[e]	−0.151	2.503	

a) Calculated at the HF/6-31+G(d,p) and the HF/6-311+G(d,p) level of the theory for chloroethylenes and bromoethylenes. b) B.R. is the branching ratio of $(M–X)^-$. c) The atomic charge of the isolated carbon. d) The atomic charge of the halogen atom at the *cis*-site of the cleaved bond. e) The atomic charge of the halogen atom at the *trans*-site of the cleaved bond. f) Ref. 4 at 333 K. g) This work at 373 K.

Cl^- and Cl_2^- are produced through the same process. This is a coincidence with the fact that electron attachment spectra of the Cl^- formation and the Cl_2^- formation are almost the same for 1,2-$C_2H_2Cl_2$. The transition state of the four-center elimination for *cis*-$C_2H_2X_2^-$ could also be optimized. Energy of the 1,2-dihaloethylidene anion is larger than that of the four-center configuration. The four-center elimination will be the main path to produce Br_2^- for *cis*-$C_2H_2Br_2^-$.

Because the branching ratio of Cl_2^- is smaller for 1,1-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4, the three- and the four-center eliminations would not occur for them. The same mechanism as that for 1,2-$C_2H_2Cl_2$, the elimination through the isomer produced from the Cl atom migration, would occur when Cl_2^- is produced from other chloroethylenes. The motion to produce the Cl atom migration will be hindered by chlorination and that will make the branching ratio of Cl_2^- smaller for C_2HCl_3. Because the motion to produce the four-center elimination will not be hindered by bromination, the branching ratio of Br_2^- for C_2HBr_3 is larger than C_2HCl_3. These assumptions fit the experimental findings. It can be considered that the elimination through 2,2-chloroethylidene produced from the Cl atom migration and the four-center elimination may occur for the formation of the halogen molecular anion from chloroethylenes and bromoethylenes, respectively. More accurate theoretical study including the reaction path is necessary to further elucidate the mechanism of the production of the halogen molecular anion from haloethylenes.

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