Negative Chemical Ionization Mass Spectrometric Study on the Dissociative Electron Attachment to Halogenated Ethane

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The temperature dependence for the formation of negative ions from C\textsubscript{3}Br\textsubscript{3}C-BrCl\textsubscript{2}, FCIBrC-BrCl\textsubscript{2}, and ClBr\textsubscript{2}C-CF\textsubscript{3} was studied using negative chemical ionization mass spectrometry. Halide ions and halogen molecular anions were observed. The intensity ratios between the halide ions and halogen molecular anions were almost equal to F\textsubscript{3}BrC-BrF\textsubscript{2}. Halogen molecular anions are produced from halogen atoms presented by each C atom: the four-center elimination. The temperature dependence of the ion intensity ratios, Br\textsuperscript{-}/Cl\textsuperscript{-} and Br\textsuperscript{-}/BrCl\textsuperscript{-}, suggests that the strength of the bonding energy of the C-Cl relative to C-Br increases in the order of ClBr\textsubscript{3}C-BrCl\textsubscript{2}<FCIBrC-BrCl\textsubscript{2} < ClBr\textsubscript{2}C-CF\textsubscript{3}.

1. Introduction

Electron attachment is an important and fundamental reaction process for radiation chemistry, plasma chemistry, ion chemistry and so on. Halocarbons have high electron affinities\textsuperscript{1} and many studies on electron attachment to halocarbons have been reported for CF\textsubscript{x}X\textsubscript{1-x} and CH\textsubscript{x}X\textsubscript{1-x} (X=Cl, Br, I).\textsuperscript{2} However, there is little information about molecules that have more than two types of halogen atoms. For CBrCl\textsubscript{3} and CBr\textsubscript{2}Cl\textsubscript{2}, we studied the negative ions produced from electron attachment using chemical ionization mass spectrometry (CIMS).\textsuperscript{3} Both chloride ions and bromide ions were observed and the intensity ratio, Br\textsuperscript{-}/Cl\textsuperscript{-}, increases with decreasing temperature. Anions produced from secondary electron attachment to radicals, formed from the dissociative electron attachment to the parent molecules, were observed. It was estimated that halide ions were produced from two processes, dissociative electron attachment to the parent molecules and to radicals formed from the former. This agrees with the result from the flowing afterglow Langmuir probe method (FALP).\textsuperscript{4} As a comparison with these results for halo-methane, we studied the electron attachment to halo-ethanes, i.e., Cl\textsubscript{3}BrC-CBrCl\textsubscript{2}, FCIBrC-BrCl\textsubscript{2}, and ClBr\textsubscript{2}C-CF\textsubscript{3}.

Experimental

C\textsubscript{3}Br\textsubscript{3}C-BrCl\textsubscript{2} (Tokyo-Kasei, purity >97%), FCIBrC-BrCl\textsubscript{2} (Tokyo-Kasei, purity >98%), ClBr\textsubscript{2}C-CF\textsubscript{3} (PCR, purity >97%), and hexane (Wako-Junyaku, purity >99%) were used as received. Our experimental apparatus has been previously described in detail.\textsuperscript{5} Electrons with an energy of 200 eV were provided from the filament and thermalized by collision with the reagent gas. The reagent gas was isobutane. To confirm that most of the electrons are thermalized when they attach to a molecule, the intensity of Cl\textsuperscript{-} from C\textsubscript{3}Cl\textsubscript{4}, depending on the flux of isobutane, was observed. According to an electron-attachment spectral study, dissociative thermal electron attachment occurred for C\textsubscript{2}Cl\textsubscript{4}.\textsuperscript{6} When the intensity of the dissociative Cl\textsuperscript{-} from C\textsubscript{2}Cl\textsubscript{4} was constantly changing with the flux of isobutane, the electrons seemed to be thermalized. Though the pressure of the ion source was not known, the pressure under the mass analytical tube was continuously monitored by an ion gauge. The monitored pressure was 1-2×10\textsuperscript{-6} and 2.5-3×10\textsuperscript{-6} Torr in both the absence and presence of isobutane, respectively. Under this condition, the intensity of the dissociative Cl\textsuperscript{-} from C\textsubscript{2}Cl\textsubscript{4} was constant and electrons were thermalized. Samples were introduced into the ion source through a capillary interface under the collision region and thermal electrons attached to the sample gas. Though the pressure of the samples at the ion source could also not be observed, the monitored pressure did not increase and the partial pressure of the samples seemed to be much smaller than that of isobutane. It was confirmed from CBrCl\textsubscript{3} and CBr\textsubscript{2}Cl\textsubscript{2} that the electron density was high enough to occur secondary electron attachment.\textsuperscript{7} Chemical ionization spectra were obtained using a Shimadzu QP1100EX GC-MS equipped for negative chemical ionization (NCI). The instrument was tuned using the NCI spectra of trifluorobenzenamine (TFPBA) at 523 K and the conditions remained 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. The samples were diluted with hexane in 1/50-1/200 mol\% and 1/10 mol\%. A 0.4-1.5 µL sample was injected. The temperature of the GC column was kept at 453 K for Cl\textsubscript{2}BrC-CBrCl\textsubscript{2} and at 323 K for FCIBrC-CBrF\textsubscript{2} and ClBr\textsubscript{2}C-CF\textsubscript{3}. The peaks were observed at the retention time of about 3.3, 4.2, and 4.1 min, respectively. Helium was used as 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 a computer. When the temperature was changed, the
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Fig. 1. Observed NCI mass spectrum of 1.0 µL injection of Cl₂BrC-CBrCl₂ (1/100 mol%) at 523 K.

Fig. 2. The temperature dependence of the intensity ratio of Br⁻/Cl⁻, Br⁻/Cl⁻, and Br₂⁻/BrCl⁻ for Cl₂BrC-CBrCl₂: Br⁻/Cl⁻ (1/200 mol%); □ Br⁻/Cl⁻ (1/10 mol%); ▲ Br⁻/Cl⁻ (1/200 mol%); × Br⁻/Cl⁻ (1/10 mol%); ○ Br₂⁻/BrCl⁻ (1/10 mol%).

Fig. 3. The temperature dependence of the intensity ratio of Br⁻/Cl⁻, Br⁻/Br⁻, and Br₂⁻/BrCl⁻ for FCIBrC-CBrF₂. ▲ Br⁻/Cl⁻ (1/100 mol%); □ Br⁻/Br⁻ (1/100 mol%); ○ Br⁻/Cl⁻ (1/10 mol%); × Br⁻/BrCl⁻ (1/10 mol%).

Fig. 4. The temperature dependence of the intensity ratio of Br⁻/Cl⁻ for CIBrC-CF₃. ▲ Br⁻/Cl⁻ (1/50 mol%); □ Br⁻/Cl⁻ (1/10 mol%).

seting 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 the isotopic masses of the ions.

Results and Discussion

The typical NCI mass spectra obtained for 1/100 mol% Cl₂BrC-CBrCl₂ are listed in Fig. 1. Both chloride ions and bromide ions were observed for all the samples. Not only halide ions (X⁻) but also halogen molecular anions (HM⁻) were produced for Cl₂BrC-CBrCl₂ and FCIBrC-CBrF₂ similar to BrF₂-CF₂Br. Three kinds of halogen molecular anions, Br₂⁻, BrCl⁻, and Cl₂⁻ were observed for Cl₂BrC-CBrCl₂ and the intensities of these anions increased in the order of Cl₂⁻ < Br₂⁻ < BrCl⁻. On the other hand, Br₂⁻ was much greater than BrCl⁻ for FCIBrC-CBrF₂. Anions produced from the secondary electron attachment to radicals were not observed. This was different from CBrCl₃ and CBr₂Cl₂. The intensity of the produced anions proportionally increased with the quantity of the sample injection. The intensity ratios, Br⁻/Cl⁻, HM⁻/X⁻, and Br₂⁻/BrCl⁻, were constant at the same temperature. These ratios are plotted in Fig. 2–4. The value of Br⁻/Cl⁻ remained constant with the change in the concentration of the sample, and the branching ratio of Cl⁻ increased and that of Br⁻ decreased with increasing temperature for FCIBrC-CBrF₂ and CIBrC-CF₃. On the other hand, the value of Br⁻/Cl⁻ at the lower sample concentration was almost constant with the temperature variations, though the branching ratio of Br⁻ decreased with the increasing temperature at the higher sample concentrations for Cl₂BrC-CBrCl₂. It is possible that a portion of the bromide ion will be produced from secondary electron attachment to Cl₂BrC-CBrCl₂ or CIBrC-CBrCl₂ at higher concentrations of the sample and this effect will be greater at lower temperature. The magnitude of HM⁻/X⁻ was on the same order as BrF₂-CF₂Br. For FCIBrC-CBrF₂, the cluster anion, Br₂Cl⁻, was observed at a temperature lower than 373 K when the concentration of the sample was 1/10 mol%. The ion molecular reaction will occur.

For CBrCl₃ and CBr₂Cl₂, secondary electron attachment to radicals produced from the electron attachment to the parent molecules occurred and halide ions were produced from the radical anions. On the other hand, anions produced from the secondary electron attachment to radicals were not observed for the haloethanes. The dissociative electron attachment to radicals will be exothermic, as the heat of formation of the halo-ethylene is low. However, it is necessary to break two single bonds to produce a double bond. The energy of the intermediate for the formation of halo-ethylene will be large. We estimate that a small proportion of the halide ions would be produced from the secondary electron attachment for the halo-ethanes. More information about secondary electron attachment will be obtained when the electron density is lower than the concentration of the sample in order to neglect the secondary electron attachment. There are two processes that produce halogen molecular anions, a dissociative electron attachment and an abstraction reaction of a halogen atom from the parent molecule. The former will occur because the abundance of halogen molecular anions was proportional to the injection.
quantity of the parent molecule similar to BrF₂C–CF₂Br.¹¹) If we neglect the secondary electron attachment for FClBrC–CBrF₂ and CBr₂C–CF₃, the reaction mechanism can be described as:

\[
M + e^- \rightarrow (M^-)^\ast \rightarrow \text{Br}^- + \cdot (\text{M-Br})
\]

\[
\text{Br}^- + \cdot (\text{M-Cl}) \rightarrow (\text{M}^-) \rightarrow \text{Cl}^- + \cdot (\text{M-Br})
\]

\[
\text{Br}^- + \cdot (\text{M-Br}) \rightarrow (\text{M}^-) \rightarrow \text{BrCl}^- + \cdot (\text{M-Br})
\]

Negative ion + \text{P}^+ \rightarrow \text{Products}

where \text{P}^+ is a positive ion.

We assumed a steady state treatment for the radiolysis in a cell. By substituting the relationship \( k_i = A_i \exp \left(-E_i/RT\right) \) \((i = 1-4)\), the intensity ratio can be described as follows:

\[
\text{Br}^-/\text{Cl}^- \rightarrow k\left(\text{Br}^-\right)/k\left(\text{Cl}^-\right) = A_1/A_2 \exp \left(-\left(E_1-E_2\right)/RT\right) \quad (1)
\]

\[
\text{Br}_2^-/\text{Br}^- \rightarrow k\left(\text{Br}_2^-\right)/k\left(\text{Br}^-\right) = A_3/A_1 \exp \left(-\left(E_3-E_1\right)/RT\right) \quad (2)
\]

\[
\text{Br}_2^-/\text{BrCl}^- \rightarrow k\left(\text{Br}_2^-\right)/k\left(\text{BrCl}^-\right) = A_3/A_4 \exp \left(-\left(E_3-E_4\right)/RT\right) \quad (3)
\]

The difference between the activation energy \(E_i - E_j\) and the relative A-factor \((A_i/A_j)\) can be determined from the slope and the intercept in Figs. 2-4.

For Cl₂BrC–CBrCl₂, the intensity ratio, Br₂⁻/Cl⁻, correlated with the atomic ratios in the molecule of 0.5. On the other hand, the branching ratio of Br⁻ was much higher than the atomic ratio of 2.0 for FClBrC–CBrF₂ and CBr₂C–CF₃ under the experimental conditions. The ratio of the Arrhenius parameter, \(A_1/A_3\), denoting the value of Br⁻/Cl⁻ at the high-temperature limit, was 2.0 and 4.3 for FClBrC–CBrF₂ and CBr₂C–CF₃, respectively. This means that the branching ratio correlates with the atomic ratios at the high-temperature limit for FClBrC–CBrF₂. There will be a higher potential barrier at the crossing point of the parent anion and the dissociative channel for Cl⁻ formation from FClBrC–CBrF₂. The differences between the activation energies for the production of halide ions, \(E_1-E_2\), were 0.04 and 0.026 eV for FClBrC–CBrF₂ and CBr₂C–CF₃, respectively. For ClBr₂C–CF₃, Br⁻ formation is favored even at the high-temperature limit. This means that the strength of the bonding energy of C-Cl relative to C-Br in ClBr₂C–CF₃ will be larger than that in FClBrC–CBrF₂, because the heats of formation of the halide ions are represented as the differences between the bonding energies of the C-halogen bonds and the electron affinities of the halogen atoms. Whether the ion intensity correlates with the atomic ratio or not, also occurs for Br₂⁻/BrCl⁻. This is reasonable because during the production of Br₂⁻, two C-Br bonds cleave and for BrCl⁻, the C-Cl bond and C-Br bond simultaneously cleave. The value of Br₂⁻/
BrCl\(^{-}\) was almost constant with the temperature variation and that of FClBrC-CBrF\(_2\) was greater than that for Cl\(_2\)BrC-CBrCl\(_2\). This means that the strength of the bonding energy of C-Cl relative to C-Br in FClBrC-CBrF\(_2\) will be greater than that in Cl\(_2\)BrC-CBrCl\(_2\). The strength of the bonding energy of C-Cl relative to C-Br increases in the order of Cl\(_2\)BrC-CBrCl\(_2\)< FClBrC-CBrF\(_2\)< ClBr\(_2\)C-CF\(_3\). Because the value of Br\(^{-}/Br\) was almost the same with the temperature variations for both Cl\(_2\)BrC-CBrCl\(_2\) and FClBrC-CBrF\(_2\), the production mechanisms are the same between both halogen molecular anions. Because halogen molecular anions were not observed for ClBr\(_2\)C-CF\(_3\), both Br\(^{-}\) and BrCl\(^{-}\) were produced from halogen atoms presented by each C atom; the four-center elimination similar to cis-C\(_2\)H\(_2\)Br\(_2\).\(^{15}\)

To estimate the differences in the branching ratio and the strength of the bonding energy of C-Cl among the molecules, we have calculated the atomic charge distribution of the parent anions. The B3LYP/6-311+G method was used for the structures of the neutral molecules optimized with the HF/6-311G(d) method. There are three and two conformers for FClBrC-CBrF\(_2\) and Cl\(_2\)BrC-CBrCl\(_2\), respectively. The calculated atomic charges are presented in Fig. 5. There are two paths for Br\(^{-}\) formation from FClBrC-CBrF\(_2\). For all three conformers, the negative charge belongs more to the Br atom in the FClBrC-group than that in the CBrF\(_2\) group. The cleavage of the C-Br bond to produce the FClC-CBrF\(_2\) radical will occur. For conformer 1 of Cl\(_2\)BrC-CBrCl\(_2\), the negative charge belongs to not only Br atoms but also to Cl which means that C\(^{-}\) formation will easily occur like Br\(^{-}\). For a comparison with ClBr\(_2\)C-CF\(_3\) and FClBrC-CBrF\(_2\), the negative charge on the Br atoms relative to Cl was greater for the former, which means that Br\(^{-}\) formation will be favored. It seems that the difference in the branching ratio and the strength of the bonding energy of C-Cl depends on the structure of the conformer.

References


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