Studies of Fragment Ion Distribution and Reaction with a Charge Spectrometer. VIII. Fragmentation Processes of Various Alkyl Halides

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The breakdown curves for C_2H_5X, n-C_3H_7X, and n-C_4H_9X ($X=Cl$, Br, and I) were obtained by the use of a double mass spectrometer of the perpendicular type. The charge exchange mass spectra for alkyl bromide and alkyl iodide are found to be similar, although those for alkyl chloride are somewhat different from these for bromide and iodide. According to the molecular orbital calculation, the difference of the electronic configuration between chloride and bromide or iodide is found to correspond to the difference of the breakdown curves. The results obtained in this study using larger molecules support our previous analysis on the breakdown processes in smaller molecules: (1) direct scission of the bond which has lost one electron by the charge exchange reaction, (2) electron redistribution, and (3) secondary decomposition (and those of higher order) from the primary fragments. In the case of alkyl chloride, formation of the ion $C_nH_{2n}^+$ is ascribed to the elimination of HX from the molecular ion in its electronically ground but vibrationally excited state.

Fragmentation processes of molecules by electron or photon impact have usually been interpreted by the quasi-equilibrium theory (QET)[1] based on the unimolecular decomposition of the molecular ion in its vibrationally excited state. Contrary to this widely accepted interpretation, some evidence of fragmentation of the molecular ion in its electronically excited state has recently been highlighted.[2-5]

On the other hand Hirota[6] and Lorquet[7] found that the scission probability of the skeletal bond was proportional to the electron density of the corresponding bond in the highest occupied MO. Although this molecular orbital theory applied to fragmentation is interesting, the validity of the theory has been shown to be doubtful.[8] In a word, a theory which is universally applicable has not been available so far.

Therefore, in order to approach the solution of these difficulties, we have proposed some new fragmentation mechanisms on the basis of a MO treatment involving the inner occupied MO's.[9] The fragmentation processes of various CH_3X ($X=NH_2$, OH, SH, Cl, Br, and I),[5,9] C_2H_5OH, $C_2H_5NH_2$,[10] various alcohols,[11] and various mercaptans[12] have been successfully explained by our interpretation.

In this paper, the breakdown curves of various alkyl halides RX (R=ethyl, propyl, and butyl, and X=Cl, Br, and I) are studied by charge exchange reactions and the effects of the length of the alkyl group (R) and that of the substituent (X) on the fragmentation processes are investigated.

Experimental

Fragmentation processes of various molecular ions produced by charge exchange reactions were studied using a double mass spectrometer of the perpendicular type. Details of the apparatus have already been described.[13] In the work, H_2S^+, $C_2H_2^+$, Xe^+, Kr^+, N_2^+, Ar^+, Xe^{++}, Ne^+, and He^+ ions were used as primary incident ions and admitted into the reaction chamber. The pressure in the reaction chamber was below 6×10^{-6} Torr.

Calculation

Eigenvectors of molecular orbitals of various alkyl halides were calculated according to the Extended Hückel Molecular Orbital method.[14] Details of the calculation were already described in the previous paper.[9] The calculation was performed at the Computer Center of Tohoku University. The models employed for this calculation are shown in Fig. 1.

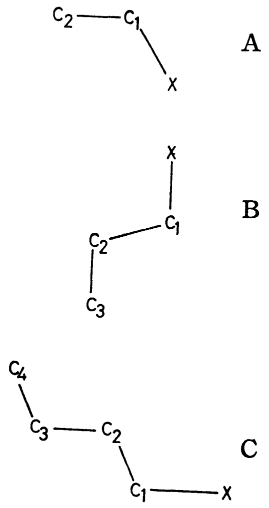

Fig. 1. Models employed for calculation (hydrogens are omitted).
A: Ethyl halide. B: Propyl halide. C: Butyl halide.

Results

(A) Ethyl Halides. The breakdown curves of ethyl chloride and ethyl iodide obtained by charge exchange reactions are shown in Fig. 2 (A) and (B). In the figure the abscissa indicates the recombination energy of the incident positive ions and the ordinate indicates the abundance of the fragment ions. The curves are normalized so that the sum of the abundances of the constituent ions at each energy is equal to 100. The production of the molecular ions must start at

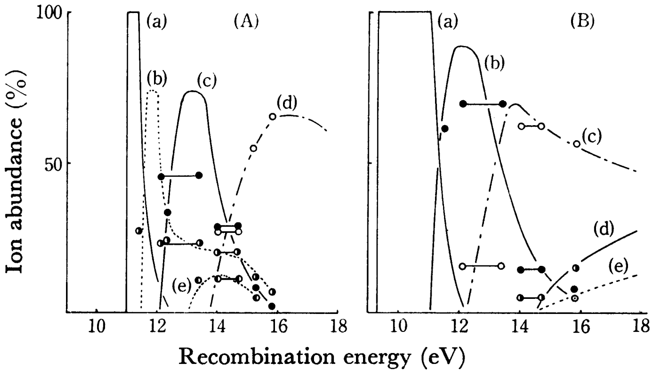

Fig. 2. Breakdown curves of ethyl chloride (A) and ethyl iodide (B).
(A) (a) $C_2H_5Cl^+$ (b) $C_2H_4^+$ (c) $C_2H_5^+$ (d) $C_2H_3^+$ (e) CH_2Cl^+
(B) (a) $C_2H_5I^+$ (b) $C_2H_5^+$ (c) $C_2H_3^+$ (d) I^+ (e) $C_2H_2^+$

the recombination energy equal to the spectroscopic ionization potential.

In ethyl chloride, the $C_2H_4^+$ ion produced by the loss of HCl from the molecular ion in the vibrationally excited state[15] follows the stable molecular ion. Formation of $C_2H_5^+$ ion starts at about 12 eV. The CH_2Cl^+ ion appears at about 13 eV as a result of scission of the C–C bond and its maximum abundance is about 15%. Formation of $C_2H_3^+$ ion produced by unimolecular decomposition of the $C_2H_5^+$ ion starts at 13.5—14.0 eV. The appearance potential of $C_2H_5^+$ ion is equal to that of the second band in the photoelectron spectrum.[16] Therefore, it is thought that the primary fragment ions from the molecular ions are $C_2H_4^+$, $C_2H_5^+$, and CH_2Cl^+, among which the $C_2H_5^+$ and CH_2Cl^+ ions are correlated to the direct fragmentation of the molecular ion in its electronically excited state.

On the other hand, in ethyl iodide the $C_2H_5^+$ ion follows the stable molecular ion. The appearance potential of this ion is equal to that of the second band in the photoelectron spectrum.[16] Formation of the $C_2H_3^+$ ion produced by unimolecular decomposition of the $C_2H_5^+$ ion starts at about 12.5 eV. Formation of the I^+ and $C_2H_2^+$ ions starts at about 14.5 eV, but the CH_2I^+ ion produced by scission of the C–C bond comprises only a few percent. Therefore, it is concluded that the product of the primary scission of the molecular ions is only the $C_2H_5^+$ ion in the low energy region (<15 eV).

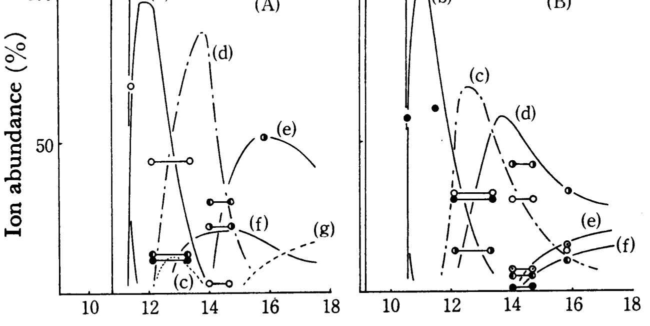

Fig. 3. Breakdown curves of propyl chloride (A) and propyl iodide (B).
(A) (a) $C_3H_7Cl^+$ (b) $C_3H_6^+$ (c) $C_3H_7^+$ (d) $C_2H_5^+$ (e) $C_2H_3^+$ (f) $C_3H_5^+$ (g) $C_3H_3^+$
(B) (a) $C_3H_7I^+$ (b) $C_3H_7^+$ (c) $C_3H_5^+$ (d) $C_2H_3^+$ (e) $C_3H_3^+$ (f) I^+

(B) Propyl Halides. The breakdown curves of propyl chloride and propyl iodide obtained by charge exchange reactions are shown in Fig. 3.

In propyl chloride, formation of the $C_3H_6^+$ ion which is produced from the molecular ion in its vibrationally excited state[15] follows that of the stable molecular ion. Formation of the $C_2H_5^+$ ion starts at about 12.0 eV after that of the $C_3H_6^+$ ion and it is thought that this $C_2H_5^+$ ion is produced by the primary scission of the molecular ion. Formation of the $C_3H_7^+$ ion also starts at about 12.0 eV and the maximum abundance of this ion is about 15%. The $C_3H_5^+$ and $C_2H_3^+$ ions are formed as a result of the consecutive decomposition of the $C_3H_6^+$, $C_3H_7^+$, and $C_2H_5^+$ ions. Therefore, these results show that the primary fragment ions of the molecular ion are $C_3H_6^+$, $C_2H_5^+$, and $C_3H_7^+$ ions, among which the $C_2H_5^+$ and $C_3H_7^+$ ions are correlated to the direct fragmentation of the molecular ion in its electronically excited state.

On the other hand, in propyl iodide the formation of $C_3H_7^+$ ion follows that of the stable molecular ion, and this $C_3H_7^+$ ion decomposes further to smaller ions ($C_3H_5^+$, $C_2H_3^+$,······). It is thought that the primary fragment ion is the $C_3H_7^+$ ion alone in the low energy region (<15 eV).

(C) Butyl Halides. The breakdown curves of butyl chloride and butyl iodide obtained by charge exchange reactions are shown in Fig. 4.

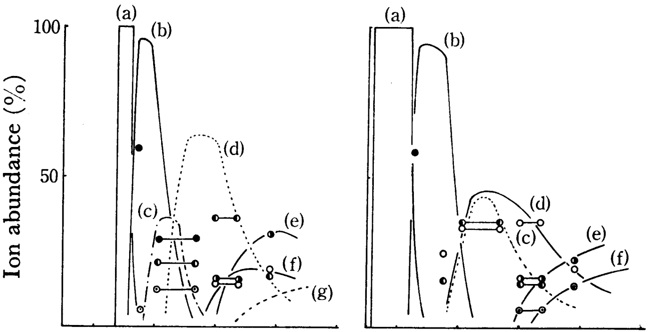

Fig. 4. Breakdown curves of butyl chloride (A) and butyl iodide (B).
(A) (a) $C_4H_9Cl^+$ (b) $C_4H_8^+$ (c) $C_3H_7^+$ (d) $C_3H_5^+$ (e) $C_2H_3^+$ (f) $C_3H_3^+$
(B) (a) $C_4H_9I^+$ (b) $C_4H_9^+$ (c) $C_3H_5^+$ (d) $C_2H_5^+$ (e) $C_2H_3^+$ (f) $C_3H_3^+$

In butyl chloride formation of the $C_4H_8^+$ ion produced by the elimination of hydrogen chloride from the molecular ion in its vibrationally excited state[15] follows that of the stable molecular ion. Formation of the $C_3H_7^+$ ion starts after the appearance of the $C_4H_8^+$ ion and this $C_3H_7^+$ ion is considered to be produced by the primary scission of the molecular ion. Formation of $C_2H_5^+$ starts at about 12.5 eV, after that of the $C_3H_7^+$ ion.

The $C_4H_8^+$, $C_3H_7^+$, and $C_2H_5^+$ ions decompose further to smaller ions. These results and Figure 4 show that the primary fragment ions of the molecular ions are the $C_4H_8^+$, $C_3H_7^+$, and $C_2H_5^+$ ions, among which the $C_3H_7^+$ and $C_2H_5^+$ ions are correlated to the decomposition of the molecular ion in its electronically excited state.

On the other hand, in butyl iodide formation of the $C_4H_9^+$ ion follows that of the stable molecular ion. This $C_4H_9^+$ ion decomposes further to smaller ions ($C_3H_5^+$, $C_2H_5^+$,……). The primary fragment ion of the molecular ion is the $C_4H_9^+$ ion alone in the low energy region (<15 eV).

From these results the dissociation schemes of various molecular ions are shown in Fig. 5.

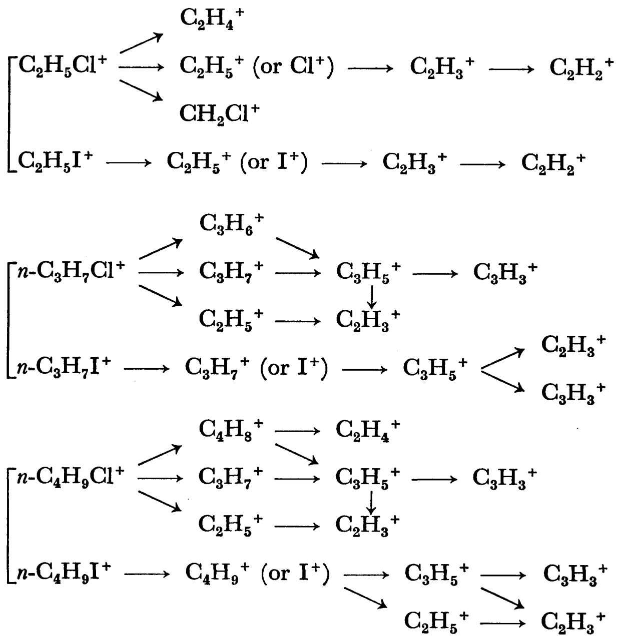

Fig. 5. Dissociation ionization schemes of various alkyl halide-moleular ions.

Discussion

Instead of an interpretation of the mass spectra using the QET[1] and Hirota's theory,[6] we have already set up a new interpretation of fragmentation processes based on the MO treatment.[5,9–12] The scission probabilities of the C–X and C–H bonds in various CH_3X^+ have been well explained by our proposal.[5,9] And the fragmentation processes of various alcohols[11] and mercaptans[12] have been also successfully accounted for. Our interpretation is composed of three basic suppositions, as follows:

(1) The scission first occurs where the electrons are exist densely in the particular occupied MO correlated to the particular ionization.

(2) Process (1) competes with the electron redistribution process after the event of ionization.

(3) In a higher energy region, secondary scission (and those of higher orders) also occurs.

Based on process(1), the primary fragment ions of the molecular ions can be predicted by the main character of the particular MO which correlates to the particular ionization, and the over-all features of the energy dependence of the fragmentation phenomena can be explained by processes (2) and (3) in addition to process (1).

TABLE 1. CALCULATED MO ENERGY, OBSERVED IONIZATION POTENTIAL AND CALCULATED BONDING CHARACTER IN ALKYL IODIDES

		Calculated MO energy (−eV)	Observed I. P. (eV)[16]	Calculated Bonding character
C_2H_5I	HOMO	10.47	9.34	non-bonding
		10.48	9.93	
	SOMO	12.36	11.66	C–I bonding
	TOMO	13.68	12.90	C–H bonding
	FOMO	13.93	13.85	C–C bonding
C_3H_7I	HOMO	10.46	9.27	non-bonding
		10.48	9.82	
	SOMO	12.36	11.43	C_1–I bonding
	TOMO	13.29	12.22	C–H bonding
	FOMO	13.48	12.78	C_1–C_2 bonding
C_4H_9I	HOMO	10.46	9.24	non-bonding
		10.48	9.79	
	SOMO	12.28	11.22	C_1–I bonding
	TOMO	13.24	11.90	C–H bonding
	FOMO	13.26	12.3	C_1–C_2 bonding

The calculated MO energy, the observed ionization potential, and the general character of the occupied MO for alkyl iodide are shown in Table 1. The highest occupied MO which is degenerated is nonbonding and the second occupied MO is C–I bonding. Therefore, the ionization of the electron in the highest occupied MO results in formation of the stable molecular ion, and the ionization of the electron in the second occupied MO results in formation of the alkyl ion, as shown in the figures. The appearance potential of the alkyl ion is equal to that of the second band in the corresponding photoelectron spectrum.[16] The primary fragment ion of the molecular ion is the alkyl ion alone in the low energy region. No formation of any fragment ions originating from ionization of the electron above the second occupied MO was observed in the present experiments. Therefore, it is considered that the molecular ion in its electronically excited state easily falls into its electronically ground state (or at least into its low-lying electronically excited states) before it decomposes. Similar considerations can be applied to the fragmentation of the molecular ion in alkyl bromide.

The MO energy and the general character of the occupied MO calculated in this work for alkyl chloride are shown in Table 2. The fragment ion produced by the elimination of hydrogen chloride is ascribed to the presence of the molecular ion in its vibrationally excited state.[15] The breakdown curves in ethyl chloride are similar to those of ethyl bromide and ethyl iodide, except for the formation of the $C_2H_4^+$ ion. Therefore, it is assumed that the general character of the various occupied MO's in ethyl chloride is similar to those of ethyl bromide and ethyl iodide.

TABLE 2. MO ENERGY AND BONDING CHARACTER CALCULATED IN THIS WORK ON ALKYL CHLORIDES

		MO energy (−eV)	Bonding character
C_2H_5Cl	HOMO	12.88	non-bonding
	SOMO	13.72	C–H bonding
	TOMO	13.90	C–C bonding
	FOMO	14.12	C–Cl bonding
C_3H_7Cl	HOMO	12.84 12.93	non-bonding
	SOMO	13.30	C–H bonding
	TOMO	13.42	C_1–C_2 bonding> C_1–Cl bonding
	FOMO	13.73	C_2–C_3 bonding
C_4H_9Cl	HOMO	12.76 12.91	non-bonding
	SOMO	13.20	C_1–C_2, C_2–C_3,⋯ bondings
	TOMO	13.25	C–H bonding
	FOMO	13.50	C_2–C_3 bonding

In propyl chloride the highest occupied MO is degenerated n(Cl). The third occupied MO is both C_1–C_2 bonding and C_1–Cl bonding. The calculated partial bond population of C_1–C_2 bonding comprises 75% and that of C_1–Cl bonding comprises 25%. Therefore, ionization of an electron in the third occupied MO results in formation of the $C_2H_5^+$ ion in abundance and a small amount of the $C_3H_7^+$ ion, as shown in Fig. 3. It is thought that the general character of the various occupied MO's in propyl chloride shown in Table 2 is correct.

In butyl chloride the calculated bonding character of the second occupied MO is C_1–C_2, C_2–C_3,⋯⋯bondings. From the experimentally obtained breakdown curve, the most dominant one is thought to be C_1–C_2 bonding.

In the molecular ions of alkyl bromide and alkyl iodide, the C–X bond dominantly dissociates and the fragment ions produced by the scission of the other bond can be scarcely observed, in contrast to the fragmentation of molecular ions of alkyl amine, alkyl alcohol, and alkyl mercaptan. This difference is explained by the difference of the general character of the various occupied MO's.

No formation of fragment ions originating from the ionization of an electron above the second occupied MO was observed. Therefore, it is considered that the molecular ion in its electronically excited state easily falls into its electronically ground state or into a less excited electronic one. Although the degree of transition between the electronic states is considered to be large in alkyl bromide and alkyl iodide, as shown in the figures, it seems this is not the case in alkyl chloride. It is likely that this degree decreases in the order of of butyl>propyl>ethyl chloride.

From these results it is shown that the electron redistribution process of our proposal also plays an important role in the higher energy region in the breakdown curve of alkyl halides. Thus, the general trends of fragmentation processes of molecular ions are concluded to be interpreted satisfactorily by our approach, although efforts to make the results more quantitative will be necessary in the future.

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