Studies on Fragment Ion Distribution and Reaction with a Charge Spectrometer. V. Applicability of the MO Theory to the Fragmentation of Alkanes by Charge Exchange

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The relation between the fragment ion distribution and recombination energy of the incident positive ions was studied by means of charge exchange reactions. The energy range which is consistent with the molecular orbital (MO) theory proposed by Hirota to account for the mass spectra by electron impact was also investigated, and the usefulness of the theory was discussed. The energy range to which the MO theory is applicable is very limited, the fragment ions produced at the high recombination energy to which it is apparently applicable, being the C_2, C_3 and C_1 ion groups. It is probable that these species are not produced directly from the parent but by degradation mechanisms *via* intermediate steps, thus causing disagreement with the MO theory. Its applicability to alkanes is open to question. The dissociation schemes on *n*-alkanes are presented from the expreimental results.

Mass spectra obtained by electron impact are utilized for the identification of organic compounds. Although mass spectroscopic analysis is widely used, only empirical or semi-empirical rules have been used to explain the experimental results.[1] The theory of mass spectra by electron impact is important for studying the initial processes of radiation actions on various substances since the interaction of radiation with materials is attributed almost substantially to excitation and/or ionization by radiation-induced electrons.

In 1952 Rosenstock *et al.*[2] proposed a quasi-equilibrium theory to account for the mass spectra of relatively simple organic substances by electron impact, the underlying assumptions of the theory being as follows:

(1) The electronically excited molecular ion produced by interaction of the molecule with an electron changes swiftly into the electronically ground but vibrationally excited molecular ion.

(2) The fragment ions are formed by unimolecular decomposition of the vibrationally excited molecular ion involving competing and successive processes.

(3) The rate constants of the elementary processes are determined by the use of the absolute rate theory.

They estimated the breakdown curve of the *n*-propane molecular ion, in qualitative accordance with the experimental results, but quantitative agreement was not so good.

Efforts were made to improve the agreement of the theory with experimental results.[3] Vestal *et al.*[4] developed a method of enumerating the states and succeeded in evaluating the mass spectra quantitatively. In this improved quasi-equilibrium theory, however, there have still been difficulties as regards its application to cases involving fragmentation processes from electronically excited states and those from superexcited states.[5]

For explanation of the fragment ionization process, Fueki and Hirota[6] proposed a theory based on the assumption that the probability of fragmentation is proportional to the electron density on the highest occupied molecular orbital in the molecule. The theory was applied to many organic compounds and fairly good accordance was observed with the experiments using electron impact of normal or cycloalkanes.[7] However, experimental evidence of the energy range fit to the theory seems to be lacking.

We have studied the relation between the distribution of fragment ions and the recombination energy of the incident ions by means of pure charge exchange reactions involving no transfer of momentum. The energy range consistent with the molecular orbital (MO) theory was also investigated, and the usefulness of the theory was discussed.

Experimental

The charge exchange reactions of various molecules were carried out with a double mass spectrometer.[8] The primary ions, produced with a bombarding electron beam (100 eV), were accelerated to 800 V and led into the reaction chamber whose repeller potential was below 10 V. The ions produced by the charge exchange reactions were drawn into the second analyzer system at 3.5 KV, and detected with an electron multiplier of 16 stages.

The pressure of the reaction chamber was 8×10^{-6} mmHg. n-C_4H_{10}, n-C_5H_{12}, n-C_7H_{16}, n-$C_{10}H_{22}$, cyclo-C_5H_{10}, cyclo-C_6H_{12}, cyclo-C_7H_{14} and cyclo-C_8H_{16} were reagent grade(Tokyo Kasei Co.) and n-C_8H_{18} was spectroscopically pure. n-C_6H_{14} was purified from starting material of reagent grade (Tokyo Kasei Co.) by means of gas chromatography.

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[2] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.*, **38**, 667 (1952).

[3] For example; H. M. Rosenstock, *J. Chem. Phys.*, **34**, 2182 (1961), B. S. Rabinovitch and R. W. Diesen, *ibid.*, **30**, 735 (1959), E. W. Schlag and R. A. Sandmark, *ibid.*, **37**, 168 (1962), M. L. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *ibid.*, **37**, 1276 (1962), E. Thiele, *ibid.*, **39**. 3258 (1963), S. H. Lin and H. Eyring, *ibid.*, **43**, 2153 (1965), P. C. Haarhoff, *Mol. Phys.*, **6**, 337 (1963).

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[5] R. L. Platzman, *J. Phys. Rad.*, **21**, 853 (1960).

[6] K. Fueki and K. Hirota, *Nippon Kagaku Zasshi*, **81**, 212 (1960).

[7] For example; M. Hatada and K. Hirota, This Bulletin, **38**, 599 (1964), M. Itoh, M. Yamamoto, and K. Hirota, *Nippon Kagaku Zasshi*, **89**, 443 (1968), K. Hirota, *ibid.*, **89**, 327 (1968), K. Hirota, *ibid.*, **91**, 585 (1970), K. Hirota, I. Fujita, M. Yamamoto, and Y. Niwa, *J. Phys. Chem.*, **74**, 410 (1970).

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CH_3^+, CH_2^+, $C_2H_2^+$, H_2O^+, Xe^+, Cl^+, H^+, Kr^+, N_2^+, Ar^+, Xe^{++}, Ar^{++}, and He^+ were used as the source of primary ions. CH_3^+ and CH_2^+ were obtained from methane, Cl^+ was the fragment ion of trichlorofluoromethane, H^+ the fragment ion of hydrogen, and $C_2H_2^+$, H_2O^+ and N_2^+ were obtained from C_2H_2, H_2O and N_2 respectively. All the other ions were produced from the corresponding rare gases.

Prior to experiments of charge exchange reactions, a re-examination of the recombination energy of the incident primary ions should be necessary because of the comparatively large velocity. However, with the use of the double mass spectrometer, Nagatani *et al.*[9] observed that the recombination energy of the comparatively fast primary ions was in good agreement with Lindholm's value of slow ones.[10] We therefore used the following Lindholm's values as the recombination energies of primary incident ions:

CH_3^+	a range around 9.8 eV
CH_2^+	10.4 eV and lower
$C_2H_2^+$	11.4 eV
H_2O^+	12.4 eV
Xe^+	12.1—13.4 eV
Cl^+	12.9—14.4 eV
H^+	13.6 eV
Kr^+	14·0—14.7 eV
N_2^+	15.3 eV
Ar^+	15.8 eV
Xe^{++}	18.0—20.0 eV
Kr^{++}	21.0 eV
Ar^{++}	24.0 eV
He^+	24.6 eV

Results and Discussion

The charge exchange reaction is generally considered as follows.

$$A + M^+ \rightarrow A^+ + M \tag{3}$$

where the energy E_c for producing the process $A \rightarrow A^+$ is dependent on the recombination energy of M^+, the ionization potential of A, and the kinetic energies of A and M^+. For the pure charge exchange reaction not involving the transfer of kinetic energy, the following equation can be applied:

$$A + M^+ \rightarrow A^+ + M + (\mathrm{R.E.})_M - (\mathrm{I.P.})_A \tag{4}$$

where $(\mathrm{R.E.})_M$ is the recombination energy of M and $(\mathrm{I.P.})_A$ the ionization potential of A. If $M=A$ in Eq. (4), the resonance process for which $E_c = (\mathrm{R.E.})_M - (\mathrm{I.P.})_A = 0$ occurs. For the case of $M \neq A$ one can excite the molecular ion A^+ by the energy $E_c = (\mathrm{R.E.})_M - (\mathrm{I.P.})_A$.

Thus the fragmentation processes from the particular excited state of the molecular ion by the charge exchange reactions can be observed with the use of a double mass spectrometer. The produced fragment ions are normalized to the sum of the total ion intensity, and the relation between the fragment ion distribution and the recombination energy of the incident ions can be illustrated as the breakdown curve of the molecular ion.

It is considered that the breakdown curve obtained by the charge exchange reactions is closely related to the mass spectra by electron impact. Mass spectra by electron impact are expressed as the sum of the mass spectra over internally excited states of various energies of the molecular ion, and calculated by the use of the breakdown curve and the internally energy distribution of the molecular ion.[11]

As an example the breakdwon curve for n-C_7H_{16} is shown in Fig. 1. The abscissa indicate recombination energy of the incident positive ions and the ordinate indicates the intensity of the ions. The plotted data were obtained in this work, and the curve in the low energy region (<14 eV) was obtained by Steiner *et al.*[12] using the photon impact. From this breakdown

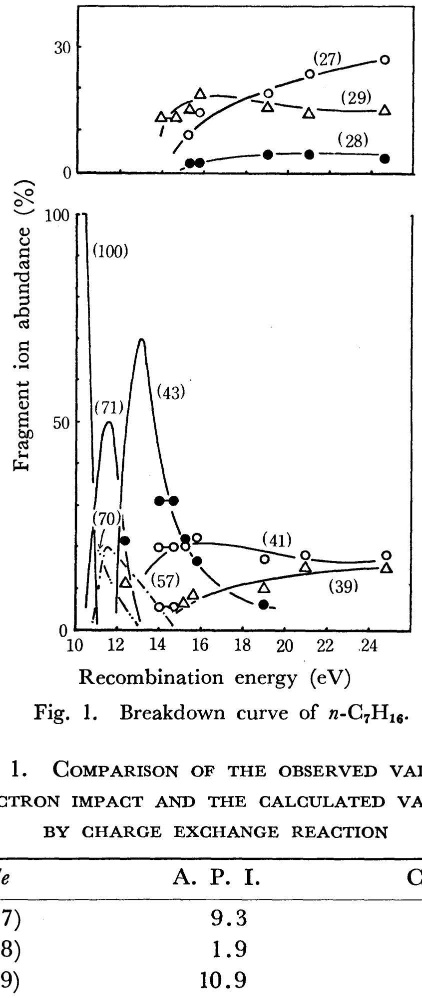

Fig. 1. Breakdown curve of n-C_7H_{16}.

Table 1. Comparison of the observed values by electron impact and the calculated values by charge exchange reaction

m/e	A. P. I.	Calcd.
(27)	9.3	7.7
(28)	1.9	1.8
(29)	10.9	8.3
(41)	12.4	11.8
(43)	23.8	23.8
(57)	11.4	6.0
(70)	4.1	3.0
(71)	10.5	9.2
(100)	3.1	2.5

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9) T. Nagatani, K. Yoshihara, and T. Shiokawa, This Bulletin, **46**, 1306 (1973).

10) E. Lindholm, "Ion Molecule Reactions in the Gas Phase," Advances in Chemistry Series **58**, American Chem. Soc., Washington, D. C. (1966), p. 1.

11) For example; H. von Koch and E. Lindholm, *Arkiv Fysik.*, **19**, 123 (1961).

12) B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

and the internal energy distribution function the composite fragment ion distribution can be calculated.[9] The result is compared with the observed values by electron impact (electron energy: 70 eV) in Table 1. The agreement is quite satisfactory. This means that the fragment ionization processes after the charge exchange reactions are almost consistent with ones by electron impact for the same energy imparted.

In contrast to the quasi-equilibrium theory, the MO theory proposed by Hatada and Hirota and others[7] to account for the mass spectra by electron impact contains three assumptions.

(1) The lifetime of the excited molecular ion is very short ($<10^{-13}$ s), the excited molecular ion being in a super-excited state, and the fragmentation occurring in the stabilization process.

(2) The scission probability of the skeletal bonds of bombarded molecule is proportional to the positive charge distribution at the corresponding bond of the molecular ion, or proportional to the electron density of the highest occupied molecular orbital at the corresponding bond of the bombarded molecule.

(3) The theory is applicable only to the primary scission, and the secondary and other scissions are explained by the quasi-equilibrium theory.

Hirota[13] pointed out that the electronically excited molecular ion is produced in a super-excited state, several eV above the ground state. The minimum energy for producing the super-excited molecular ions can be estimated by the following equation:

$$\mathrm{V(min)} = \mathrm{I.P.} + nRT + D(\mathrm{c\text{-}c}) \tag{5}$$

where I.P. is the ionization potential of the starting molecule, n the number of the degree of freedom, D the dissociation energy for the carbon bonds, T absolute temperature (K) and R the gas constant. 20 eV was obtained for the molecule having 50 degrees of freedom.

In order to examine this theory it is important to study the energy dependence of the fragment ion distribution especially in the recombination energy region of about 20 eV. From the breakdown curve (Fig. 1), it is necessary to study the energy region which is consistent with the MO theory (or to check the fragment ion distribution predicted by the theory).

In the MO theory, Fueki and Hirota[6] could not determine which of the ruptured fragment groups was in the positive state *i.e.* which one lost an electron on the rupture event. C_i+C_{n-i} was therefore used to represent the scission probability for the i-th bond from the end. The summation C_i+C_{n-i} was normalized to be 100 except for the parent ion group. Thus we first obtain the breakdown curve of the molecular ion by the charge exchange reaction and next the abundance of the C_i group. Finally the relation between C_i+C_{n-i} and the recombination energy of the incident ion can be obtained, and the energy in which the MO theory holds can be determined. The relation of C_i+C_{n-i} versus energy in n-C_7H_{16} is shown in Fig. 2 with the data in Fig. 1. The predicted values on n-C_7H_{16} by the MO theory are as follows: $C_3+C_4=54$ (%), $C_2+C_5=35$ (%), $C_1+C_6=11$ (%).

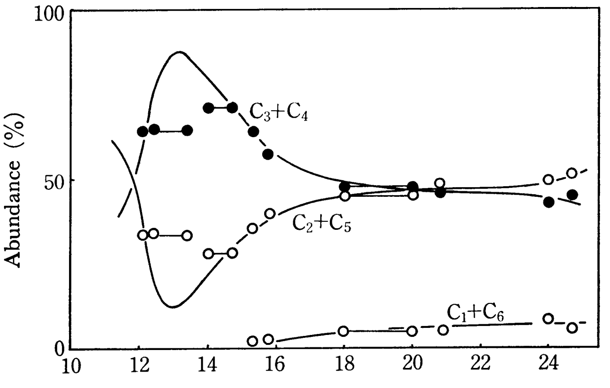

Fig. 2. Relation between C_i+C_{n-i} and recombination energy of incident positive ions on n-C_7H_{16}.

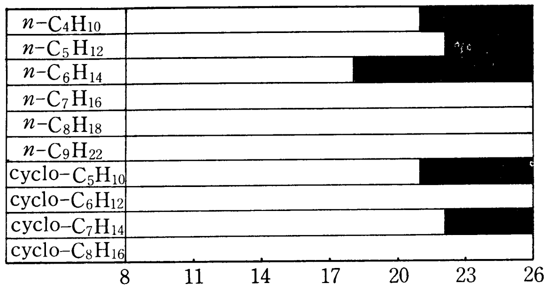

Fig. 3. Energy range of fragmentation consistent with the MO theory.

The energy range to which the MO theory is applicable is thus determined for n-alkanes and cycloalkanes. In Fig. 3, the black portion shows the energy range apparently consistent with Hirota's MO theory. We see that the energy range to which the MO theory is applicable is very limited. There are no energy regions to fit the MO theory in n-C_7H_{16}, n-C_8H_{18}, n-$C_{10}H_{22}$, cyclo-C_6H_{12} and cyclo-C_8H_{16}. The results for n-C_7H_{16} and n-C_8H_{18} were re-estimated more rigorously than in the previous communication.[14]

The mass spectra by electron impact can be calculated by the breakdown curve and the internal energy distribution function. It is assumed, however, that the maximum of the internal energy distribution func-

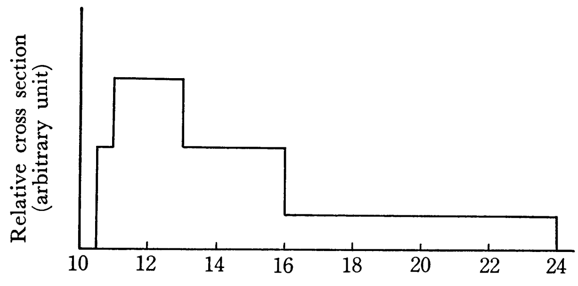

Fig. 4. Internal energy distribution of n-C_7-H_{16} molecular ion.

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13) K. Hirota, *Shitsuryo Bunseki*, **20**, 101 (1972).

14) S. Ikuta, K. Yoshihara, and T. Shiokawa, *Chem. Lett.*, **1972**, 685.

tion is about 1 eV plus the ionization potential. Figure 4 shows the internal energy distribution on *n*-C_7H_{16} molecular ion which was used to calculate the mass spectra. The breakdown phenomenon in the high recombination energy range seems to contribute very little to the whole mass spectra. This means that the mass spectra in the energy range which are consistent with the MO calculation (Fig. 3) contribute little to the whole mass spectra by electron impact.

Although Hirota *et al.* could not quantitatively predict which of the fragment C_n and C_m ($m=N-n$; where N is the total number of carbon atoms) was to be in the positive charge, they qualitatively proposed that the abundance of the C_n ion group was larger than that of the C_m ion group in case of $n>m$, since the charge density of the C_n ion group was larger than that of the C_m ion group. It seems that there is a comparatively large ion group ($>C_{N/2}$: C_N is the parent ion group) in the energy range to which the MO theory is applicable.

Figure 5 shows the breakdown curve of the *n*-hexane parent ion obtained by the charge exchange reactions. It is evident that the fragment ions produced at the high recombination energy, to which the MO theory is applicable are the C_2, C_3 and C_1 ion groups. These C_2, C_3 and C_1 groups are predominant in the mass spectra at the high recombination energy on all alkanes. These results do not agree with the MO theory.

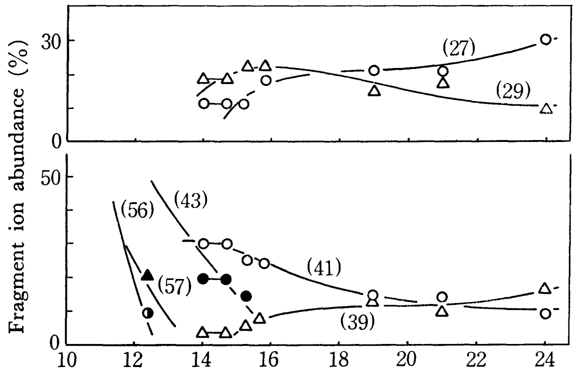

Fig. 5. Breakdown curve of *n*-C_6H_{14}.

From the above results, there arise some doubts about the applicability of the MO theory to alkanes. It is probable that the agreement between the observed values by electron impact and the predicted values by the MO theory happens to be given by integration of the breakdown curve along the internal energy distribution by chance. The argument seems to hold in the case of cycloalkanes in which double scissions are necessary to give the fragment ion distribution in the present study. We cannot exclude a possibility that there is a discrepancy in the mechanism between electron impact and charge exchange resulting in fragmentations. The possibility that the mechanism involving the pre-ionization from the super-excited state should also be considered but we do not believe this will alter the discussion given above.

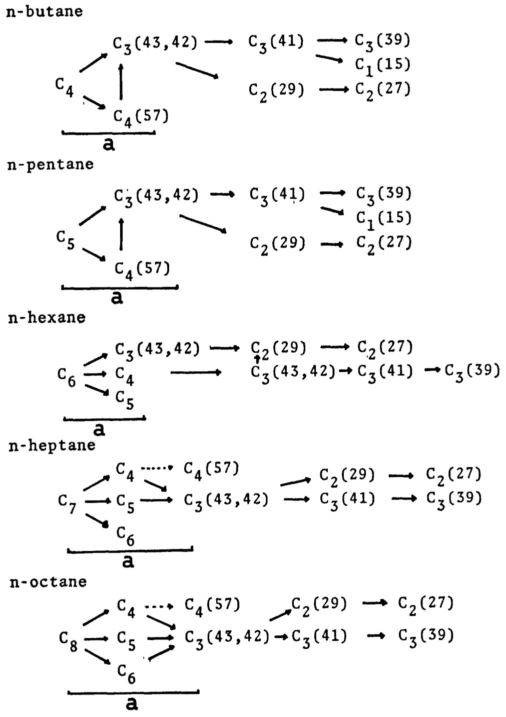

Fig. 6. Dissociation schemes of *n*-alkanes.

It seems that application of the MO theory to the fragmentation of the alkanes ($>C_4$) as a whole is difficult.

The dissociation scheme on alkanes is given in Fig. 6. At the high recombination energy (>17 eV) fragment ions were always C_2, C_3 and C_1 ion groups. Figure 6 [a] shows comparatively swift fragmentation processes. It is assumed that the molecular ions produced change swiftly to the C_3 or C_2 ion groups, and thereafter the C_3 or C_2 ion groups comparatively slowly change to the C_3', C_2' and C_1 ion groups experimentally observed. In the swift process one can imagine that availability of the molecular orbital consideration may be possible, although it is far from proven in the results of this study.

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