CHEMISTRY LETTERS, pp. 289-292, 1975. Published by the Chemical Society of Japan

BREAKDOWN CURVES OF ETHYL AND METHYL RADICALS AND THEIR MASS SPECTRA

Shigeru IKUTA, Kenji YOSHIHARA, and Takanobu SHIOKAWA
Department of Chemistry, Faculty of Science, Tohoku University,
Aramaki, Aoba, Sendai 980

The breakdown curves of ethyl and methyl radicals were estimated based on those of corresponding alkyliodides. Mass spectra of the radicals calculated from these breakdown curves using an estimated internal energy distribution are in good accordance with those obtained by electron impact.

The authors have studied on the mass spectra after charge exchange with positive ions for the fundamental study of radiation action on the matter and for the interpretation of mass spectra.[1,2] And it is pointed out that the breakdown curves (mass spectra as a function of energy) are very useful for the identification of the bands in photoelectron spectra.[3,4] The authors have already proposed the fragmentation mechanisms of the molecular ion based on the molecular orbital calculation.[5] According to this proposal, the primary fragment ions can be predicted by the MO assignment in the particular molecular orbital which correlates to the particular ionization.

There are few papers on the study of the breakdown curves of radicals.[6,7,8] This is due to the difficulty in obtaining the abundant flux of radicals for this type of experiments. In order to overcome this difficulty, the present authors propose a simple procedure which enables us to construct the correct breakdown curves of radicals. For this purpose, the breakdown curves of alkyliodides obtained by the use of a double mass spectrometer of a perpendicular type are available.

In the experiment using TOHOKU CS,[9] the pressure in the reaction chamber was kept below 6×10^{-6} mmHg to avoid the consecutive reactions.

In principle the breakdown curves of radicals must be obtained by charge exchange reactions between the positive ions and radicals such as equation (1). It is,

$$R\cdot(\text{radical}) + M^{+} \longrightarrow R^{+} + M \qquad (1)$$

however, very difficult to get the abundant radicals under the present condition using photon impact, and therefore the authors have estimated the breakdown curves of the radicals as follows. From the breakdown curve of alkyliodide(RI) it is found that the R^+ ion is produced by the primary scission.[10] For instance in ethyliodide (C_2H_5I) the $C_2H_5^+$ ion amounts to almost 100 % as the primary fragment ion, and this ion decomposes further to the smaller ions in unimolecular decomposition. Then, it is considered that R^+ which should be obtained by equation (1) is very similar to R^+

which is obtained from the breakdown curve of alkyliodide as the primary fragment ion, except the view-point of the internal excitation energy. Therefore, it is found that the breakdown curves of the radicals can be estimated on the basis of unimolecular decomposition process of the alkyl ion (R^+) obtained from the breakdown curve of alkyliodide.

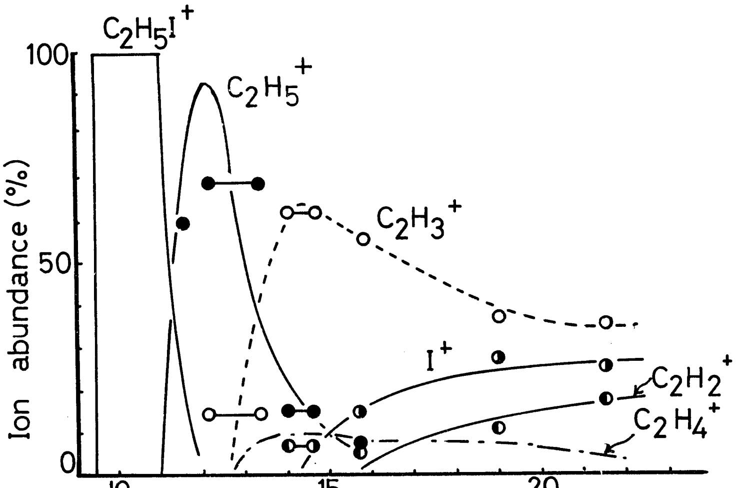

Fig. 1. Breakdown curve of ethyliodide.

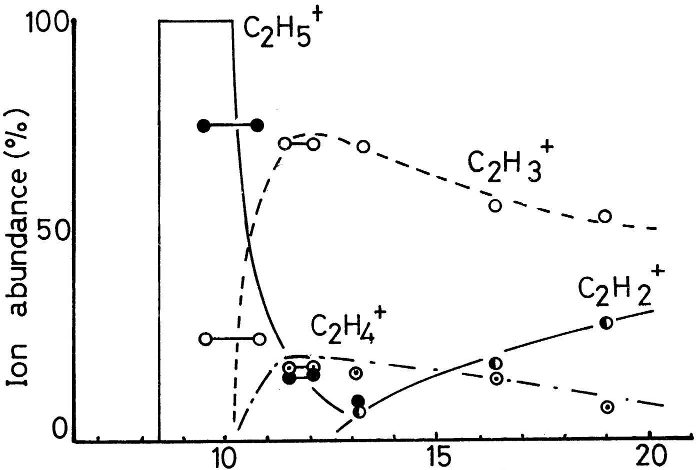

Fig.2. Breakdown curve of ethyl radical.

(i) Ethyl radical

The breakdown curve of ethyliodide (C_2H_5I) after charge exchange studied in the previous paper[10)] is reproduced in Fig.1. The abscissa indicates the recombination energy of the incident ions which is the measure of the endowed energy to the molecular ion. As we have already found, the primary fragment ions can be discriminated from the secondary ones, etc.[5,10)] Figure 1 shows that the primary fragment ion from the molecular ion ($C_2H_5I^+$) is $C_2H_5^+$. In order to get a breakdown curve of ethyl radical, therefore, the abundance of the molecular ion and I^+ (they have no relation to the breakdown curve of the ethyl radical) in the breakdown curve in Fig.1 may be omitted, so that the breakdown curve may start from the $C_2H_5^+$ ion, and further the abscissa of the breakdown curve should be shifted to the value 8.34 eV[11)] which is known as the ionization potential of ethyl radical. The breakdown curve thus obtained is shown in Fig.2. It is necessary to study whether the mass spectrum calculated from this breakdown curve with a suitable internal energy distribution is similar to one obtained by electron impact or not.

In Fig.3-(A) the internal energy distribution used in this calculation is shown. The mass spectrum calculated in this work is compared with one obtained by Yamashita[6)] in Table 1. There is a good agreement with each other. Therefore, it is obvious that the breakdown curve of ethyl radical can be estimated on the basis of the breakdown curve of ethyliodide.

(ii) Methyl radical

Figure 4 shows the breakdown curve of methyl radical, which is estimated based on that of methyliodide in a similar manner as in ethyl radical. It is impossible that the breakdown curve of methyl radical is estimated from those of CH_4, CH_3Cl, and CH_3Br, because in these molecules there is an abrupt increses of CH_2^+ at about 19 eV derived from the excited state.[12,13] The calculated mass spectrum using a suitable internal energy distribution (Fig.3-(B)) is shown in Table 1. Again there is a good agreement between the calculated and observed mass spectra.

Therefore, it is clear that the breakdown curves of some radicals can be estimated based on those of suitable molecules such as alkyliodides in which the scission of the C-I bond is dominant. And it is possible to calculate the mass spectra by electron impact with a suitable internal energy distribution.

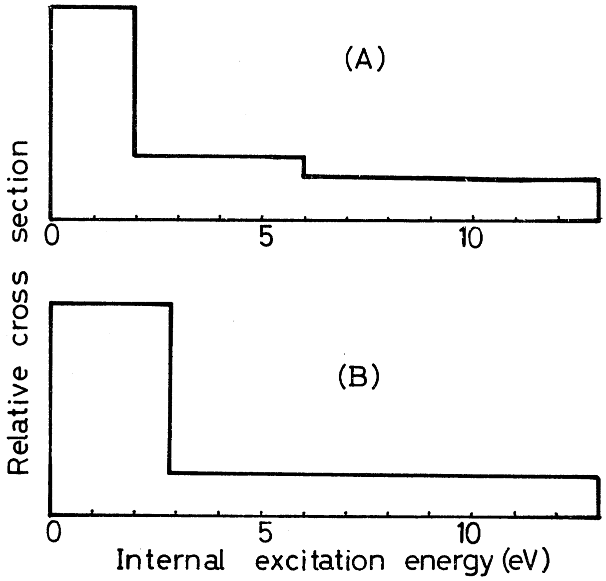

Fig.3. Internal energy distribution of $C_2H_5^+$(A) and CH_3^+(B).

Table 1. Comparison of the observed values by electron impact[6)] and the calculated ones in this work.

	m/e	cacl.	obs.[6)]
C_2H_5 radical	$C_2H_5^+$	100	100
	$C_2H_4^+$	21.6	44 ± 10
	$C_2H_3^+$	80.3	82 ± 12
	$C_2H_2^+$	15.3	13 ± 3
	m/e	cacl.	obs.[6)]
CH_3 radical	CH_3^+	100	100
	CH_2^+	25.8	25 ± 8
	CH^+	4.2	11 ± 6

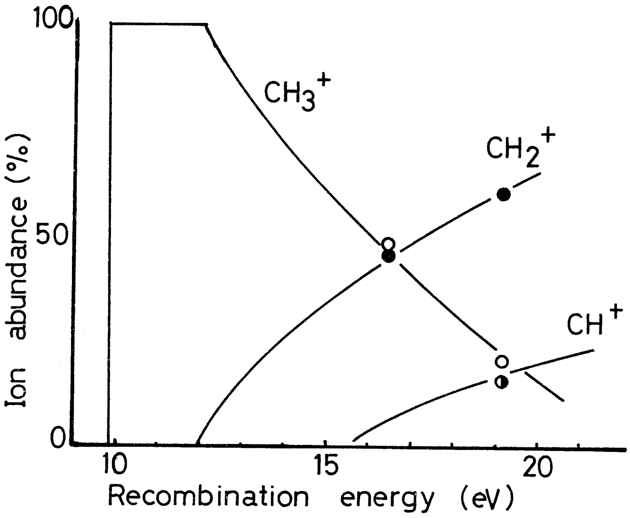

Fig.4. Breakdown curve of methyl radical.

References

1) S. Ikuta, K. Yoshihara, and T. Shiokawa, Bull. Chem. Soc. Japan, 46, 3648 (1973).
2) T. Nagatani, K. Yoshihara, and T. Shiokawa, Bull Chem. Soc. Japan, 46, 1036 (1973).
3) E. Lindholm, "Ion-Molecule Reactions", Vol.2, Ed.by Franklin, Plenum Press, New York (1972) p.457.
4) S. Ikuta, K. Yoshihara, and T. Shiokawa, Mass Spectroscopy, (1974) No.4, to be published.
5) S. Ikuta, K. Yoshihara, and T. Shiokawa, Bull. Chem. Soc. Japan, to be published.
6) S. Yamashita, Bull. Chem. Soc. Japan, 47, 1373 (1974).
7) O. Osberghaus and R. Taubert, Z. Phys. Chem., 4, 264 (1955).
8) C. Ottinger, Phys. Letters, 17, 269 (1965).
9) T. Shiokawa, K. Yoshihara, M. Yagi, T. Omori, H. Kaji, M. Hiraga, and Y. Takita, Mass Spectroscopy, 18, 1230 (1970).
10) S. Ikuta, K. Yoshihara, and T. Shiokawa, Bull. Chem. Soc. Japan, to be published.
11) J. M. Williams and W. H. Hamill, J. Chem. Phys., 49, 4467 (1968).
12) H. Sjögren, Arkiv Fysik, 31, 159 (1965).
13) S. Ikuta, K. Yoshihara, and T. Shiokawa, to be published.

(Received January 21, 1975)