Study on Unimolecular Decomposition of Excited Olefin Ions

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Since Eyring and his co-workers[1] first used statistical theory in the interpretation of the mass spectra of polyatomic molecules, several authors[2-5] have reported applications of the theory. They have adopted some alkanes, esters as well as aliphatic alcohols, and discussed mass spectra, appearance potentials, yields of fragment ions, frequency factors, decomposition processes and such other things. The present author reported in a previous paper[6] on his experimental results concerning the mass spectra of some paraffins and olefins and discussed the bond dissociation of molecular ions.

In this paper, frequency factors, rate constants and decomposition probabilities are estimated from the mass spectra of olefins by the quasi-equilibrium theory, and the decomposition processes of olefins are briefly discussed in comparison with those of paraffins.

Theory

According to the quasi-equilibrium theory[1], the rate constant for the unimolecular dissociation of a polyatomic ion with the excitation energy of E is given by:

$$K(E)=\int_{0}^{E-\varepsilon_0}\frac{1}{h}\cdot\frac{\rho^{+}(E,\varepsilon_0,\varepsilon_t)}{\rho(E)}\mathrm{d}\varepsilon_t \tag{1}$$

where $\rho(E)$ is the density of the states of the ion with an energy of E, $\rho^{+}(E, \varepsilon_0, \varepsilon_t)$ is the density of the states of the ion in the activated complex configuration with the potential energy of ε_0 and the translational energy of ε_t, and h is Planck's constant. The internal energy of the transition complex is, then, $E-\varepsilon_0$. Neglecting the contribution of the electronic state to the state density function, and assuming the oscillations in normal and activated complex configurations of the molecular ion to be harmonic, Eq. 1 can be rewritten as:

$$K(E)=z\left(1-\frac{\varepsilon_0}{E}\right)^{p}(E-\varepsilon_0)^{q} \tag{2}$$

Here, z is the frequency factor; the exponents p and q are defined by the following equations:

$$p=(3N'-6)-L/2-1$$
$$q=(L-L^{*})/2$$

where N' is the number of atoms in the parent ion, L is the number of internal rotational degree of freedom, and the symbol* indicates the quantities relating to the activated complex.

In such a system of unimolecular reaction, the amount of parent ions left at time t is given by:

$$n_t=n_0\exp(-\sum_{i}^{n}K_i t) \tag{3}$$

Here, n_0 is the amount of parent ions at the beginning. In practical calculation, the time, t, is usually assumed to be a certain constant value of the order of 10^{-5} sec. according to the dimension of the ion source as well as of the ion-accelerating voltage. The relative abundance of fragment ions is given by:

$$(I_t)_j=\frac{K_j}{\sum_{i}K_i(E)} \tag{4}$$

It is very difficult to calculate theoretically the frequecy factor. In general, the frequency factor is estimated from the experimental data concerning the reactant and activated complex states in spectroscopy. In other cases, the frequency factor is determined inversely from the relative yields of the principal ions in mass spectrometry. Thus, low-energy reaction paths for the unimolecular decomposition of the polyatomic ion have been studied through mass spectrometry[1,4-8].

Experimental

The instrument used was a Hitachi mass spectrometer, RMS-3, of a single focusing, 60°-sector type with a radius of 100 mm. Ionization is carried out by electron impact. The appearance potentials and the relative yields of the principal ions produced from some paraffins and olefins were measured and reported on in the previous paper[6].

For the case of propylene, a block diagram for the unimolecular decomposition is shown in Fig. 1.

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

[2] A. Krope, E. M. Eyring, A. L. Wahrhaftig and H. Eyring, *J. Chem. Phys.*, **32**, 149 (1960).

[3] L. Friedman, F. A. Long and M. Wolfsberg, ibid., **27**, 613 (1957).

[4] A. B. King and F. A. Long, ibid., **29**, 374 (1958).

[5] L. Friedman, F. A. Long and M. Wolfsberg, ibid., **30**, 1605 (1959).

[6] I. Omura, This Bulletin, **34**, 1227 (1961).

[7] W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1951).

[8] B. Steiner, C. F. Ciese and M. G. Inghram, ibid., **34**, 189 (1961).

TABLE I. LOW VOLTAGE PATTERNS AND APPEARANCE POTENTIALS FOR OLEFINS

Mass	Propylene ion yeild	 A. P., eV.	1-Butene ion yield	 A. P., eV.	*cis*-2-Butene ion yield	 A. P., eV.
$C_4H_8^+$			34.5	9.72	42.5	9.25
$C_4H_7^+$			9.5	12.01	6.3	11.20
$C_3H_6^+$	57.4	9.74				
$C_3H_5^+$	30	12.11	34.5	11.73	29.5	11.60
$C_3H_4^+$	8.5	12.52				
$C_3H_3^+$	4.5	14.21	2.5		3.0	
$C_2H_5^+$					1.5	12.25
$C_2H_4^+$		12.85	9.0	12.38	6.8	12.19
$C_2H_3^+$	2.6	13.80		13.6		

$V_e—I$: 4 eV.

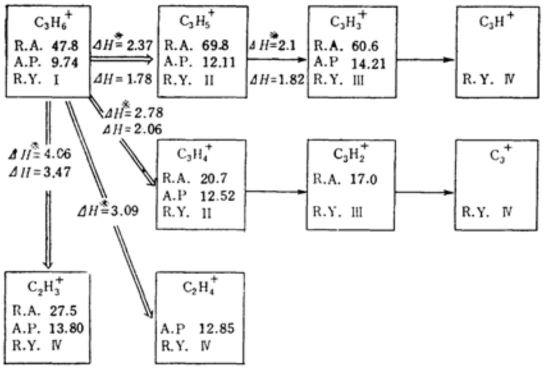


Fig. 1. Unimolecular decomposition scheme for propylene ion by electron impact.

R.A.	Relative abundance (%)
A.P.	Appearance potential (eV.)
R.Y.	Type of relative yield curve[6]
Δ H*	Heat of activation (eV.)
Δ H	Heat of reaction (eV.)

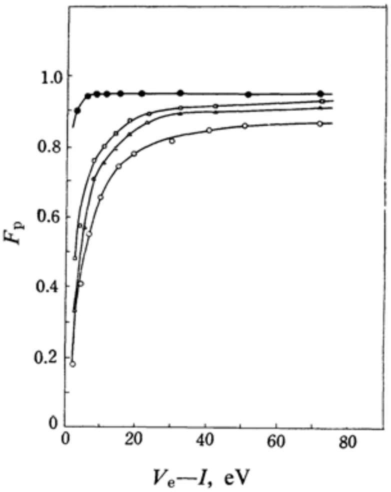


Fig. 2. Decomposition probability of parent ions.

○ Propylene
△ 1-Butene
□ *cis*-2-Butene
● *n*-Butane.

In each block are shown the chemical formula of the ion, the relative abundance (R. A.), and the type of relative yield curve (R. Y.)[6]. The bold lines connecting two blocks show primary reaction paths, fine lines, secondary or higher reaction paths, and broken lines, energetically impossible paths. Over and along the arrow are shown the heat of activation (ΔH^*) and the heat of reaction (ΔH). Table I shows the appearance potentials of principal fragment ions from propylene, 1-butene and *cis*-2-butene, and also the relative abundances at the ionizing voltage four volts higher than the ionization potantial of the parent molecule.

Figure 2 shows the decomposition probability of the parent ion calculated from the following equation:

$$F_p = \frac{\sum_j (I_f)_j}{I_p + \sum_j (I_f)_j} \tag{5}$$

where I_p is the intensity of the undecomposed parent ions and $\sum_j (I_f)_j$ is the total sum of all the other fragment ions in the mass spectrum. Abscissa, V_e-I, is the excess energy of the ionizing electron over the ionization potential of the parent molecule. The curve for *n*-butane is taken as an example of paraffins.

Similarly, the probability of the secondary decomposition of $C_3H_5^+$ ions is shown in Fig. 3. In this case, the $C_3H_5^+$ ion intensity corresponds to I_p in Eq. 6, while the total sum of fragment ions expected from the decomposition of $C_3H_5^+$ ions corresponds to $\sum (I_f)$. The ratio of the intensity of the $C_3H_5^+$ ion to that of the parent ion, as well as the ratio of the intensity of the $C_3H_3^+$ ion produced from the $C_3H_5^+$ ion by secondary decomposition to that of the $C_3H_5^+$ ion, are shown in Fig. 4.

TABLE II. RATE CONSTANT FOR OLEFIN IONS

Molecule	Ion	Rate constant 10^5 sec^{-1}
C_2H_4	$C_2H_4^+$	1.39
C_3H_6	$C_3H_6^+$	4.21
1-C_4H_8	1-$C_4H_8^+$	7.59
cis-2-C_4H_8	*cis*-2-$C_4H_8^+$	4.78

TABLE III. FREQENCY FACTORS FOR DECOMPOSITION PROCESSES

Parent ion	Primary decomposition				
	H	CH_3	C_2H_4	C_2H_5	H_2
$C_3H_6^+$	1.74×10^{11}	4.07×10^{18}			1.13×10^{14}
1-$C_4H_8^+$	1.25×10^{15}	1.35×10^{13}	5.62×10^{17}	1.0×10^{14}	
cis-2-$C_4H_8^+$	8.65×10^{12}	1.55×10^{15}	6.4×10^{20}	3.54×10^{20}	

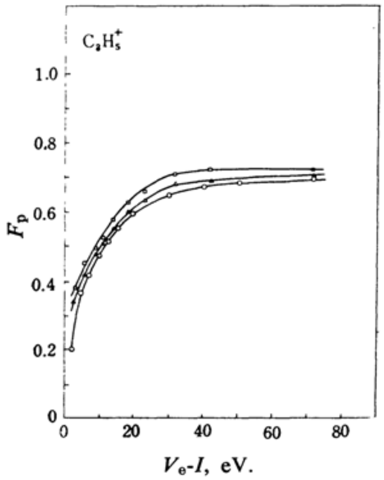


Fig. 3. Decomposition probability of $C_3H_5^+$ ions.
○ $C_3H_5^+$ from propylene
△ $C_3H_5^+$ from 1-butene
□ $C_3H_5^+$ from *cis*-2-butene

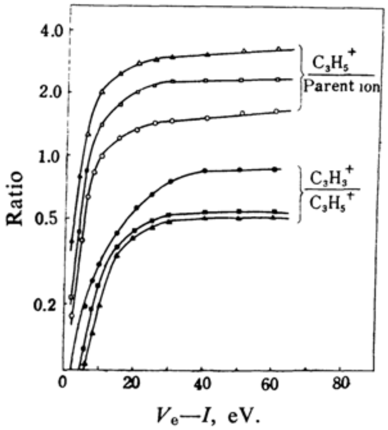


Fig. 4. Ratios of yields.
○, ● Propylene
△, ▲ 1-Butene
□, ■ *cis*-2-Butene

The rate constants for the $C_3H_6^+$, $C_3H_5^+$ and $C_3H_3^+$ ions from propylene are calculated from the mass spectrometric data and are shown in Fig. 5, where the time is assumed to be 1×10^{-5} sec. In Table II are listed the rate constants of the parent ions of some olefins at an ionizing voltage four volts higher than the ionization potential. The frequency factors are also calculated and listed in Table III.

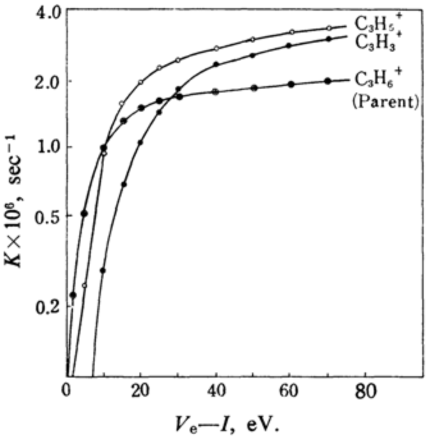


Fig. 5. Unimolecular decomposition rate constant — propylene —.

Discussion

In the estimation of the rate constant, the time, t, in Eq. 3 is assumed to be 1×10^{-5} sec. because the time between the formation of the ions and their entering the focusing system is presumed to be of the order of 10^{-5} sec. The absolute value of the rate constant obtained depends greatly on this assumption and is not very important. It should be discussed in relation with the assumption as well as with the value obtained from theory or other kinds of experiment. The frequency factor is of the same type.

The frequency factor obtained for the hydrogen atom abstraction from propane ion and that obtained for the methyl radical abstraction are in the ratio of about 1 : 10^3, as has been reported by Friedman[5)]. It seem there are no gross mistakes in the present experiment.

The rate constant of the parent ion in a homologous series seems to increase with the size of the ion, as is shown in Table II. This may be due to the increase in possible reaction paths.

It might be simply considered that the character of the fragment ion, $C_3H_5^+$, is independent of the parent ion. Contrary to this simple expectation, the secondary decomposition probabilities of the $C_3H_5^+$ ion in the cases of propylene, 1-butene, and *cis*-2-butene are slightly different from each other,

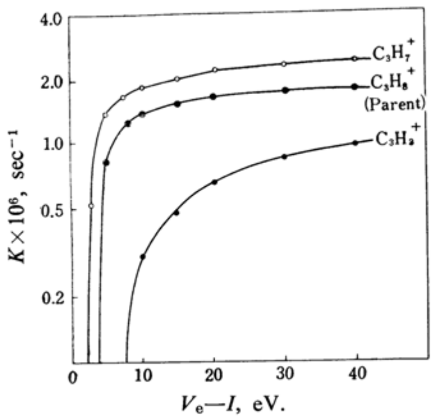
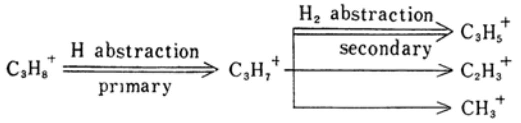


Fig. 6. Unimolecular decomposition rate constant — propane —.

as is shown in Fig. 3. The $C_3H_3^+/C_3H_5^+$ ratio for the ions from propylene considerably differs from those for the ions from 1-butene and *cis*-2-butene, as is shown in Fig. 4. The cause remains to be further investigated.

The rate constants of the principal ions from propane are shown in Fig. 6 in comparison with those of propylene, as in Fig. 5. The decomposition paths of the propane ion are as follows:

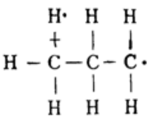


Here, bold lines indicate principal paths and fine lines, reaction paths energetically possible but of secondary importance. The secondary decomposition path from $C_3H_7^+$ to $C_3H_5^+$ in the case of propane corresponds to the path from $C_3H_5^+$ to $C_3H_3^+$ in the case of propylene. Comparing Fig. 5 with Fig. 6, we can see that the rate constant for the secondary decomposition probability is larger in the case of propylene than in the case of propane. This may be caused by the fact that the probability of the abstraction of the hydrogen molecule is closely related with the distribution of the positive charge or the ionic structure of the activated complex. According to the quasi-equilibrium theory, the density of the positive charge associated with the bonds has an effect on the bond rupture, and the relative yield of ions is related with the distribution of the positive charge⁶⁾. Inversely, the effect of positive charge distribution may be presumed from the rate constant or the activation energy.

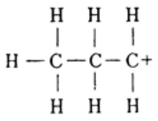
The decomposition paths to the $C_3H_3^+$ ion from the propylene ion are as follows:

$$C_3H_6^+ \xrightarrow[\text{primary}]{\text{H abstraction}} C_3H_5^+ \xrightarrow[\text{secondary}]{H_2\text{ abstraction}} C_3H_3^+$$

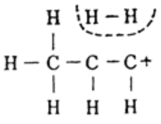
The ionic structure of the $C_3H_7^+$ ion from propane is presumed to be of the last type of the follwing three structures;



I

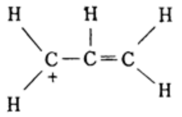


II

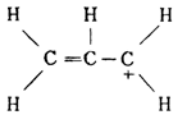


III

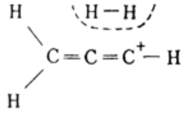
Similarly, the ionic structure of the $C_3H_5^+$ ion from propylene is presumed to be of the last type of the following three structures:



I′



II′



III′

In the case of propylene, the activation energy for the secondary reaction (hydrogen molecule abstraction) is smaller than twice the activation energy for the primary reaction (hydrogen atom abstraction), as is shown in Table IV. In the case of propane, on the other hand, the energy for the secondary reaction (hydrogen molecule abstraction) is larger than twice the energy for the primary reaction (hydrogen atom abstraction). These interesting results seem to be very important for the study of the dissociation of these molecular ions.

Tabie IV. Energy for the abstraction of a hydrogen atom and a hydogen molecule

Parent ion	Primary H, eV.	Secondary H_2, eV.	H_2-2H eV.
$C_3H_6^+$	2.37	2.10	−2.64
1-$C_4H_8^+$	2.29	2.09	−2.49
cis-2-$C_4H_8^+$	1.95	2.15	−1.75
$C_3H_8^+$	0.56	3.2	+2.08
n-$C_4H_{10}^+$	0.78	2.54	+0.98
iso-$C_4H_{10}^+$	1.37	3.39	+0.65

Summary

The decomposition probabilities, rate constants, and frequency factors for some olefins have been calculated on the basis of mass spectrometric data and the quasi-equilibrium theory.

The rate constant of the parent ion in a homologous series increases with the size of the ion. Fragment ions of the same form but from different parent ions sometimes reveal different rate constants.

The scheme of hydrogen molecule abstraction in the secondary decomposition processes of propane is analogous to that of propylene, and reasonable ionic structures of primary ions can be presumed.

For a more quantitative discussion, however, there remain some indistinct points in the application of the quasi-equilibrium theory. For instance, the time of reaction along with the rate constant is assumed to be 1×10^{-5} sec. and to be constant for all ions. Further studies should be carried out both in theory and experiments.

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