December, 1977]　BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (12), 3103—3106 (1977)　3103

The Effect of Temperature on the Mass Spectra of 1-Alkenes. II

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(Received January 20, 1977)

The mass spectra of 1-alkenes ranging from C_5 to C_{10} were measured at temperatures of the ion source 120—250 °C. Fragmentation $M^+ \xrightarrow{m_{28}} (M-28)^+$ and $M^+ \xrightarrow{m_{29}} (M-29)^+$, where m_{28} and m_{29} denote the metastable peaks of the fragmentations, were studied. The behavior of the curve of the intensity ratios $R'_{28}=m_{28}/F_{28}$ and $R'_{29}=m_{29}/F_{29}$ (F_{28} and F_{29} denote the intensities of the $(M-28)^+$ ion and the $(M-29)^+$ ions, respectively), *versus* temperature T of the ion source of the mass spectrometer is explained by the quasi-equilibrium theory (QET).

Many theoretical studies have been carried out[1-7] on the mechanism of fragmentation of ions produced by elecron impact from various organic compounds. These works can be divided roughly into two categories, one using QET and the other based on the molecular orbital calculation (MOT).[2,4] So far nothing definite has been given on a comparison of the two methods. It seems difficult to interpret the mechanism of each fragmentation by either one of the methods. It was shown[2] that the intensities of some peak in the mass spectra of a few derivatives of aromatic compounds can be interpreted by MOT. Subsequently, QET was applied to explain some experimental results for a series of primary alcohols and of 1-alkenes,[6] and found to give satisfactory results. QET was also successfully applied to the elucidation of the behavior of common ions, such as $C_5H_5^+$,[8] $C_6H_5CO^+$,[9] and $C_7H_7^+$ [10] from various precursors.

For 1-hexene, the slope of the curve R'_{28} *versus* T becomes positive though it is expected to take a negative value according to QET, when a simple form is assumed for the internal energy distribution function, $P(E)$, for M^+. The behavior of the curve can be explained by using the measured photoelectron spectrum as $P(E)$ instead of a simple function.[6]

We have obtained the curves R'_{29} *versus* T for C_5—C_{10} 1-alkenes and a curve R'_{28} *versus* T for 1-pentene, and studied the behavior of these curves and the R'_{28} curves for C_6—C_{10} 1-alkenes. The slopes of a few curves for smaller compounds take a negative sign as expected with QET having a simple $P(E)$ function. In contrast, the tangents of most of the curves for larger compounds are found to take a positive sign. The behavior of these curves can be elucidated on the same basis as in the case of R'_{28} for 1-hexene.

Experimental

A CEC 21-103C mass spectrometer was used to obtain the mass spectra. $R'_{28}=m_{28}/F_{28}$ and $R'_{29}=m_{29}/F_{29}$ were measured in the temperature range 120—250 °C. The results for R'_{28}, including those for C_6—C_{10}, and for R'_{29} are given in Figs. 1 and 2, respectively, the curves being given in Table 1. The result was investigated by QET. For the investigation, curve log k *versus* E, where k is the rate constant for the decomposition of M^+ into F^+, and E is the internal energy of M^+, should be drawn in order to estimate the location,* of the "metastable window" on the E axis. The corresponding curve for 1-hexene is given in Fig. 11 in a previous report.[6] In order to construct curve log k *versus* E, the ionization potential, I, of M^+ and the appearance potential, A, of F^+ were measured at the ion source temperature 250 °C using the EDD technique[11] (Table 1).

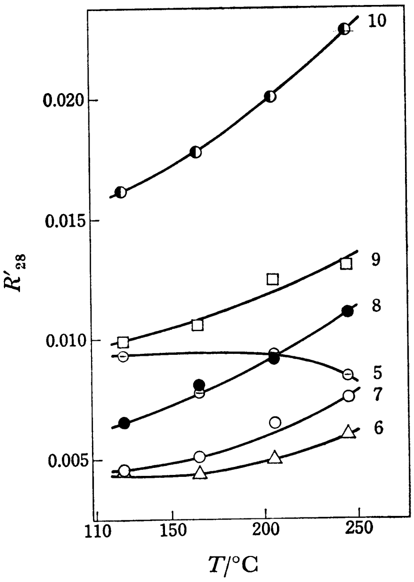

Fig. 1.

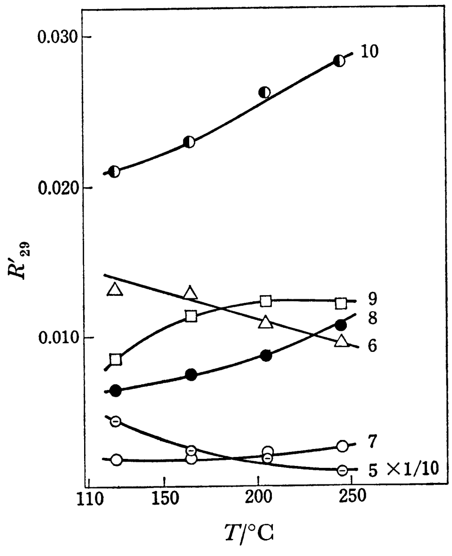

Fig. 2.

Figs. 1 and 2. The relation of intensity ratios of ions, R'_2 and R'_{29}, *versus* the temperature, T, of the ion source. The numbers on the curves are those of the carbon atoms of the 1-alkenes.

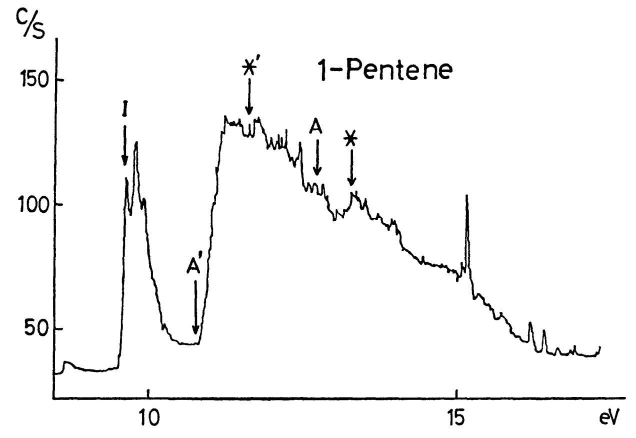

Fig. 3.

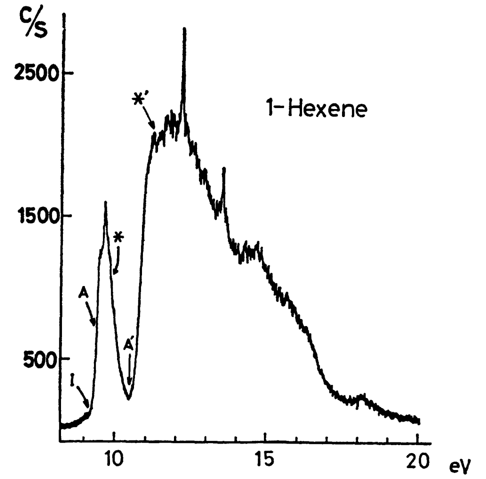

Fig. 4.

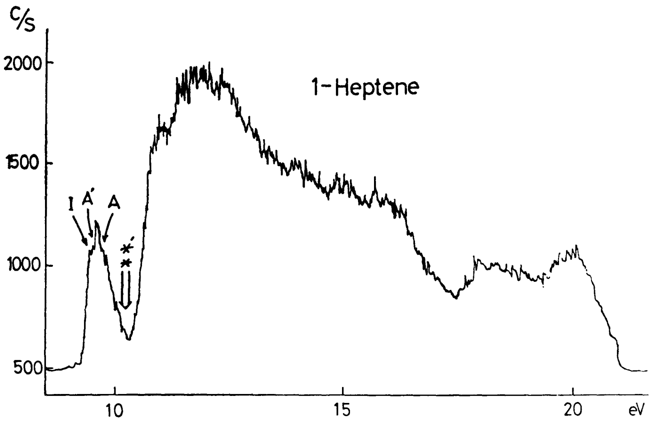

Fig. 5.

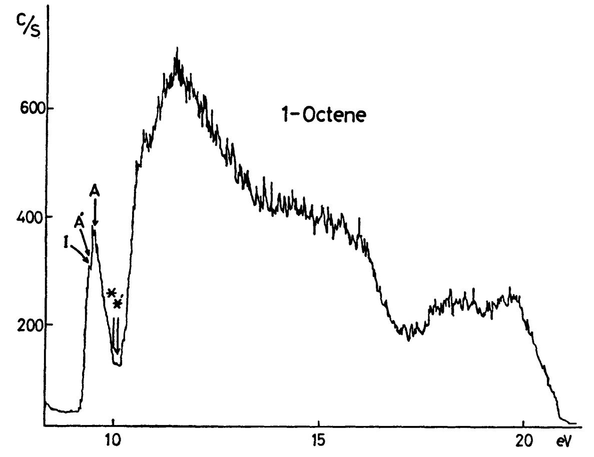

Fig. 6.

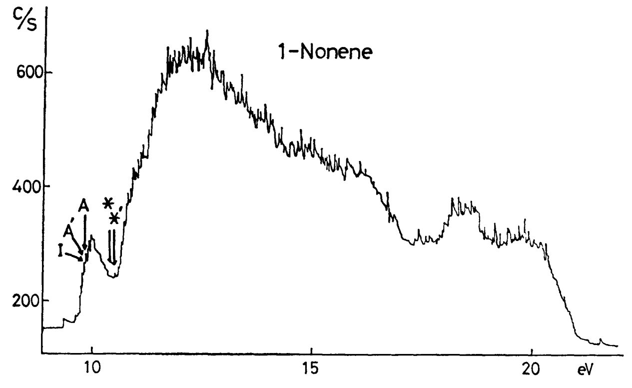

Fig. 7.

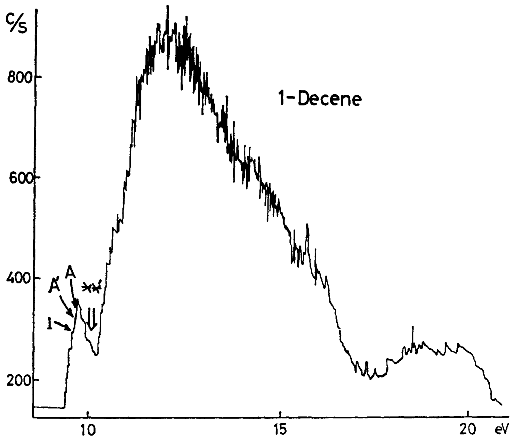

Fig. 8.

Figs. 3—8. The photoelectron spectra of 1-alkenes. The meanings of the notations are given in the text.

A JASCO PE-1 photoelectron spectrometer was used to obtain photoelectron spectra with HeI as a light source. The photoelectron spectra measured were used as $P(E)$. The spectra for each compound are shown in Figs. 3—8. The conditions of measurement are the same as already described.[6]

The olefins used were API standard samples, the purity being greater than 99.7%. All the reagents were mass-spectroscopically confirmed to be pure.

Results and Discussion

The relation between the temperature of the ion source, T, and the intensities, $[M^+]$, $[m]$, and $[F^+]$, of the ions in the following fragmentation was investigated by QET.

$$M^+ \xrightarrow{m} F^+$$

Though more sophisticated expressions are proposed for

Table 1. Ionization potential, I, activation energies, ε_{28} and ε_{29}, in eV, and the schematic curves of the behavior of R' *versus* T (Figs. 1 and 2)

$\varepsilon_n = A(\mathrm{M-n})^+ - I$, where $A(\mathrm{M-n})^+$ is the appearance potential of the fragment ion $(\mathrm{M-n})^+$. Errors in the measured I and A values are estimated to be ±0.1 eV.

Number of C atom	I a)	I Present result	ε_{28}	ε_{29}	R'_{28}	R'_{29}
5	9.66	9.76	1.25	2.92		
6	9.59	9.54	0.11	1.18		
7	9.54	9.53	0.10	0.26		
8	9.52	9.54	0.06	0.21		
9	—	9.56	0.02	0.10		
10	9.51	9.52	0.03	0.08		

a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc. (1957), p. 108.

the rate constant and intensities of ions, the rate constant for the fragmentation was assumed to be given by

$$k = \nu(1-\varepsilon/E)^{n-1}$$

where the notations have their usual meanings.[6] The intensities of the ions were assumed to be given by[12]

$$[\mathrm{M}^+] = \int_0^{\varepsilon} P(E)\mathrm{d}E + \int_{\varepsilon}^{\infty} P(E)\exp[-k(E)t_4]\mathrm{d}E, \tag{4}$$

$$[\mathrm{F}^+] = \int_{\varepsilon}^{\infty} P(E)[1-\exp\{-k(E)t_1\}]\mathrm{d}E, \tag{5}$$

$$[\mathrm{m}] = \int_{\varepsilon}^{\infty} P(E)[\exp\{-k(E)t_2\} - \exp\{-k(E)t_3\}]\mathrm{d}E. \tag{6}$$

The mean time spent by a newly-formed ion in the ionization chamber is t_1. After being accelerated, the ions dissociated between the times t_2 and t_3 are observed as a metastable peak, and the M^+ ions which do not dissociate until t_4 are observed as the parent ion, M^+. The internal energy distribution function, $P(E)$, was assumed to be

$$P(E) = \exp[-E/kT]E/(kT)^2. \tag{7}$$

The values of t were estimated from the dimensions of the mass spectrometer and the conditions of measurement. Substituting these values in Eqs. 4—7, graphs showing the relationship between $R=[\mathrm{F}^+]/[\mathrm{M}^+]$, $R^*=[\mathrm{m}]/[\mathrm{M}^+]$ and $R'=[\mathrm{m}]/[\mathrm{F}^+]$ *versus* T were obtained and compared with the experimental results. The graphs for R and R^* obtained by calculation increased, and the graph for R' decreased with rise in temperature. Comparing the behavior of these curves with those obtained by experiments for M^+, $\mathrm{F}^+=(\mathrm{M}-28)^+$, R_{28}, R^*_{28} and R'_{28} *versus* T, it was found that while values of R_{28} and R^*_{28} for 1-alkenes of C_5—C_{10} increase with rise in temperature in line with the theoretical prediction, those of R'_{28} for 1-alkenes for C_6—C_{10} also increase, contrary to the prediction based on the assumption mentioned above. Taking R'_{28} for 1-hexene as an example, this anomaly was shown[6] to be adequately explained if the photoelectron spectrum for the compound was used as $P(E)$, instead of Eq. 7.

In the present study, R_{29}, R^*_{29}, and R'_{29} for 1-alkenes of C_5—C_{10} are measured in addition to R'_{28} for 1-pentene, and their behavior, when the temperature of the ion source is increased, is compared with that expected by QET using Eq. 7 as $P(E)$. As the result, the behavior of the curves for R' is found to be inconsistent with the expectation by QET with Eq. 7, except for R'_{28}, R'_{29} for 1-pentene and R'_{29} for 1-hexene, while the behavior of R'_{29} and R^*_{29} is found to be consistent with the prediction, *i.e.*, both the ratios increase with rise in temperature. Namely, the schematic curves shown in the 6 and 7th columns of Table 1, (*cf.* Figs. 1 and 2) increase with the temperature increase, except for R'_{28}, R'_{29} for 1-pentene and R'_{29} for 1-hexene.

The experimentally obtained ionization potential, I, appearance potentials, A and A', of $(\mathrm{M}-28)^+$ and $(\mathrm{M}-29)^+$ ions, respectively, and approximate positions of the metastable windows, * and *′, of the $(\mathrm{M}-28)^+$ and $(\mathrm{M}-29)^+$ ions, respectively, estimated by the same procedure as described,[6] are shown by arrows in Figs. 3—8. In calculating the location of * and *′, ν was assumed to be 10^7 for $(\mathrm{M}-28)^+$, the rearrangement ion, and 10^{13} for $(\mathrm{M}-29)^+$, the ion considered to be produced by simple cleavage of a bond.

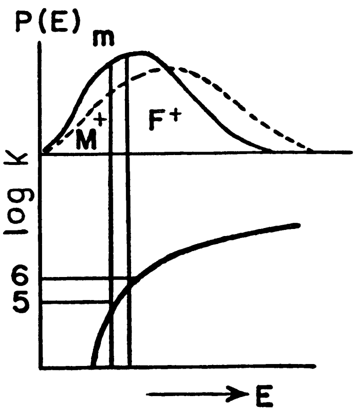

Fig. 9. Relationship of $P(E)$ and k (E) for unimolecular ion decompositions in the mass spectrometer; see text for definitions.

Using the positions * and *′, of the metastable windows, the behavior of curves of R, R^*, and R' *versus* T can be explained as follows. For the sake of simplicity, the internal energy distribution function, $P(E)$, is assumed to be given by Eq. 7 for the moment. Figure 9 shows the relation between $P(E)$ and the internal energy, E, and the position, m, of metastable window schematically. The positions of the origin and the onset of the curve in the lower diagram are located by the measured I and A, respectively. The dotted curve in the upper diagram shows the behavior of the $P(E)$ curve schematically when the temperature T increases.[14] The intensities of molecular ion, $[\mathrm{M}^+]$, metastable ion, $[\mathrm{m}]$, and fragment ion, $[\mathrm{F}^+]$, are assumed to be proportional to the area under the $P(E)$ curve (upper diagram) denoted by M^+, m, and F^+, respectively. As the temperature rises and the $P(E)$ takes a flatter shape, shown by the dotted curve in Fig. 9, the areas for both M^+ and m decrease and that for F^+ increases and consequently $R=[\mathrm{F}^+]/[\mathrm{M}^+]$ increases and $R'=[\mathrm{m}]/[\mathrm{F}^+]$ decreases. As for R,* the calculated result based on Eqs. 4—7, and shown in Fig. 9 of the previous report,[6] suggests its increase with the temperature increase.

First, R' curves obtained by experiments are compared with those predicted by the theory. In the following investigation, the photoelectron spectrum for each compound is assumed to represent the internal energy distribution function, $P(E)$, for the compound instead of Eq. 7. In the case of 1-pentene given in Fig. 3, since the metastable windows * and *′ are both situated near the shoulder of the wider band of its photoelectron spectrum (*cf.* the $P(E)$ curve in Fig. 9), the behavior of R'_{28} and R'_{29}, with the temperature increase is consistent with that expected from the simple consideration mentioned above. The behavior of R'_{29} in the case of 1-hexene (Fig. 1 and Table 1) can be explained in exactly the same manner from the location of *′ given in Fig. 4.

The values of * and *′ for all other compounds studied including * for hexene[6] are located on the higher energy side of the narrower band of the photoelectron spectrum of each compound. This band is considered to originate from the π electron. When T increases and the band takes a flatter shape, the area corresponding to the metastable peak increases, while the fractional increase of the area for F^+ is very small, resulting in the increase in R'_{28} or in R'_{29}, in contrast to the theoretical expectation based on Eq. 7.

The values of $R=[F^+]/[M^+]$ and $R^*=[m]/[M^+]$ show no "anomaly," *i.e.*, they both increase with temperature. This can easily be explained by the consideration for R'.

As far as these phenomena are concerned, they can be qualitatively elucidated by QET with photoelectron spectra used as the internal energy distribution functions. Various investigations[13–18] have been made of possible methods for the evaluation of the internal energy distribution functions resulting in ions from the impact of energetic electrons. Meisels *et al.*[19] postulate that the photoelectron spectrum of a compound gives a reasonable representation of the actual function under certain conditions. Innorta *et al.*[20] report that it is too crude an approximation to use photoelectron spectra as a representation of the internal energy distribution function for some compounds in interpreting their mass spectra. The former idea receives support from the present investigation for a series of 1-alkenes ranging from C_5 to C_{10}.

The diagrams of the measured appearance potentials of $(M-28)^+$ and $(M-29)^+$ ions *versus* the number of carbon atoms were found to be smooth curves which decrease at first and then approach gradually nearly constant values as the carbon number increases. The behavior of these curves deserves further investigation.

It is not clear whether the reactions producing $(M-28)^+$ and $(M-29)^+$ are competing reactions or reactions starting from different electronic states, into which the sample molecules are excited with certain probabilities. Judging from the present result, the effect of the reaction mechanism on the result is not so large that it influences the qualitative elucidation based on QET, aside from whether the reactions compete with each other or not.

In conclusion the "anomaly" in the mass spectra of 1-alkenes ranging from C_5 to C_{10} is explained qualitatively by QET using photoelectron spectra of the compounds as the internal energy distribution functions, $P(E)$.

The authors are indebted to Mr. Hiroshi Matsumoto and Mr. Tadashi Miyazaki for carrying out the photoelectron spectrometry experiment.

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