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The Effect of the Temperature on the Mass Spectra of Aliphatic Primary Alcohols and 1-Alkenes. I.

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The decomposition of the $(M-18)^{\ddagger}$ ion of aliphatic alcohols and that of the $M^{\ddagger}$ ion of 1-alkenes are studied. The temperature effect of the ion source of a mass spectrometer on the ratios of the intensities of these ions, those of the ions produced from them by C_2H_4 elimination, and those of the metastable ions for the corresponding fragmentation was measured and was compared with the results to be expected from a simple QET consideration. A discrepancy between the result expected and the experimental result was found for 1-alkenes. In order to clarify the cause of the discrepancy, the photoelectron spectrum was measured for 1-hexanol and for 1-hexene and was assumed to represent the internal energy distribution function, $P(E)$, for each of these substances. Taking the shape of the $P(E)$ into account, the result for 1-alkenes was explained.

It is well known that there is so striking a similarity between the mass spectra of aliphatic primary alcohols and those of 1-alkenes that a group of peaks in the mass spectra of alcohols is called as "olefin peaks," this has prompted studies of the fragmentation mechanism of these alcohols. By study of the appearance potentials of the ion corresponding to the "olefin molecule" or by study of the time variation in the intensity of the "olefin peaks" in the mass spectra of alcohols, it has been shown that no olefin molecule is actually formed by, for instance, any surface reaction, in the ionization chamber before ionization takes place.1) The mass spectra of primary alcohols, particularly the intensities of the $(M-18)^{\ddagger}$ ion peak and the peaks related to the ion, are known to be strongly dependent on the conditions of measurement, such as the temperature or the materials of the sample manifold of the instrument used.2) However, the details of these phenomena have not yet been clarified.

It is of primary importance to obtain reproducible mass spectra in the various applications of mass spectrometry to organic chemistry. As a first step to finding the conditions under which we can obtain reproducible results, it is desirable that the mechanism of fragmentation resulting in the poorly reproducible peaks be clarified. In the present work, the effect of the temperature of the ion source of a mass spectrometer on a few peaks, mentioned above, in the mass spectra of primary alcohols and those of 1-alkenes was investigated.

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1) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publ. Co., Amsterdam (1960),

2) R. A. Brown, W. S. Young, and N. Nicolaides, *Anal. Chem.*, **26**, 1653 (1954),

Experimental

A CEC21-103C mass spectrometer was used to obtain the mass spectra of aliphatic primary alcohols and the corresponding 1-alkenes. The number of carbon atoms of the alcohols and the 1-alkenes investigated ranged from 5 to 12 and from 6 to 10, respectively. For alcohols, ions in the following decompositions were investigated, because the (alcohol$-$H$_2$O)$^{+\cdot}$ ion is known to be sensitive to the temperature of the ion source:

$$\begin{aligned} &C_nH_{2n+1}OH \rightarrow (C_nH_{2n+1}OH)^{+\cdot} \\ &\rightarrow (C_nH_{2n})^{+\cdot} + H_2O \\ &\;\;{*'}\big\lfloor\!\longrightarrow (C_nH_{2n}-28)^{+\cdot} + C_2H_4 \end{aligned} \tag{1}$$

In the decomposition, the intensities of the $(C_nH_{2n})^{+\cdot}$ and $(C_nH_{2n}-28)^{+\cdot}$ ions and that of the metastable ion, $*'$, are denoted as M', F', and m' respectively. For 1-alkenes, the following decomposition was studied:

$$C_nH_{2n} \rightarrow C_nH_{2n}^{+\cdot} \overset{*}{\rightarrow} (C_nH_{2n}-28)^{+\cdot} + C_2H_4 \tag{2}$$

In the decomposition, the intensities of the $(C_nH_{2n})^{+\cdot}$, and $(C_nH_{2n}-28)^{+\cdot}$ ions and that of the metastable ion, $*$, are denoted as M, F and m respectively. The height of the metastable peak was taken as the m or m′ intensity. When the metastable peak was partly masked by an adjacent peak, the height of the metastable peak was determined after it had been resolved with a Du Pont 310 Curve Resolver.

F'/M', m'/M', and m'/F' for alcohols, and F/M, m/M, and m/F for 1-alkenes were measured under various temperatures, and the relation between the values of these intensity ratios and the temperature of the ion source was investigated from the standpoint of QET. The temperature range covered was between 120 and 250 °C.

The appearance potentials, A, of the $C_nH_{2n}^{+\cdot}$ ions from hexanol and 1-hexene, A(M′) and A(M) respectively, and that of the $(C_nH_{2n}-28)^{+\cdot}$ ion from the hexene, A(F), were measured at the ion-source temperature of 250 °C using the EDD technique.[3] The constant, b, in the EDD calculation was taken as 0.67. In the measurement, the influence of the filament-shielding voltage of the ion source on the appearance potential obtained was taken into account.[4] Xenon was used for the correction of the energy axis. The results obtained were $A(\mathrm{M})=9.33$ eV and $A(\mathrm{M})-A(\mathrm{F})=0.12$ eV. The photoelectron spectra of hexanol and 1-hexene were measured with a photoelectron spectrometer, PE-1, made by the Japan Spectroscopic Co., Ltd., using He I. The temperature of the sample in the measurement was less than 100 °C. Xenon was used for calibrating the energy axis again.

The alcohols were obtained from the Tokyo Kasei Co., Ltd., and were used after distillation. The olefins were API Standard Samples, the purity of which was guaranteed to be more than 99.7%. All the reagents were mass-spectroscopically confirmed to be pure.

Results and Discussion

The relations between the temperature of the ion source and the m'/M', m'/F', F'/M', m/M, m/F, and F/M ratios are shown in Figs. 1—6 respectively. As may be seen from the figures, the tangents of the curves for the m/M, m'/M', F/M, F'/M' and m/F ratios *versus* the temperature are positive, whereas the tangent of the curve for the m'/F' ratio is negative. Though Figs. 1—6 were obtained with an electron-accelerating voltage, V_e, of 70 eV, the tangent for each curve was found to keep the same sign when V_e was lowered until $V_e=10.0$ eV.

According to QET in its simplest form,[5] the rate constant, k, for the unimolecular fragmentation with a metastable ion, m:

$$A^+ \longrightarrow B^+ \tag{3}$$

is written as:

$$k = \nu\left(1 - \frac{\varepsilon}{E}\right)^{n-1} \tag{4}$$

where ν is the frequency factor, ε is the activation energy, E is the internal energy of the A$^+$ ion, and n is the effective number of harmonic oscillators of which the A$^+$ molecule is assumed to be composed. In Reaction (3), it is assumed that B$^+$ does not decompose further.

Before applying QET to the results shown in Figs. 1—6, the effect of the potential successive decompositions from $F'^{+\cdot}$ or $F^{+\cdot}$ and that of the potential competitive decompositions from $M'^{+\cdot}$ or $M^{+\cdot}$ on the results shown in Figs. 1—6 have to be investigated in order to examine whether the rate constant in the form of Eq. (4) can be used for Reactions (1) and (2).

When bombarded by electrons of $V_e=70$ eV, the $(\mathrm{M'}-28)^{+\cdot}$ ions from alcohols and the $(\mathrm{M}-28)^{+\cdot}$ ions from 1-alkenes are shown to decompose further into the $(\mathrm{M'}-43)^+$, and $(\mathrm{M'}-45)^+$ ions, and into the $(\mathrm{M}-43)^+$, $(\mathrm{M}-45)^+$ ions, respectively, by the appearance of the corresponding metastable peaks. However, in the spectra obtained at electron-acceleration voltages lower than $V_e=12$ eV, the intensities of the ions produced by the successive fragmentations were found to be nearly zero. Because the signs of the tangent of the curves shown in Figs. 1—6 remain the same down to $V_e=10.0$ eV, it is reasonable to assume that the rate constant in the form of Eq. (4) can be used to discuss qualitatively the temperature effect on the intensity of the ions in Reactions (1) and (2) without taking the influence of the successive fragmentations into account.

At low electron-acceleration voltages, two reactions, (5) and (6), competing with Reactions (1) and (2) respectively, were observed:

$$\mathrm{M'}^{+\cdot} \longrightarrow (\mathrm{M'}-29)^+ \tag{5}$$

$$\mathrm{M}^{+\cdot} \longrightarrow (\mathrm{M}-29)^+ \tag{6}$$

The appearance potentials for these ions, A, were measured for 1-alkenes, such as 1-hexene and 1-octene, and were found to be $A(\mathrm{M}-28) < A(\mathrm{M}-29)$, as was to be expected for the reasons to be given below. As for the appearance potentials of the corresponding ions for alcohols, $A(\mathrm{M'}-28)^{+\cdot}$ is inferred to be smaller than $A(\mathrm{M'}-29)^+$, because the $(\mathrm{M'}-28)^{+\cdot}$ ion is considered to be produced by rearrangement, and the $(\mathrm{M'}-29)^+$

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[3] R. E. Winters, J. H. Collins, and W. L. Courchene, *J. Chem. Phys.*, **45**, 1931 (1966).

[4] S. Tajima, Y. Shimizu, and T. Tsuchiya, This Bulletin, **45**, 931 (1972).

[5] H. M. Rosenstock and M. Krauss, *Adv. Mass Spectrometry*, **2**, 251 (1962).

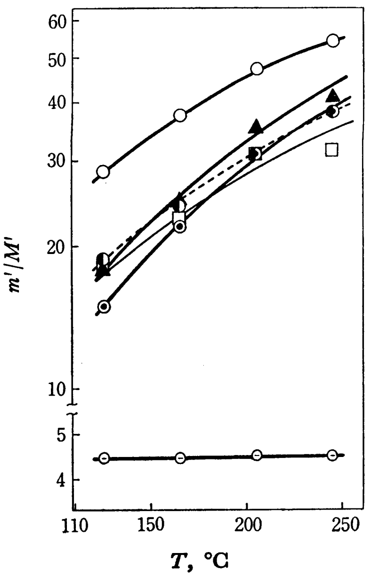

Fig. 1.

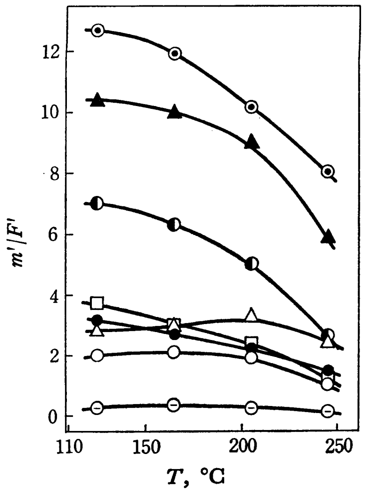

Fig. 2.

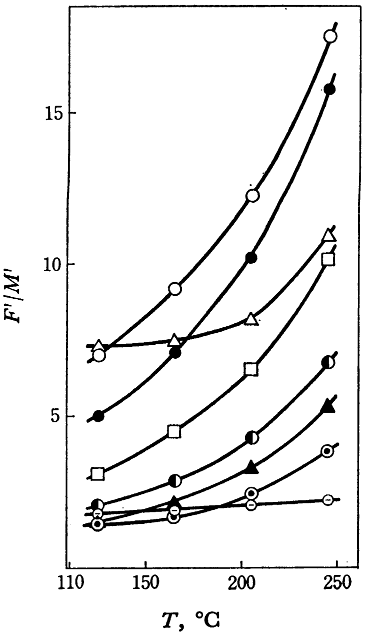

Fig. 3.

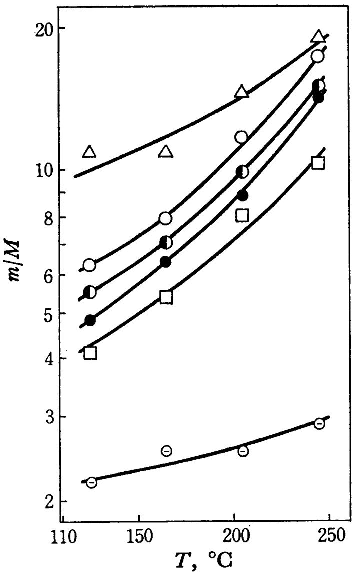

Fig. 4.

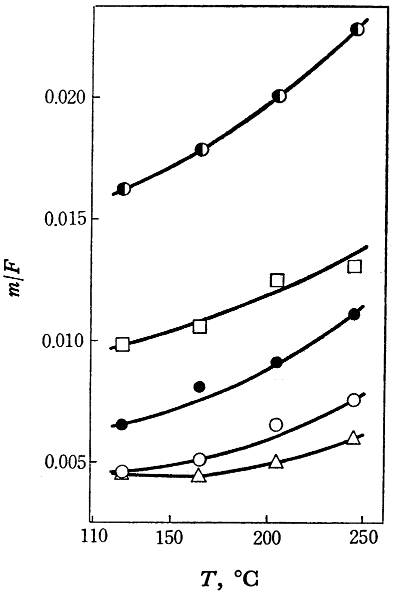

Fig. 5.

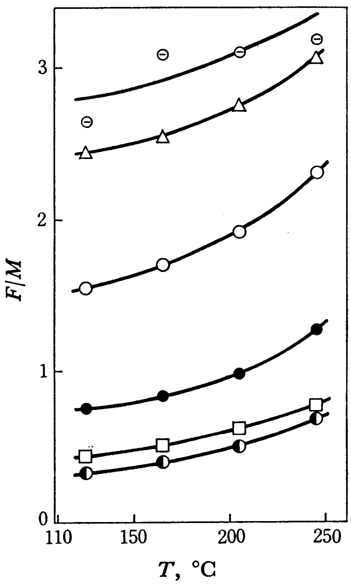

Fig. 6.

Figs. 1—6 show the relation of intensity ratios of ions in Reaction (1) or (2) *versus* the temperature of the ion source. The mark for each curve stands for the carbon number of the compound as indicated below.
⊖ 5; △ 6; ○ 7; ● 8; □ 9; ◐ 10; ▲ 11; ⊙ 12.

ion, to be a simple cleavage of a bond from the M^{+} ion[6,7]. Actually, the values of the $(M'-29)^{+}/(M'-28)^{+}$ and $(M-29)^{+}/(M-28)^{+}$ intensity ratios, which were 1—0.5 at $V_e=70$ eV, were found to decrease as the electron energy was lowered. The implication of these results is that the competitive reactions, (5) and (6), have no serious effect upon the general behavior of the curves shown in Figs. 1—6, at least not in the low-electron energy range, the sign of the tangent of the curves can, therefore, be investigated without taking the influences of these reactions into account as long as the qualitative considerations are concerned, although the influences of Reactions (5) and (6) on the intensities of M'^{+} or M^{+} respectively can not be neglected in any quantitative consideration. Such being the circumstances, the results of Figs. 1—6 were investigated as follows. In the investigation, the M'^{+} ion, produced by water elimination from alcohol, is considered to be the parent ion for Reaction (2), since the F'^{+} ion is shown to be produced from the M'^{+} ion by the presence of the metastable ion.

Using the expression given by Eq. (4) for the rate constant, McLafferty *et al.*,[8] Cooks *et al.*,[9] Jennings

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[6] D. H. Williams and R. G. Cooks, *Chem. Comm.*, **1968**, 663.

[7] A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **92**, 3984 (1970).

[8] F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967).

[9] R. G. Cooks and D. H. Williams, *Chem. Comm.*, **1968**, 627.

et al.[10] and Williams *et al.*[6,11] have investigated quantitatively the effects of n[8,9], ε[10], E[11] and ν[6] in Eq. (4) on the fragmentation patterns of an appropriate series of compounds or of appropriate combinations of compounds.

In the present investigation, the A^+ ion in the unimolecular decomposition reaction, (3), is assumed to have an internal energy distribution function of $P(E)$. The times spent by an ion in various parts of the mass spectrometer were assumed to be as follows. 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 A^+ ions which do not dissociate until t_4, are observed as the parent ion, A^+. Then, of the total ions produced, the fractions of the ions, A, B, and m, are given by:[12]

$$[\mathrm{A}] = \int_0^{\varepsilon} P(E)\mathrm{d}E + \int_{\varepsilon}^{\infty} P(E)\exp\{-k(E)t_4\}\mathrm{d}E \tag{7}$$

$$[\mathrm{B}] = \int_{\varepsilon}^{\infty} P(E)[1-\exp\{-k(E)t_1\}]\mathrm{d}E \tag{8}$$

$$[\mathrm{m}] = \int_{\varepsilon}^{\infty} P(E)[\exp\{-k(E)t_2\}-\exp\{-k(E)t_3\}]\mathrm{d}E \tag{9}$$

Ehrhardt *et al.*[13] have given an expression for $P(E)$, based on statistical mechanics, as follows:

$$P(E) = F(E)G(T)\exp(-E/kT)$$

For the sake of simlicity, the following expression for $P(E)$ was assumed in the present investigation:

$$P(\mathrm{E}) = \frac{E}{(kT)^2}\exp(-E/kT) \tag{10}$$

where k is the Boltzmann constant and where T is the temperature of the molecule. Figure 7 shows schematically the behavior of $P(E)$ for two different temperatures. As the temperature rises, the maximum value of $P(E)$ decreases and the mean value of E increases. This tendency is in accordance with the results previously reported.[13-15]

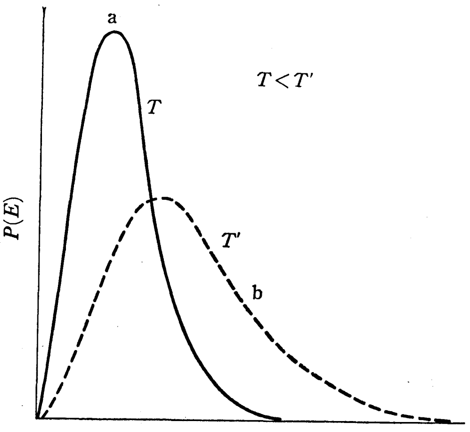

Fig. 7. Illustration of typical behavior expected for a simple internal energy distribution function.
a : lower temperature.
b : higher temperature.

Assuming Eq. (10) for $P(E)$, the $R\equiv[\mathrm{B}]/[\mathrm{A}]$, $R'\equiv[\mathrm{m}]/[\mathrm{B}]$, and $R^*\equiv[\mathrm{m}]/[\mathrm{A}]$ ratios were calculated using Eqs. (7)—(9). In the calculation, it was assumed that the $m/e=100$ ion is focused at the ion-acceleration voltage of 1000 V and that $t_1=t_2=3$ μs, $t_3=4$ μs, and $t_4=12$ μs. The results are shown in Fig. 8. From the figure, it may be seen that, under these assumptions, as the temperature of the molecules increases and as, consequently, the mean internal energy and the rate constant increase, both R and R^* increase and R′ decreases in the range of $kT < 1.5$ eV.

The results shown in Fig. 8 can be applied to Reactions (1) and (2), and the ratios, *F/M*, *m/M*, *etc*, given in Figs. 1—6 can be expected to behave qualitatively, in accord with the curves shown in Fig. 8 under the assumption cited.

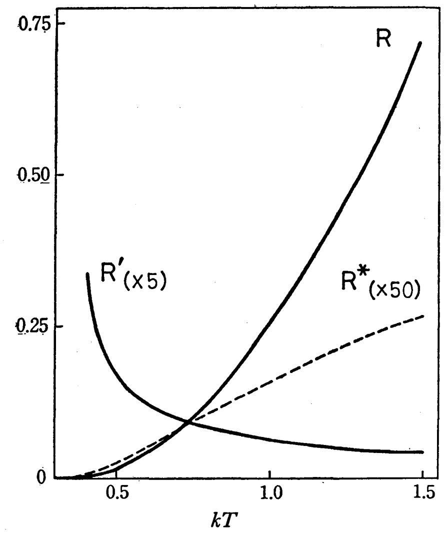

Fig. 8. Intensity ratios of ions calculated from Eqs. (7)—(9) *versus* internal energy *E*.

A comparison of Figs. 1—6 with each of the corresponding curves in Fig. 8 reveals that the expectation is met in all with the exception of Fig. 5; *i.e.*, the signs of the tangents of the curves in Figs. 1—4 and Fig. 6 are in accord with those of the corresponding curves in Fig. 8. On the contrary, the sign of the tangent for the curve in Fig. 5 is positive, whereas that for the curve, R', in Fig. 8 is negative.

In order to explain this discrepancy, the shape of the internal energy distribution function, $P(E)$, was investigated as follows. McLafferty *et al.*,[14] in their study of substituent effects in unimolecular decompositions of diphenylethane derivatives, have taken the effect of the shape of $P(E)$ curves into account in explaining the temperature dependence of the ratio of the intensity of the metastable ion to the parent ion, R^* in the present study, for their sample substances. They synthesized the photoelectron spectrum for a substance from the known spectrum for each moiety

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[10] K. R. Jennings and J. H. Futrell, *J. Chem. Phys.*, **44**, 4315 (1966).
[11] D. H. Williams, R. G. Cooks, and I. Howe, *J. Amer. Chem. Soc.*, **90**, 6759 (1968).
[12] I. Howe and D. H. Williams, *ibid.*, **91**, 7137 (1969).
[13] H. Ehrhardt and O. Osberghaus, *Z. Naturforschg.*, **15a**, 575 (1960).
[14] F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *J. Amer. Chem. Soc.*, **92**, 6867 (1970).
[15] W. A. Chupka, *J. Chem. Phys.*, **54**, 1936 (1971).

compound of which the substance was composed, and used the synthesized photoelectron spectrum as $P(E)$ for the substance. Using the structure of the synthesized $P(E)$ curve and the value of internal energy corresponding to the range of the abscissa called the "metastable window," which is considered to mainly contribute to the production of the metastable ion observed, they explained the temperature effect on metastable ions.

There have been various investigations[16–19] of possible methods for the evaluation of the internal energy distribution functions resulting in ions from the impact of energetic electrons; their shortcomings have been analysed by Meisels *et al.*[20] According to them, the photoelectron spectrum gives a resonable representation of the actual functions for molecules where multiple ionization and autoionization occur to only a relatively minor extent. On the other hand, another report notes[21] 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. It seems difficult to reach a decisive conclusion concerning the problem for the time being.

Under these circumstances, the photoelectron spectra were used as an approximate representation of the internal energy distribution function in the present study, and the temperature effects shown in Figs. 1—6, especially the effect shown in Fig. 5, were investigated following McLafferty *et al.*[14]

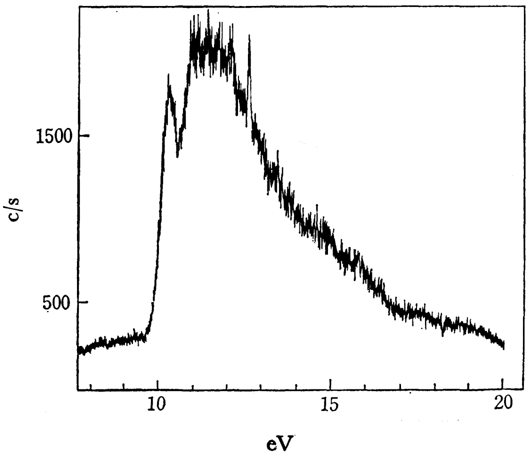

Fig. 9. Photoelectron spectrum of 1-hexanol.

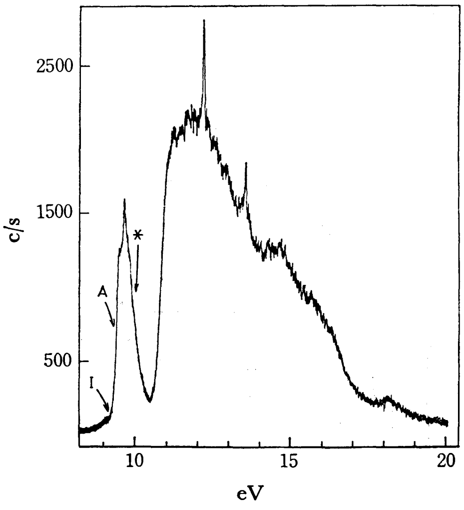

Fig. 10. Photoelectron spectrum of 1-hexene.
I, Ionization potential.
A, Appearance potential of $C_4H_8^+$.
*, "Metastable Window."

In the present report, *n*-hexanol and 1-hexene were taken as examples, and the photoelectron spectrum of each of these compounds was measured. Figures 9 and 10 show the spectra for *n*-hexanol and 1-hexene respectively. The ionization potentials of $^2P_{1/2}$ and $^2P_{3/2}$ for xenon, 13.44 eV and 12.14 eV respectively, were used for energy calibration. The vertical ionization potential and the adiabatic ionization potential[22] for 1-hexene were found to be 9.61 eV and 9.31 eV respectively. The ionization potential of 1-hexene, measured by the photoionization method, has been reported to be 9.45±0.02 eV[17] and 9.46±0.02 eV.[23] The appearance potentials of M^+ and F^+ for 1-hexene, A(M) and A(F), respectively, as measured by electron impact in the present study, are shown by arrows in Fig. 10. The A(M) value thus obtained, 9.33 eV, coincides with the result obtained from the photoelectron spectrum mentioned above, but it is lower than the literature value. Though the reason for the disagreement is not clear, it is noticeable that the mean value, 9.46 eV, of the vertical and the adiabatic ionization potentials obtained from the photoelectron spectrum is consistent with the literature value.

In order to obtain the internal energy value corresponding to the "metastable window," as is shown in the report of McLafferty *et al.*,[14] $\log k(E)$ was calculated for 1-hexene by Eq. (4) as a function of E. In the calculation, ε was taken as 0.12 eV and n was assumed to be $n=(3N-6)/3$, where N is the number of atoms in the molecule. Figure 11 shows the results. Generally, the ν value for a fragmentation with a rearrangement, such as the McLafferty rearrangement, is smaller than that for a simple cleavage of a bond[5,6]. Yeo *et al.*[7] used $\nu=3\times10^6$ for fragmentations with the rearrangement of a hydrogen atom or an oxygen atom and thus obtained results which are close to those obtained in their experiments. Both the log $k(E)$ *versus* E curves for $\nu=10^7$ and $\nu=10^6$ were calculated; they are shown in Fig. 11. The real value for ν was assumed to be in the range between these two values. It may be seen from the figure that the

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16) H. Ehrhardt, F. Linder, and T. Tekaat, *Adv. Mass Spectrometry*, **4**, 705 (1968).

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

18) J. D. Morrison, *ibid.*, **21**, 1767 (1953).

19) H. von Koch, *Arkiv Fysik*, **28**, 559 (1965).

20) G. G. Meisels, C. T. Chen, B. G. Giessner, and R. H. Emmel, *J. Chem. Phys.*, **56**, 793 (1972).

21) G. Innorta, S. Torroni, and S. Pignataro, *Org. Mass Spectrom.*, **6**, 113 (1972).

22) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc., Ser. B*, **1968**, 22.

23) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

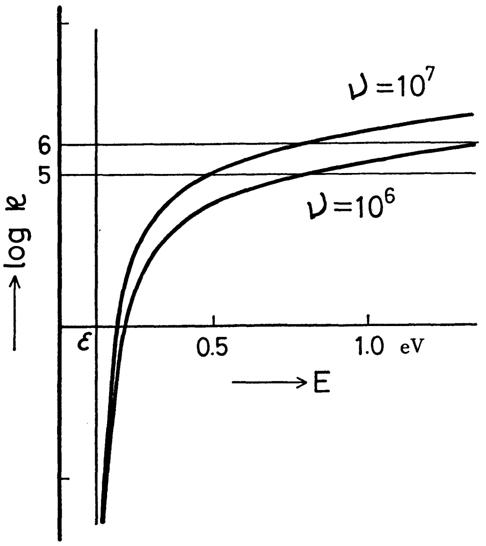

Fig. 11. log *k* *versus* internal energy *E* calculated by Eq. (4) for 1-hexene.

internal energy corresponding to the "metastable window" in this case is in a small range centered about $E = 1$ eV, as is shown by an asterisk in Fig. 10. As the temperature is increased, the curve in Fig. 10 takes a flatter form as a whole, like the broken curve in Fig. 7, and the fraction of the area under the curve, which covers the energy region marked by an asterisk in Fig. 10, gets larger, resulting in an increase in the metastable-ion intensity. On the other hand, because the fractional change in the area under the curve corresponding to the fragment ion F^+, as the temperature is increased, is relatively small, as may be seen from Fig. 3 cited above,[14] the behavior of the curves shown in Fig. 5 is explained. The results given in Figs. 4 and 6 can be understood as has been discussed before.

The signs of the tangents of all the curves, shown in Figs. 1—3, for 1-hexanol, are as would be expected from the simple consideration, in which no particular structure is assumed for the internal energy distribution function for the precursor ion, M'^+, which itself, in this case, is produced from the molecular ion. This suggests that the internal energy distribution function for M'^+ is of a simple form, as is the curve given in Fig. 7, which has no structure, in contrast to the photoelectron spectrum of 1-hexene (Fig. 10). This implies that no 1-hexene molecule is actually produced in the ion source of the mass spectrometer; this is consistent with an observation cited before.[1]

Danby *et al.*[24] report that the sum of the coincident electron spectra corresponding to the parent ion and the fragment ion from methylene chloride agrees with the photoelectron spectra for all the electrons. If this result is also valid for 1-hexanol, it follows from the inference described above that the internal energy distribution function for the fraction of the molecular ion, which is observed as the parent ion in the mass spectrum of 1-hexanol, may be of a simple form without any marked structure, at least in the vicinity of the "metastable window," because the photoelectron spectrum of 1-hexanol is of a simple form without any marked structure, as may be seen in Fig. 10.

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[24] C. J. Danby and J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, **8**, 153 (1972).