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An Investigation of the Decomposition of the Intermediate Ions Produced by Electron Impact. I. $C_7H_7^+$ Ions from Several Substituted Toluenes

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The decomposition of the $C_7H_7^+$ ions produced by electron impact from toluene, *o*-, *m*-, *p*-xylene, *o*-, *m*-, *p*-chlorotoluene, *o*-, *m*-, *p*-methylbenzoic acid, *p*-nitrotoluene, and *p*-methylacetophenone has been investigated. By the determination of the relative abundances of normal and metastable ions, these $C_7H_7^+$ ions are shown to be identical in structure, except for the $C_7H_7^+$ ion from *p*-nitrotoluene. The relative rates of decomposition of these ions are compared in terms of the relative abundances of the ions $65^+/91^+$ ($=R$) and $46.5^*/91^+$ ($=R^*$) (where 46.5^* is the abundance of the metastable ion for the $91^+ \rightarrow 65^+ + 26$ decomposition; 91^+ and 65^+ denote the abundance of ions at *m/e* 91 and 65 respectively). Further, using the internal energy, the relative rates are estimated by comparing their R and R^* values with the IRE curve (*i.e.*, R and R^* *versus* the bombarding electron energy) for *p*-methylacetophenone (PMAP), which was used as the standard compound.

By the quasi-equilibrium theory (QET),[1] the rate constant, k, for the decomposition of an ion produced by electron impact varies with the internal energy, E, according to Eq. (1):

$$k(E) = \nu(1-\varepsilon_0/E)^{n-1} \qquad (1)$$

where ν is a frequency factor, where ε_0 is the activation energy for the decomposition, and where n is the number of effective harmonic oscillators of which the compound is assumed to be composed. Many authors have explained the influence of ν,[2] E,[3,4] and n[5] in the equation on the rate of the decomposition of the ions produced by electron impact. McLafferty *et al.*,[6] Cooks *et al.*,[7] and Jennings and Futrell[8] have studied the relative rates of the decomposition of a common intermediate ion, X^+, from different precursors. They investigated the following reaction:

$$M^+ \longrightarrow X^+ \xrightarrow{m^*} A^+ \qquad (2)$$

where M^+ is a different precursor ion, where X^+ is a common intermediate ion, and where m^* is the metastable ion for the $X^+ \rightarrow A^+$ decomposition. They investigated the relative rates of the decomposition of X^+ in terms of such ratios of abundances of ions as X^+/A^+, X^+/m^*, and/or m^*/A^+; then, using QET, they explained the relative rates qualitatively by the degrees of vibrational freedom in M^+ or the apparent heat of formation, which was assumed to be associated with the internal energy, E, for X^+.

In this paper, the rates of decomposition of $C_7H_7^+$ ions produced from certain toluene derivatives substituted by electron-withdrawing substituents are investigated. In the mass spectra of these toluene derivatives, the $C_7H_7^+$ ion is very prominent, and the ion decomposes successively through the $C_7H_7^+$ (*m/e* 91) $\xrightarrow{m^*(m/e\ 46.5)}$ $C_5H_5^+$(*m/e* 65)$+C_2H_2$ process, with the metastable peak at *m/e* 46.5. On the base of QET, we will examine the decomposition of the $C_7H_7^+$ ions as a function of the internal energy, E. The procedure is as follows: 1) the relative ion abundances ($65^+/91^+=R$, $m^*/91^+=R^*$) for the $C_7H_7^+$ ion produced by electron impact from *p*-methylacetophenone (PMAP) are measured; 2) the "ion abundance ratio efficiency curve" (IRE curve), which gives the relation of R and R^* to the electron accelerating voltage (V_e), is plotted; 3) the structure and the internal energy, E, of the $C_7H_7^+$ ions from substituted toluenes are estimated from these curves, *i.e.*, by comparing the R and R^* values obtained from each compound.

Experimental

The mass spectra were obtained by voltage scanning with a CEC 21-103C mass spectrometer. The V_e was measured with a potentiometer of Leeds & Northrup Co., Ltd. The electron-trap current was 10 μA. The temperatures of the ion source and the sample manifold were 250 and 125°C respectively.

With scanning, the voltage applied to the repeller electrodes varies in proportion to the ion-accelerating voltage. Because the bombarding electron energy is known to be affected by the repeller voltage,[9,10] it is desirable to measure the abundances of the *m/e* 91, *m/e* 65, and *m/e* 46.5 ions under the same ion-accelerating voltage, so that the effect of the repeller voltage on V_e can be nearly the same for all the ions studied. In this study, the optimum ion-accelerating voltage

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[1] H. M. Rosenstock and M. Krauss, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press Inc., New York (1963), Chap. 1.

[2] D. H. Williams and R. G. Cooks, *Chem. Commun.*, **1968**, 663.

[3] W. A. Chupka and M. Kaminsky, *J. Chem. Phys.*, **35**, 1991 (1961).

[4] M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *ibid.*, **37**, 1276 (1962).

[5] W. A. Chupka, *ibid.*, **30**, 191 (1959).

[6] F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89**, 5951 (1967); W. T. Pike and F. W. McLafferty, *ibid.*, **89**, 5954 (1967).

[7] R. G. Cooks and D. H. Williams, *Chem. Commun.*, **1968**, 627; D. H. Williams, R. G. Cooks, and I. Howe, *J. Amer. Chem. Soc.*, **90**, 6759 (1968).

[8] K. R. Jennings and J. H. Futrell, *J. Chem. Phys.*, **44**, 4315 (1966).

[9] I. Omura, K. Higashi, and H. Baba, This Bulletin, **29**, 501 (1956).

[10] L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.*, **31**, 755 (1959).

for the most intense metastable peak was obtained first, and then all the ions were measured under this same accelerating voltage by adjusting the magnetic field.

The 180° mass spectrometer used does not have the field-free region in front of the magnetic analyser; however, it is known that the apparent mass (m*) of the metastable ion can be obtained by means of the same equation ($m^* = A^2/X$) as is used with other sector-type mass spectrometers.[11,12] The metastable ion-abundance measurements were based on the peak heights for the data.

All the samples studied were of a research grade, were obtained from Tokyo Kasei Co., Ltd., and were used without further purification upon checking the purity with the mass spectrometer. The ion abundances of the *m/e* 91, *m/e* 65, and *m/e* 46.5 of PMAP were measured at 1.0 eV intervals of the bombarding-electron energy. The abundances of these ions from the other compounds studied were measured at V_e= 20.0 eV. The probable error in the measurement of V_e is estimated to be less than ±0.2 eV.

Results and Discussion

The "IRE curves" for PMAP are given in Fig. 1. The ordinates denote R and R^* (×100); hereafter, these curves will be termed the "R-standard curve" and the "R^*-standard curve" respectively. According to QET, the rate constant, k, for the decomposition of an ion is given by Eq. (1). An ion has its own distribution function of the internal energy, E, and an ion with a particular internal energy decomposes with a rate constant corresponding to the internal energy. For the decomposition of ions identical in structure, the rate constant, k, increases with an increase in the internal energy, E, of the ion, as can be seen from Eq. (1), since the frequency factor, ν, the activation energy, ε_0, and the number of harmonic oscillators, n, are the same for ions identical in structure.

For simplicity, it is assumed that all the X^+ ions are produced at the same time in the ionization chamber and that the A^+ ions do not decompose further. The latter assumption is reasonable when a low electron energy is used. Then, the intensities of the various ions in Eq. (2) are given by:[13]

$$I(X^+) = \int_0^{\varepsilon_0} P(E)\mathrm{d}E + \int_{\varepsilon_0}^{\infty} P(E)\exp\{-k(E)t_4\}\mathrm{d}E \qquad (3)$$

$$I(A^+) = \int_{\varepsilon_0}^{\infty} P(E)[1-\exp\{-k(E)t_1\}]\mathrm{d}E \qquad (4)$$

$$I(\mathrm{m}^*) = \int_{\varepsilon_0}^{\infty} P(E)[\exp\{-k(E)t_2\}-\exp\{-k(E)t_3\}]\mathrm{d}E \qquad (5)$$

where $P(E)$ is the number of X^+ with the internal energy, E, (internal energy distribution function). In the above equation, we assumed further that the X^+ ions created at $t=0$ reach the exit slit in the ion source at time t_1, the field-free region at time t_2, the magnetic field at time t_3, and the end of the magnetic field at time t_4. R and R^* are given by:

$$R = I(\mathrm{A}^+)/I(\mathrm{X}^+) \qquad (6)$$

$$R^* = I(\mathrm{m}^*)/I(\mathrm{X}^+) \qquad (7)$$

From Eqs. (1), (6), and (7), R and R^* can be treated as function of the internal energy, E.

Using, for simplicity, the expressions for $I(\mathrm{X}^+)$, $I(\mathrm{A}^+)$, and $I(\mathrm{m}^*)$ given by Chupka[5] instead of Eqs. (3)—(5), the relations of R and R^* to the rate constant, k, calculated by a FACOM 270-30 computer are shown in Fig. 2. In this calculation, we used $t_1=t_2=2.5$ μsec, $t_3=3.3$ μsec, and $t_4=9.5$ μsec. These times were estimated from the dimensions of the mass spectrometer used in this study and from the conditions of measure-

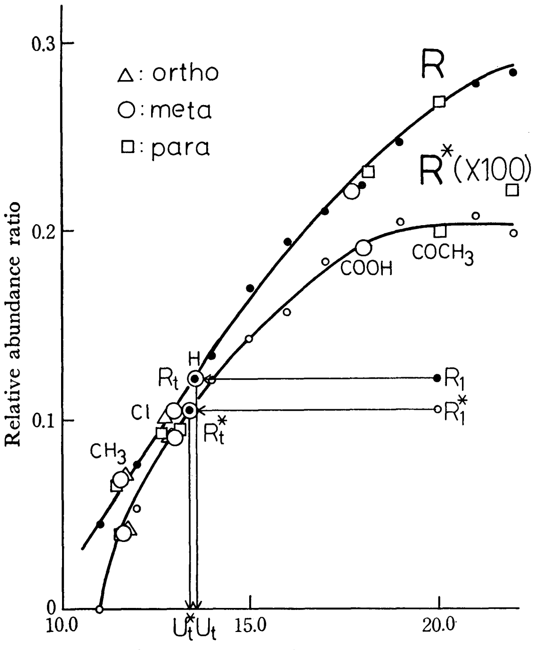

Fig. 1. IRE curves for *p*-methylacetophenone and relative abundance ratios of each compound at V_e=20.0 eV.

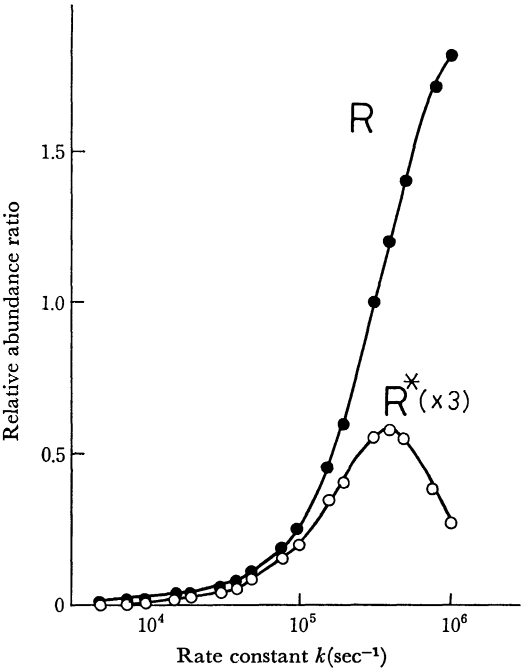

Fig. 2. Calculated relative abundance ratios $65^+/91^+$ and $\mathrm{m}^*/91^+$ *vs.* rate constant k by using Chupka's equations.[5]

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[11] N. D. Coggeshall, *ibid.*, **37**, 2167 (1962).

[12] A. S. Newton, *ibid.*, **44**, 4015 (1966).

[13] I. Howe and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 7137 (1969).

ment. The internal energy of the parent ion, M^+, increases with an increase in V_e, so the internal energy, E, of X^+, produced by the decomposition of M^+, will also increase with an increase in V_e. Consequently, the greater the V_e value, the greater the average rate constant, $\bar{k}$. The behavior of R and R^* with V_e in Fig. 1 can be explained qualitatively when the curves in Fig. 1 are compared with those in Fig. 2, assuming k values lower than 5×10^5 sec^{-1}. The X^+ produced by the decomposition of M^+ from PMAP at a given V_e will have an internal energy corresponding to the V_e. The ion abundances related to the decomposition of X^+ give R and R^* values corresponding to the ordinates in Fig. 1. Thus, R and R^* can be taken as measures of the internal energy of X^+ in the sense mentioned above. The corresponding values on the abscissa show the internal energy of X^+ in this measure. When the average internal energy of X^+ is estimated in this measure, the R and R^* obtained for the X^+ must lie on a line perpendicular to the abscissa. In this study, we used the IRE curves for PMAP as a measure of the internal energy of the $C_7H_7^+$ ions from various compounds.

TABLE 1. RELATIVE ABUNDANCE RATIOS $65^+/91^+(R)$ AND $m^*/91^+(R^*)$ IN THE MASS SPECTRA OF EACH SUBSTITUTED TOLUENE AT $V_e=20.0$ eV

Substituent	R	$R^*(1\times00)$
H	0.122	0.105
o-CH_3	0.071	0.053
m-CH_3	0.068	0.048
p-CH_3	0.065	0.048
o-Cl	0.104	0.095
m-Cl	0.108	0.095
p-Cl	0.095	0.094
o-COOH	0.304	0.221
m-COOH	0.221	0.189
p-COOH	0.230	0.220
p-$COCH_3$	0.269	0.200
p-NO_2	0.460	0.491

In order to investigate the structure and the internal energy of the $C_7H_7^+$ ion from each substituted toluene, the R and R^* values for each compound in Table 1 have been compared with the standard curves. The data in Table 1 were measured at $V_e=20.0$ eV, because the abundance of the *m*/*e* 46.5 metastable ion peak was masked by other normal peaks (for example, by the *m*/*e* 47 peak) and the abundance of the metastable ion could not be determined exactly when V_e was higher.

The effective internal energy from every compound in Table 1 was estimated as follows. The R and R^* values were determined experimentally for each compound at $V_e=20.0$ eV. Two lines were drawn parallel to the abscissa from points on the ordinate corresponding to the R and R^* values. R_1 and R_1^* were determined where the lines intersected the R- and R^*-standard curves respectively. When perpendiculars passing through these points were drawn, the feet, U and U^*, were found to coincide within the limits of experimental error. The value of V_e corresponding to the feet was assumed to be a measure of the internal energy in the sense mentioned above. For example, in the case of toluene, the two feet are denoted as U_t and U_t^* in Fig. 1. U_t and U_t^* are found to be 13.6 and 13.4 eV respectively. This suggests that the structure and the internal energy distribution of the $C_7H_7^+$ ions from toluene at $V_e=20.0$ eV correspond to those of the $C_7H_7^+$ ions from PMAP at about $V_e=13.5$ eV. That is, if the structure and the internal energy distribution of the $C_7H_7^+$ ions from toluene at $V_e=20.0$ eV are identical with those of the $C_7H_7^+$ ions from PMAP at $V_e=13.5$ eV, ν, ε_0, and n in Eq. (1), and $P(E)$ in Eqs. (3)—(5) will be the same, respectively, for each of the $C_7H_7^+$ ions from the two compounds. Therefore, the relation between R_t and R_t^* in toluene is exactly the same as the relation between R and R^* in PMAP, and U_t will agree with U_t^*. If the $C_7H_7^+$ ions from toluene were not identical in structure and/or in internal energy with those from PMAP, ν, ε_0, and n in Eq. (1) would be different for these ions and $P(E)$ in Eqs. (3)—(5) would also be different. Therefore, the relation between R_t and R_t^* in toluene will differ from that in PMAP, and U_t will not generally coincide with U_t^*. The U and U^* values for other compounds in Table 1 coincide with each other within the limits of experimental error, as can be seen in Fig. 1. Therefore, the $C_7H_7^+$ ions produced from these compounds at $V_e=20.0$ eV have the same structure and internal energy distribution as the $C_7H_7^+$ ion produced from PMAP at each corresponding V_e. By using the isotope labelling technique, Meyerson *et al.*[14] have reported that the $C_7H_7^+$ ions from toluene, *p*-xylene, and *p*-chlorotoluene are "tropylium ions." Thus, the $C_7H_7^+$ ions produced from the compounds in Table 1 and PMAP in the V_e range of the present investigation can be inferred also to be tropylium ions which have various effective internal energies, as is indicated in Table 2.

TABLE 2. THE ELECTRON ACCELERATING VOLTAGE (U), AT WHICH THE INTERNAL ENERGY DISTRIBUTION OF THE $C_7H_7^+$ ION FROM PMAP IS EQUAL TO THAT OF THE $C_7H_7^+$ ION FROM EACH COMPOUND AT $V_e=20.0$ eV

Compound	U(eV)
Toluene	13.5
Xylene	11.8
Chlorotoluene	13.0
Methylbenzoic acid	~18.0

In the case of *p*-nitrotoluene, we could not plot the R and R^* in Fig. 1 because these values were too high in comparison with the values of the other compounds. When the IRE curves of *p*-nitrotoluene are regarded as the standard curves instead of that of PMAP, U does not agree with the U^* value in other compounds. These facts suggest that the structure of the $C_7H_7^+$ ion from *p*-nitrotoluene is not identical with that of the $C_7H_7^+$ ions from the other compounds studied here.

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[14] S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press Inc., New York (1963), Chap. 10.

Beynon *et al.*[15] have studied in detail the decomposition mechanism of nitrobenzene derivatives by electron impact. They have explained that the compounds decompose to fragment ions through some complicated intermediates. Recently, Westwood *et al.*[16] have reported the difference between the decomposition mechanism of *p*-nitrobenzene derivatives and that of *m*-isomers. One reason why the structure of the $C_7H_7^+$ ion from *p*-nitrotoluene is not identical with that of the $C_7H_7^+$ ions from other compounds may be these complicated decomposition processes.

From Table 1 it may be seen that while the U values for compounds with different substitutents differ from one another, the U values for the *o*-, *m*-, *p*-isomers containing the same set of substituents are nearly the same, except for methylbenzoic acid. This indicates that the internal energy distribution of the tropylium ion is affected by the species of substituents and not by the position of the substituents. The U values obtained for compounds in Table 1 are shown in Table 2. For example, in the case of toluene, the internal energy distribution of the $C_7H_7^+$ ion obtained at $V_e=20.0$ eV corresponds to that of the $C_7H_7^+$ ion from PMAP at about $V_e=13.5$ eV. One reason why the U values for *o*-, *m*-, *p*-methylbenzoic acid are distributed over a rather wide range compared to the case of the other compounds may be that the R and R^* values of methylbenzoic acid are in a relatively insensitive portion of the bombarding electron energy. In such a range, a slight error in measurement of ion abundances will result in a rather large spread in the corresponding electron energy. According to the results given in Table 2, the order of the internal energy of the $C_7H_7^+$ ions produced by the electron bombardment of the 20.0 eV energy is: methylacetophenone$\simeq$methylbenzoic acid$>$toluene$>$chlorotoluene$>$xylene. This order reveals an approximate tendency for the amount of the internal energy of the $C_7H_7^+$ ion from the compound to be larger as the electron-withdrawing property of the substituent is stronger.

Recently, Gross and McLafferty[17] have reported that substituted benzophenone, YϕCOϕ, with a weaker Yϕ-COϕ bond (ϕ and Y representing a benzol ring and a substituent respectively), yields the less energetic benzoyl ion when bombarded by electrons. On the contrary, Shapiro *et al.*[18] have indicated that substituted benzamide, described as YϕNHCOϕ, with a stronger YϕNH-COϕ bond, yields the less energetic benzoyl ion. Based on the information about the competing fragmentation of benzophenone, they have explained[18] the results of Gross and McLafferty.[17] It has been shown recently[19] that, when bombarded by electron, a disubstituted benzene, A-ϕ-Y (A being a common substituent for a series of compounds), gives a larger value of the summation of ions (Aϕ^++Y$^+$) when the substituent Y has a stronger electron-withdrawing property. If this result is understood to indicate that the summation of the ions increases as the bond strength between the substituent, Y, and the aromatic moiety decreases, and if it is assumed that all of the molecular ions studied here have nearly the same internal energy distribution, the compound possessing a weak bond between the substituent, Y, and the aromatic moiety will leave a large internal energy to the Aϕ^+ ion, *i.e.*, the tropylium ion in the present investigation. That is, as the energy spent to break the (Aϕ-Y)$^+$ bond is smaller, a larger internal energy is left in the residual Aϕ^+ ion. If this simple explanation is accepted, the relationship between the amount of internal energy of the $C_7H_7^+$ ions corresponding to Aϕ^+ ions and the electron-withdrawing property of the substituents can be explained qualitatively in accordance with the conclusions of Shapiro *et al.*[18] Like the compounds studied by Shapiro *et al.*,[18] the molecular ions of the compounds in Table 1 do not undergo competing reactions to any appreciable extent, and they decompose almost exclusively into $C_7H_7^+$ ions at any ionizing energy.

In addition to the two parameters used in this study, the m*/A$^+$ parameter is used by many authors to obtain the relative rate constant, k, for the decomposition. When the internal energy of X$^+$ for PMAP is smaller with a decrease in the V_e, this parameter is less reliable, since both the numerator, m*, and the denominator, A$^+$, are very small in this V_e region. Therefore, the m*/A$^+$ parameter was not used in this study.

Conclusions

A procedure for investigating the identity of an ion produced by electron bombardment in mass spectrometry is proposed. "IRE curves" are first obtained for a standard compound, and the ion abundance ratio R and R^* from the comound to be studied is compared with the standard curve. By this procedure, the identity of the ion can be checked and the internal energy imparted to the ion can be estimated semiquantitatively.

The $C_7H_7^+$ ions from various toluene derivatives were investigated by this method. While the $C_7H_7^+$ ions from isomeric compounds possessing the same combination of substituents (Table 1) contain nearly equal amounts of internal energy, the $C_7H_7^+$ ions from compounds containing different sets of substituents contain quite different amounts of internal energy. The amount of internal energy contained by the ion from derivatives of toluene increases as the electron-withdrawing property of the substituent other than CH_3 increases.

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[15] J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier Publishing Co., Amsterdam (1968), Chap. 5.

[16] R. Westwood, D. H. Williams, and A. N. H. Yeo, *Org. Mass Spectrom.*, **3**, 1485 (1970).

[17] M. L. Gross and F. W. McLafferty, *Chem. Commun.*, **1968**, 254.

[18] R. H. Shapiro, J. Turk, and J. W. Serum, *Org. Mass Spectrom.*, **3**, 171 (1970).

[19] S. Tajima, N. Wasada, and T. Tsuchiya, This Bulletin, in press.