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On the Decomposition of $C_6H_5CO^+$ Ions Produced from Several Alkyl Phenyl Ketones by Electron Impact

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The decomposition of $C_6H_5CO^+$ ions produced by electron impact from seven alkyl phenyl ketones, C_6H_5-COR (R=H, CH_3, C_2H_5, *n*-C_3H_7, *iso*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}), has been studied. By determining the heats of formation, the $C_6H_5CO^+$ ions produced from the different precursors in the vicinity of the threshold are shown to have the same structure, and it is also shown that there is a linear relationship between the heat of formation of the activated complex for the reaction $C_6H_5CO^+ \rightarrow C_6H_5^+ + CO$ and the vibrational degrees of freedom of the neutral fragment, R.

Many authors have studied[1-7] the decomposition of a common intermediate ion produced from various precursors, in order to study how the difference of the precursors reflects on the decomposition of the common intermediate ions assuming quasi-equilibrium theory (QET) of mass spectra[8] to be valid.

The present paper describes the decomposition of the benzoyl ions, $C_6H_5CO^+$, produced from seven alkyl phenyl ketones, benzaldehyde, acetophenone, ethyl phenyl ketone, *n*-propyl phenyl ketone, isopropyl phenyl ketone, *n*-butyl phenyl ketone, and *n*-amyl phenyl ketone, on the basis of the following assumption: As is usually assumed in QET,[8,9] when a molecular ion with internal energy E decomposes into a neutral and an ionic fragments, the energy, E_M, in excess of the activation energy, is partitioned in proportion to the number of vibrational degrees of freedom in the neutral and the ionic fragments.

Experimental

The appearance potentials (AP) of the various ions were measured with a CEC 21—103 C mass spectrometer. The temperatures of the ion source and the sample manifold were about 250 °C and 100 °C, respectively. The electron-trap current was 10 μA. The electron accelerating voltage was supplied by a battery, and set with a 20-turn potentiometer (Sakae Tsushin Kogyo Co., Ltd.).

AP values were obtained by the energy distribution difference (EDD) technique[10] after the ionization efficiency curves were smoothed by the least-squares method. The constant, *b*, used in the EDD calculation was 0.67. The details have already been given.[11] Krypton (IP=14.00 eV) was used as calibrating gas for the electron energy scale.

All the samples studied were of research grade, and were obtained from Tokyo Kasei Co., Ltd., and were used without further purification.

Results and Discussion

Calculation of the Heat of Formation. The heat of formation of the $C_6H_5CO^+$ ion and that of the state which can be taken to be the activated complex for the reaction (1), $\Delta H_f(C_6H_5CO^+)$ and $\Delta H_f(C_6H_5^+ \cdots CO)$, are calculated by the Eqs. (2) and (3).

$$C_6H_5CO^+ \longrightarrow C_6H_5^+ + CO \quad (1)$$

$$\Delta H_f(C_6H_5CO^+) = AP(C_6H_5CO^+) + \Delta H_f(M) - \Delta H_f(R) - E_1 \quad (2)$$

$$\Delta H_f(C_6H_5^+ \cdots CO) = AP(C_6H_5^+) + \Delta H_f(M) - \Delta H_f(R) - E_2 \quad (3)$$

where $AP(X^+)$ is the appearance potential of the ion X^+, $\Delta H_f(M)$ and $\Delta H_f(R)$ are the heats of formation

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

2) (a) F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89**, 5951 (1967); (b) F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5953 (1967); (c) W. T. Pike and F. W. McLafferty, *ibid.*, **89**, 5954 (1967); (d) M. L. Gross and F. W. McLafferty, *Chem. Commun.*, **1968**, 254.

3) (a) R. G. Cooks and D. H. Williams, *ibid.*, **1968**, 627; (b) D. H. Williams, R. G. Cooks, and I. Howe, *J. Amer. Chem. Soc.*, **90**, 6759 (1968); (c) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 137 (1969).

4) P. Brown, *ibid.*, **2**, 1805 (1969).

5) (a) R. H. Shapiro, J. Turk, and J. W. Serum, *ibid.*, **3**, 171 (1970); (b) J. Turk and R. H. Shapiro, *ibid.*, **6**, 189 (1972).

6) S. Tajima, Y. Niwa, M. Nakajima, and T. Tsuchiya, This Bulletin, **44**, 2340 (1971).

7) H. Nakata, A. Tatematsu, H. Yoshizumi, and S. Naga, *Chem. Lett.*, **1973**, 75.

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

9) A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.*, **5**, 135 (1971).

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

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

of the neutral molecule, M, and radical, R, respectively, and E_n is the excess energy of the fragments at the threshold.

The AP values of the $C_6H_5CO^+$ ions and the $C_6H_5^+$ ions from seven alkyl phenyl ketones measured in this experiment are given in Table 1. Each value represents an average taken from at least three measurements, and the given experimental errors are maximum deviations.

The values of the heat of formation used for the neutral molecules and free radicals, $\Delta H_f(M)$ and $\Delta H_f(R)$, are given in Table 2. These values are taken from the literature.[12] Some $\Delta H_f(M)$ values which are not given in the literature were calculated by approximation methods used by Franklin.[13]

Using the AP values in Table 1 and the values of heat of formation shown in Table 2, the heat of formation of the $C_6H_5CO^+$ ions and that of the activated complexes for the reaction (1) were calculated by Eqs. (2) and (3), respectively. The results are shown in Fig. 1. The values in Fig. 1 are obtained by taking E_n as zero.

$C_6H_5CO^+$ Ions. As seen in Fig. 1, the values for heat of formation of the $C_6H_5CO^+$ ions from seven alkyl phenyl ketones studied here are the same within the experimental error. Therefore, these $C_6H_5CO^+$ ions produced in the vicinity of the threshold are considered to have the same structure.[14,15] Consequently,

TABLE 1. APPEARANCE POTENTIALS (eV) OF THE $C_6H_5CO^+$ IONS AND THE $C_6H_5^+$ IONS FROM ALKYL PHENYL KETONES

C_6H_5COR	AP($C_6H_5CO^+$)	AP($C_6H_5^+$)
Benzaldehyde	10.2±0.10	13.5±0.06
Acetophenone	9.8±0.08	13.5±0.10
Ethyl phenyl ketone	9.5±0.10	13.6±0.15
n-Propyl phenyl ketone	9.8±0.07	13.9±0.06
Isopropyl phenyl ketone	9.3±0.08	13.7±0.05
n-Butyl phenyl ketone	10.0±0.10	14.3±0.10
n-Amyl phenyl ketone	9.8±0.06	14.5±0.10

TABLE 2. HEATS OF FORMATION ΔH_f(kcal/mol) OF NEUTRAL ALKYL PHENYL KETONES AND RADICALS

Compound	$\Delta H_f(C_6H_5COR)$	$\Delta H_f(R)$
Benzaldehyde	−10.5	52.1
Acetophenone	−23.0	33.2
Ethyl phenyl ketone	−24.7	25.0
n-Propyl phenyl ketone	−29.6[a]	22.1
Isopropyl phenyl ketone	−30.9[a]	16.8
n-Butyl phenyl ketone	−34.5[a]	18.5
n-Amyl phenyl ketone	−39.4[a]	9.1

a) These values were calculated by approximation methods used by Franklin.[9]

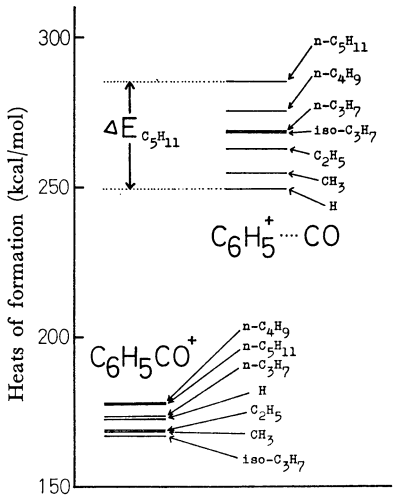

Fig. 1. The heats of formation (kcal/mol) of the $C_6H_5CO^+$ ions and the activated complexes for the reaction (1), $\Delta H_f(C_6H_5CO^+)$ and $\Delta H_f(C_6H_5^+\cdots CO)$.

the decomposing $C_6H_5CO^+$ ions of reaction (1), produced from various precursors, will also have the same structure, that is, the values for heat of formation of the activated complexes for the reaction (1) will be the same.[14,16]

The Activated Complexes for the Reaction (1). As seen in Fig. 1, the heats of formation of the activated complexes for the Reaction (1) show some scatter, compared with that of $C_6H_5CO^+$ ions, and furthermore, the values increase systematically as the number of atoms in R is large. In this study, we have investigated the source of the difference in the values, on the basis of the above assumption.

A few authors have reported[17,18] that during the dissociation of a molecular ion, the energy, E_M, in excess of the activation energy, is partitioned to the neutral and the ionic fragments, R and $C_6H_5CO^+$ in this study, respectively, and consequently, that the appearance potentials for the secondary ions, $C_6H_5^+$ in the present study, will be somewhat higher than the "true" values. In this experiment, the number of vibrational degrees of freedom of the R differs from compound to compound, and a part of the energy E_M will be carried away by the R. Therefore, as a consequence of the assumption, the extent of the effect on the AP($C_6H_5^+$) will also vary, and each AP($C_6H_5^+$) will be high according to the number of the vibrational degree of freedom of the R.

In this study, benzaldehyde was taken as the standard, since the number of the vibrational degree of freedom of the R in the compound is zero. ΔE_R is defined as the difference between the heat of formation of the activated complex for the reaction (1) of a compound, C_6H_5COR, and that of benzaldehyde. In Fig. 1, the $\Delta E_{C_5H_{11}}$ for $C_6H_5COC_5H_{11}$ is shown as an example. ΔE_R is considered to be the energy which

12) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseuos Positive Ions", National Bureau of Standard, U.S.A., (1969).
13) J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953).
14) J. L. Occolowitz and G. L. White, *Aust. J. Chem.*, **21**, 997 (1968).
15) S. Tajima and T. Tsuchiya, This Bulletin, in press.
16) S. Tajima and T. Tsuchiya, *Org. Mass Spectrom.*, in press.
17) S. Wexler, G. R. Anderson, and L. A. Singer, *J. Chem. Phys.*, **32**, 417 (1960).
18) M. B. Wallenstein and M. Krauss, *ibid.*, **34**, 929 (1961).

is partitioned to the radical R during the decomposition of the molecular ion. From the assumption, it is reasonable to expect that the following equation holds:

$$\Delta E_R/\alpha = f_R/f_{\phi-CO}$$

Therefore, $$\Delta E_R = (\alpha/f_{\phi-CO}) \times f_R \quad (4)$$

where α is the energy which is partitioned to the $C_6H_5CO^+$ ion during the decomposition of the molecular ion; f_R and $f_{\phi-CO}$ are the numbers for vibrational degree of freedom of the radical R and the $C_6H_5CO^+$ ion, respectively.

The plot of ΔE_R *vs.* f_R is given in Fig. 2. As expected from Eq. (4), the plot gives a straight line which passes through the origin. The experimental formula shown in Fig. 2 is obtained by the least-squares method. From the slope of the line, the value $\alpha=27.4$ kcal/mol was obtained taking $f_{\phi-CO}=33$. By definition, $\alpha=27.4$ kcal/mol is the energy which is partitioned to the $C_6H_5CO^+$ ion during the decomposition of the $C_6H_5COR^+$ ion, while the difference between the heat of formation of the activated complex and that of the $C_6H_5CO^+$ ion for benzaldehyde is about 75 kcal/mol (refer to Fig. 1). For benzaldehyde, the value $\Delta H_f(C_6H_5^+)=275.6$ kcal/mol was obtained taking $\Delta H_f(CO) = -26.4$ kcal/mol,[12] this value is comparable to the value $\Delta H_f(C_6H_5^+)=284$ kcal/mol which was obtained from phenyl radical by Lossing *et al.*[19] Therefore, it can be seen that these $C_6H_5^+$ ions in this study are produced in the vicinity of the ground state of the $C_6H_5^+$ ion. It is reasonable that the excess energy of H-atom in this case is taken as zero, because if there is any energy partition to the H-atom, values for heat of formation of the $C_6H_5^+$ ion from benzaldehyde will be higher than that of the $C_6H_5^+$ ion from phenyl radical.

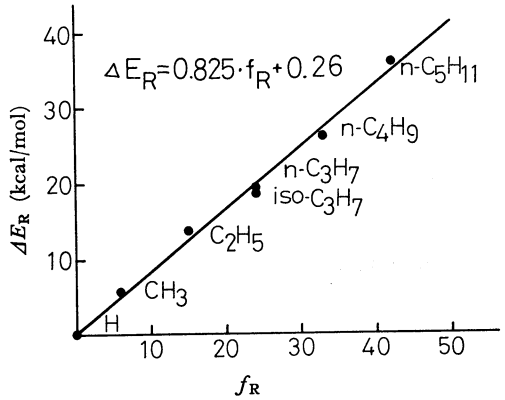

Fig. 2. The plot of the energy difference between the heats of formation of the activated complexes for the reaction (1), ΔE_R, *vs.* the number of vibrational degree of freedom of the radical R, f_R.

As a consequence of the above consideration, if the assumption is valid, the experimental results lead us to conclude that CO loss occurs from the $C_6H_5CO^+$ ion after the $C_6H_5CO^+$ ion, produced from the decomposition of the molecular ion in an excited electronic state, is transferred to a vibrationally excited state of its ground electronic state. An alternative explanation is that the assumption is not valid. Each decomposition reaction occurs from a vibrationally excited state of the ground electronic state of each ion, and only a part of the excess energy E_M is partitioned in proportion to the number of the vibrational degrees of freedom in radical R and the ion $C_6H_5CO^+$, and all of the remaining energy of E_M is partitioned to the $C_6H_5CO^+$ ion.

Conclusions

1) By using the data concerning the heat of formation, the decomposition of the $C_6H_5CO^+$ ions produced from seven alkyl phenyl ketones, are studied, on the basis of an assumption. The $C_6H_5CO^+$ ions produced in the vicinity of the threshold can be considered to have the same structure.

2) It was found that there is a linear relationship between the number of the vibrational degree of freedom, f_R, of the alkyl radical R and the difference of the values for heat of formation, ΔE_R, of the activated complex for the reaction (1). Two different conclusions on the mechanism of the decomposition of the $C_6H_5CO^+$ ions are derived, depending upon whether the assumption is valid or not.

19) I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, **86**, 2741 (1964).