BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3291—3292 (1973)

Energetic Consideration of $C_5H_5^+$ Ions Produced from Various Precursors by Electron Impact

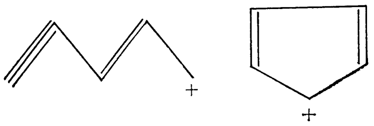
Susumu TAJIMA and Toshikazu TSUCHIYA

National Chemical Laboratory for Industry, 1-1-5, Honmachi, Shibuya-ku, Tokyo 151

(Received March 31, 1973)

It is well known[1] that the $C_7H_7^+$ ions produced from various precursors (C_7H_7Z) decompose into the $C_5H_5^+$ ions by losing C_2H_2. The structure of the $C_7H_7^+$ ions has been investigated by various methods.[1-3] To the authors' knowledge, however, the structure of the $C_5H_5^+$ ions produced by the $C_7H_7Z^+ \rightarrow C_7H_7^+ + Z \rightarrow C_5H_5^+ + C_2H_2$ reaction has not yet been examined.

Occolowitz and White have concluded[4] that the structure of the $C_5H_5^+$ ions derived from some compounds can be identified as the (a) structure rather than the (b) structure shown in Fig. 1 by measuring the heat of formation.[5] Natalis and Franklin have also reported[6] similar conclusions reached by the same method.



(a) ΔH_f: 277 kcal/mol (Ref. 4)
(b) ΔH_f: 240 kcal/mol (Ref. 5)

Fig. 1. Schematic diagram of the structure of the $C_5H_5^+$ ion from 3-penten-1-yne (a) and cyclopentadienyl radical (b).

In order to examine the structure of the $C_5H_5^+$ ions produced from the derivatives of toluene and benzene, we have now measured the heat of formation of the $C_5H_5^+$ ions from these compounds and compared them with that of 3-penten-1-yne and the cyclopentadienyl radical.[4,5]

The apparent heat of formation of the $C_5H_5^+$ ions, $\Delta H_f(C_5H_5^+)$, is calculated from the following equation:

$$\Delta H_f(C_5H_5^+) = \Delta H_f(M) + \text{A.P}(C_5H_5^+) - \sum \Delta H_f(N) - E \qquad (1)$$

where $\Delta H_f(M)$ is the heat of formation of the neutral molecule; $\text{A.P}(C_5H_5^+)$ is the appearance potential of the $C_5H_5^+$ ion, $\sum \Delta H_f(N)$ is the algebraic sum of the heat of formation of the neutral fragments, and E is the excess energy of the fragments at the threshold.

TABLE 1. APPEARANCE POTENTIALS (eV) AND HEATS OF FORMATION (kcal/mol) OF THE $C_5H_5^+$ ION FROM VARIOUS COMPOUNDS

Compounds	$\text{A.P}(C_5H_5^+)$		ΔH_f $(C_5H_5^+)$		Neutral products
	This work	Ref. 4	This work	Ref. 4	
Toluene	16.4		284.8		$H + C_2H_2$
p-Xylene	16.3		292.1		$CH_3 + C_2H_2$
o-Nitrotoluene	13.5		306.8 (Eq. 2)		$OH + CO + HCN$
			259.2 (Eq. 3)		$NO_2 + C_2H_2$
m-Nitrotoluene	15.2		298.4		$NO_2 + C_2H_2$
p-Nitrotoluene	14.9		291.0		$NO_2 + C_2H_2$
Ethylbenzene	16.2		292.6		$CH_3 + C_2H_2$
n-Propylbenzene	15.5		279.9		$C_2H_5 + C_2H_2$
o-Chlorotoluene	15.7		282.7		$Cl + C_2H_2$
m-Chlorotoluene	15.7		282.5		$Cl + C_2H_2$
p-Chlorotoluene	15.7		281.4		$Cl + C_2H_2$
o-Bromotoluene	15.2		285.3		$Br + C_2H_2$
m-Bromotoluene	15.2		284.5		$Br + C_2H_2$
p-Bromotoluene	15.2		285.2		$Br + C_2H_2$
o-Iodotoluene	14.3		279.9		$I + C_2H_2$
m-Iodotoluene	14.5		281.9		$I + C_2H_2$
p-Iodotoluene	14.7		286.2		$I + C_2H_2$
Aniline	15.2	15.24	290.2	288.0	$HCN + H$
Phenol	14.2	14.25	278.2	273.0	$CO + H$

The values of $\text{A.P}(C_5H_5^+)$ from the compounds obtained in the present experiment using a CEC 21-103C mass spectrometer are given in the second column in Table 1. These A.P values were obtained by the E.D.D technique;[7] the details of the experiment have already been described.[8] Each value is the average of at least three measurements. The experimental error is within ±0.2 eV.

The values for the heat of formation of the $C_5H_5^+$ ions calculated from Eq. (1) using the A.P values in Table 1 and the literature values[9] for $\Delta H_f(M)$ and $\Delta H_f(N)$ are given in the fourth column in Table 1. The value of E is usually determined from the width of the observed metastable peak.[4,10] The value seldom exceeds 10 kcal/mol, with a few exceptions, such as is the case of NO loss. In this experiment, we estimated

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[1] H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press Inc., New York (1963), Chap. 10.

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

[9] 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 Gaseous Positive Ions," National Bureau of Standard, U.S., (1969).

[10] J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier Publishing Co., London (1968), Chap. 1.

the heat of formation by neglecting E. Therefore, the data will show a tendency to have a little higher value. Taking the experimental error into consideration, the overall error is considered to be less than 20 kcal/mol. It is evident from the data of the heat of formation (Table 1) that all these values coincide with the heat of formation of 3-penten-1-yne (277 kcal/mol)[4] within the limits of experimental error, except for the values from *o*-nitrotoluene (the value of *m*-nitrotoluene is slightly higher than the limit of the experimental error, but it probably belongs to the former group). The values for the former group are considerably higher than the heat of formation of the $C_5H_5^+$ ion from the cyclopentadienyl radical (240 kcal/mol).[5] According to the results of Occolowitz and White,[4] we can also regard the $C_5H_5^+$ ions from the compounds studied here as having the (a) structure in Fig. 1.

Beynon *et al.* have reported[11] that the $C_5H_5^+$ ions are produced from *o*-nitrotoluene molecular ions by the following two reactions:

$$C_7H_7NO_2^+ \xrightarrow{-OH} C_7H_6NO^+ \xrightarrow{-CO} C_6H_6N^+ \xrightarrow{-HCN} C_5H_5^+ \qquad (2)$$

$$C_7H_7NO_2^+ \xrightarrow{-NO_2} C_7H_7^+ \xrightarrow{-C_2H_2} C_5H_5^+ \qquad (3)$$

Therefore, the heat of formation of the $C_5H_5^+$ ion for *o*-nitrotoluene, calculated from both Eq. (2) and Eq. (3), is given in Table 1. The structure of the $C_5H_5^+$ ion produced from Reaction (2) cannot be assigned on the basis of the present experiment alone. The value calculated from Reaction (3) is considerably lower than that of *m*- and *p*-nitrotoluene. The value (259.2 kcal/mol) shown in Table 1 as having been obtained from Reaction (3) was calculated by using A.P.= 13.5 eV. However, taking the mechanism of the production of the $C_5H_5^+$ ion given in Eq. (3) into account, the structure of the $C_5H_5^+$ ion of *o*-nitrotoluene produced by Reaction (3) seems to be identical with that of the *m*- and *p*-compounds. If this assumption is valid, the $\Delta H_f(C_5H_5^+)$ obtained from Eq. (3) for *o*-nitrotoluene should be close to that obtained for *m*- and *p*-compounds. In that case, assuming the $\Delta H_f(C_5H_5^+)$ is about 290 kcal/mol, the A.P value of the $C_5H_5^+$ ions for *o*-nitrotoluene obtained from Eq. (3) must be close to 14.8 eV. Therefore, a break in the ionization efficiency curve of the $C_5H_5^+$ ion for *o*-nitrotoluene is expected to occur at about 14.8 eV. As may be seen in Fig. 2, there is a break at about 14.8 eV. Consequently, it may be inferred that, while the onset of the $C_5H_5^+$ ion from Reaction (2) is at 13.5 eV (shown by the a arrow in Fig. 2), that of the $C_5H_5^+$ ion from Reaction (3) is at about 14.8 eV (shown by the b arrow).

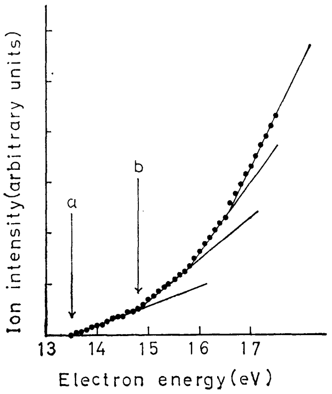

Fig. 2. Ionization efficiency curve for the $C_5H_5^+$ ion from *o*-nitrotoluene.

If the appearance potentials of the metastable ions corresponding to the $C_6H_6N^+ \rightarrow C_5H_5^+ + HCN$ and $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$ reactions can be measured, then the above assumption will be confirmed.

The authors wish to thank Mr. Nobuhide Wasada of this Laboratory for his valuable discussions.

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