

Energetic Study of $[C_5H_3]^+$ Fragment Ion Produced from some Benzyl Derivatives

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ABSTRACT. The different processes for formation of $[C_5H_3]^+$ fragment ion, for a range of 3 eV above threshold, from benzyl alcohol, benzyl amine and benzyl cyanide have been suggested and discussed. Appearance energies for the ion have been measured using electron impact technique. The results indicate, that at threshold as well as at higher energies, the $[C_5H_3]^+$ ion generated from the three precursors is a linear ion. A MNDO SCF method is used to calculate the heats of formation for the linear and cyclic structures of the ion. The substituent effect of $-OH$, $-NH_2$ and $-CN$ groups on the activation energy as well as excess energy term is also discussed.

The formation and structure of $[C_5H_3]^+$ fragment ion produced from different aromatic molecules had been rarely investigated (Franklin and Carroll 1969, Baer *et al.* 1979 and Dannacher *et al.* 1981) using mass spectrometric technique. Furthermore, the heat of formation of $[C_5H_3]^+$ ion is not well established. Baer *et al.* (1979) and Dannacher *et al.* (1981) reported an upper limit of $\sim 1431 \text{ kJ mol}^{-1}$ for the heat of formation of $[C_5H_3]^+$ produced from hexadyne isomers using breakdown diagrams obtained by photoelectron-photoion coincidence experiments. In the present work, we have studied the formation of $[C_5H_3]^+$ fragment ion produced from benzyl alcohol, benzyl amine and benzyl cyanide at and near threshold. Appearance energies (AE) as well as apparent heats of formation (ΔH_f) for the ion are reported. A correlation between the activation energy as well as the excess energy term and the substituent effect of $-NH_2$, $-OH$ and $-CN$ are also reported.

The electron impact technique was used for measuring the ionization efficiency curves for the fragment ion studied. By combining the inverse

convolution procedure of Vogt and Pascual (1972) with the first derivative technique we had been able to study the AE at threshold as well as higher AE's in the three studied curves. The results (Selim and Helal 1982, Selim *et al.* 1984, Selim 1985 and Selim *et al.* 1987) obtained by this combined technique are reliable and sufficiently accurate for comparison with similar values in the literature. The metastable peaks associated with the different dissociation processes have been also detected.

Experimental Technique

Ionization efficiency data were obtained using an Atlas CH-4 mass spectrometer with a normal electron impact ion source (AN4). The conditions of measurements and the method of the calibration of energy scale were the same as previously reported (Selim 1976). The electron energy was varied in 0.05 eV steps using a 10-turn helipot potentiometer and was measured with a digital multimeter Model VR-3511 of Hitachi. The energy scale was calibrated using the 15.76 eV threshold value of argon.

The directly measured ionization efficiency curves were smoothed by a 5-point smoothing (Savitzky and Golay 1964) computer technique in order to decrease the random noise in the raw data. Once again using a computer technique the smoothed data were treated (Savitzky and Golay 1964) to obtain the first derivative curves, and then the inverse convolution technique of Vogt and Pascual (1972) was applied to obtain the deconvoluted first differential (DFD) ionization efficiency curves. The complete details of the application of the combined technique had been reported elsewhere (Selim 1985) together with merits and limitations of the technique.

Metastable peaks had been detected at 70 eV using an MM16F mass spectrometer. However, the metastable signals were too weak to determine the translational energy associated with them with any reasonable accuracy.

Results and Discussion

The deconvoluted first differential ionization efficiency curve for $[\text{C}_5\text{H}_3]^+$ ions, measured (by 0.05 eV steps) up to about 3 eV above threshold, are given in Fig. 1. The AE values as well as calculated thermochemical threshold (ΔE_{th}) values for the suggested processes of formation are presented in Table 1, together with the estimated ΔH_f values. In the calculation of ΔE_{th} values we assumed a linear structure for the $[\text{C}_5\text{H}_3]^+$ ion with $\Delta H_f = 1213 \text{ kJ mol}^{-1}$ since, anything other than a linear structure appears implausible (Franklin and Carroll 1969). However, we have performed a molecular orbital calculations using MNDO

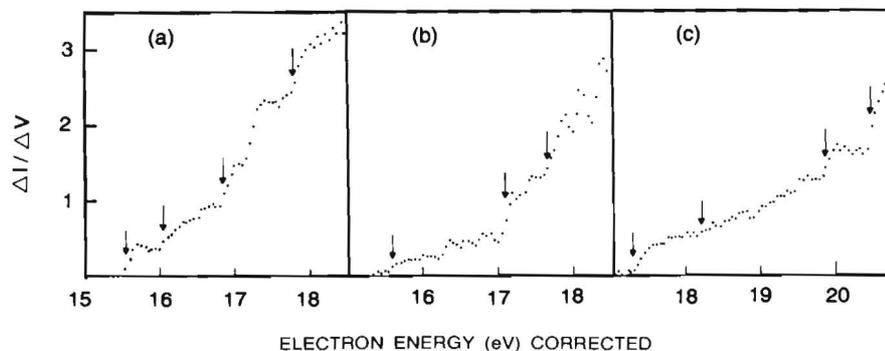


Fig. 1. The deconvoluted first differential IE curves for $[C_5H_3]^+$ ($m/z=63$) fragment ion obtained from: (a) benzyl alcohol (b) benzyl amine and (c) benzyl cyanide.

method (modified Neglect of differential overlap) for $[C_5H_3]^+$ ion with linear structure (a) and cyclic structure (b), and found that $\Delta H_f[a]^+$ is 1254 kJ mol^{-1} compared with $\Delta H_f[b]^+ = 1750 \text{ kJ mol}^{-1}$. These results indicate the much higher stability of the linear structure relative to the cyclic one as suggested by Franklin and Carroll (1969).



Since the suggested processes for the formation of $[C_5H_3]^+$ ions from the three precursors are all secondary decomposition processes, one expects (Franklin and Carroll 1969, Refaey and Chupka 1968) that they are associated with significant values of excess energy ($\epsilon_{exc.}$). Also, it is known (Holmes and Osborne 1978) that for secondary decomposition, the excess energy may contain some contribution from kinetic shift in addition to reverse activation energy (ϵ_o^r) and so $\epsilon_{exc.}$ should be regarded as upper limit for ϵ_o^r .

$[C_5H_3]^+$ from benzyl alcohol

There are two processes (1) and (2) leading to $[C_5H_3]^+$ which are accessible in the energy range considered. The thermochemical calculated thresholds (ΔE_{th}) are 14.55 (1) and 15.20 eV (2). Therefore, the experimental threshold at 15.49 eV must be associated with process (1) while the higher AE's at 16.86 eV is associated with processes (2). It might be noted that process (2) is partially confirmed by the metastable transition of $[C_7H_6]^+$ to $[C_7H_5]^+$ to $[C_5H_3]^+$.

Table 1. Energetics of the processes forming $[C_5H_3]^+$ fragment ion from benzyl alcohol, benzyl amine and benzyl cyanide

Molecule	AE $[C_5H_3]^+$ (eV) ^a	Suggested Process	Calculated ^b ΔE_{th} (eV) linear $[C_5H_3]^+$	Apparent $\Delta H_f[C_5H_3]^+$ (kJ mol ⁻¹)	ϵ_{exc} (eV)
Benzyl alcohol	15.49 ± 0.09	$[C_7H_8O]^+ \cdot \rightarrow [C_5H_3]^+ + \cdot OH + C_2H_4$ (1)	14.55	1304	0.94
	16.86 ± 0.11	$[C_7H_8O]^+ \cdot \rightarrow [C_5H_3]^+ + H_2O + \cdot H + C_2H_2$ (2)	15.70	1325	1.16
Benzyl amine	15.61 ± 0.10	$[C_7H_9N]^+ \cdot \rightarrow [C_5H_3]^+ + \cdot NH_2 + C_2H_4$ (3)	14.04	1365	1.57
		$[C_7H_9N]^+ \cdot \rightarrow [C_5H_3]^+ + NH_3 + H + C_2H_2$ (4)	15.84	1347	1.39
	17.23 ± 0.11	$[C_7H_9N]^+ \cdot \rightarrow [C_5H_3]^+ + \cdot NH_2 + H_2 + C_2H_2$ (5)	16.27	1349	1.41
	17.68 ± 0.13	$[C_7H_9N]^+ \cdot \rightarrow [C_5H_3]^+ + NH + \cdot C_2H_5$ (6)			
Benzyl cyanide	17.31 ± 0.10	$[C_8H_7N]^+ 1 \cdot \rightarrow [C_5H_3]^+ + HCN + \cdot H + C_2H_2$ (7)	16.76	1266	0.55
	18.36 ± 0.12	$[C_8H_7N]^+ \cdot \rightarrow [C_5H_3]^+ + \cdot CN + H_2 + C_2H_2$ (8)	17.61	1286	0.75

(a) AE values are the average of five determinations and the errors quoted are the standard deviations.

(b) Calculated using ΔH_f [linear- C_5H_3]⁺ = 1213 kJ mol⁻¹ from Franklin and Carroll (1969), ΔH_f (C_7H_8O) from Cox and Pilcher (1970), ΔH_f (C_7H_9N) and (C_8H_7N) from Franklin *et al.* (1969), ΔH_f for: H, OH, CN, HCN, H₂O, NH, NH₂, NH₃, CH₃, C₂H₂, C₂H₄ and C₂H₅ from Rosenstock *et al.* (1977).

Table 2. Activation energy and excess energy term for the process $[C_6H_5CH_2X]^{+\cdot} \rightarrow [C_5H_3]^+ + XH \cdot + C_2H_2$ for the dissociation of benzyl amine, benzyl alcohol and benzyl cyanide

Substituent	Activation energy (ϵ) (AE - IE*) eV	Excess energy (ϵ_{exc}) (eV)
NH ₂	8.74	1.39
OH	8.60	1.16
CN	7.99	0.55

* IE's for benzyl amine, benzyl alcohol and benzyl cyanide are taken from Selim *et al.* (1987).

$[C_5H_3]^+$ from benzyl amine

It is assumed that the ion is formed at threshold by the successive loss of $\cdot NH_2 + C_2H_4$ from benzyl amine (process 3). This scheme is partially confirmed by the observation of the metastable transition of $[C_7H_7]^+$ to $[C_5H_3]^+$. ΔE_{th} calculated for $[C_5H_3]^+$ ion according to process (3) is 14.04 eV while the experimental AE at threshold is measured at 15.61 eV.

A higher AE at 17.23 eV is assumed to be due to the ion formation by the successive loss of $NH_3 + \cdot H + C_2H_2$ (process 4) and/or $\cdot NH_2 + H_2 + C_2H_2$ (process 5). These schemes are partially confirmed by the detection of the metastable transition: $[C_7H_5]^+ \rightarrow [C_5H_3]^+ + C_2H_2$. ΔE_{th} calculated for the formation of $[C_5H_3]^+$ ion according to either process (4) or (5) is equal to 15.84 eV in comparison with 17.23 eV for the higher AE measured. A higher threshold at 17.68 eV is assumed to be due to $[C_5H_3]^+$ ion formation by the successive loss of $NH + \cdot C_2H_5$ (process 6). Process (6) has a calculated $\Delta E_{th} = 16.27$ eV, suggesting $\epsilon_{exc} = 1.41$ eV.

$[C_5H_3]^+$ from benzyl cyanide

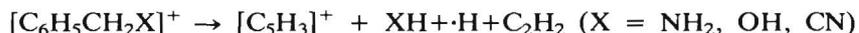
It is assumed that the ion is formed at threshold by successive loss of $HCN + \cdot H + C_2H_2$ (process 7). This scheme is confirmed by the observation of the metastable transitions of $[C_8H_7N]^+$ to $[C_7H_6]^+$ to $[C_7H_5]^+$ to $[C_5H_3]^+$. The calculated ΔE_{th} for the formation of the ion according to process (7) is 16.76 eV in comparison with 17.31 eV for the experimentally measured AE at threshold.

A higher threshold is measured at 18.36 eV in the DFD curve of $[C_5H_3]^+$ produced from benzyl cyanide. This AE is assumed to be associated with process (8) due to the formation of the ion by the successive loss of $\cdot CN + H_2 + C_2H_2$. The calculated ΔE_{th} value for process (8) is equal to 17.61 eV suggesting $\epsilon_{exc} = 0.75$ eV.

Note from table 1 that all the processes of formation of $[\text{C}_5\text{H}_3]^+$ are associated with significant excess energy values. Since the only possible structure for $[\text{C}_5\text{H}_3]^+$ is a linear structure (Franklin and Carroll 1969) and since the estimated heat of formation for the ion is 1213 kJ mol^{-1} (Franklin and Carroll 1969) which is in reasonable agreement with our calculated value (1254 kJ mol^{-1}), it seems very likely (knowing that $[\text{C}_5\text{H}_3]^+$ ions are formed in the present work, with significant excess energy values) that the $[\text{C}_5\text{H}_3]^+$ ion produced from the three precursors is linear ion.

The ionization efficiency curves of $[\text{C}_5\text{H}_3]^+$ ions obtained from benzyl alcohol and benzyl cyanide show additional higher AE's (steps) at 16.01 ± 0.09 , $17.76 \pm 0.12 \text{ eV}$ and at 19.81 ± 0.10 , $20.44 \pm 0.10 \text{ eV}$, respectively. These AE's correspond to steps (or peaks) at approximately the same energies (within experimental uncertainties) for the corresponding molecular ions (benzyl alcohol: $16.16 \pm 0.12 \text{ eV}$ and $17.69 \pm 0.15 \text{ eV}$, benzyl cyanide: 19.56 ± 0.10 and $20.53 \pm 0.15 \text{ eV}$) and for some other fragments (C_6H_5^+ , and C_3H_3^+) (Selim *et al.* 1989), probably suggesting the onset of formation of excited states of the corresponding molecular ions. On the other hand, the ionization efficiency curve for $[\text{C}_5\text{H}_3]^+$ ion obtained from benzyl amine show three peaks (not completely resolved) between ~ 17.90 and $\sim 18.40 \text{ eV}$ which do not appear in the molecular ion curve of benzyl amine. A tentative explanation is that these peaks are due to an autoionization process. Clearly in this case the electron emitted in autoionization carries away relatively little energy.

The effect of the substituent on the activation energy (ϵ) (AE-IE) value as well as excess energy value ($\epsilon_{\text{exc.}}$) for the formation of $[\text{C}_5\text{H}_3]^+$ according to the process:



is summarized in Table 2. It is apparent that for the molecules with electron-donating substituents (benzyl amine and benzyl alcohol), the ϵ values are relatively large with ϵ (8.74 eV) (benzyl amine) $\geq \epsilon$ (8.60 eV) (benzyl alcohol), while for the molecule with electron-withdrawing substituent (benzyl cyanide) the ϵ value (7.99 eV) is smaller. This is in accordance with the observation of many authors (Brown 1970) that introduction of an electron donating substituent leads in most cases to an increase in (AE-IE) and thus to increased activation energy, although several instances are known where the opposite behaviour has been observed (McLafferty *et al.* 1970, Brown 1970).

It is also interesting to note that the excess energy term ($\epsilon_{\text{exc.}}$) associated with the last process is affected by substitution. The order of decreasing $\epsilon_{\text{exc.}}$ is $\epsilon_{\text{exc.}}$

(1.39 eV) (benzyl amine) $\rangle \epsilon_{exc}$. (1.16 eV) (benzyl alcohol) $\rangle \epsilon_{exc}$. (0.55 eV) (benzyl cyanide). This may reflect the influence of the substituent on the excess energy term.

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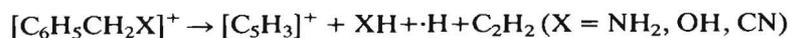
(Received 22/01/1989;
in revised form 24/09/1989)

دراسة طاقات تكوين الايون $[C_5H_3]^+$ الناتج من بعض مشتقات الجزئيات البنزيلية

عزت طه محمد سليم و محمد عبدالفتاح ربيع و مجد الدين فهمي أحمد و أحمد شلبي^١

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تم في هذا البحث اقتراح ومناقشة الطرق المختلفة لتكوين الأيون $[C_5H_3]^+$ من جزئيات الكحول البنزيلي والأمين البنزيلي والسيانيد البنزيلي. وقد قيست طاقات الظهور لتلك الأيونات لمدى قدرة ٣ الكترون فولت باستخدام طريقة التناطح الالكتروني، وطاقات الظهور المقاسة عند البداية للأيون هي ١٥, ٤٩, ١٥, ٦١, ١٧, ٣١ الكترون فولت (الكحول البنزيلي)، ١٥, ٦١, ١٧, ٣١ الكترون فولت (الأمين البنزيلي) وتم قياس طاقات الظهور ومستويات الطاقة الأعلى لكل أيون من خلال منحنيات كفاءة التأين، ولقد استخدم المؤلفون طاقات الظهور المقاسة عند البداية وعند الطاقات الأعلى في استنتاج حرارة التكوين للأيون الناتج من الجزئيات الثلاثة السابقة. والنتائج التي تم الحصول عليها تدل على أن الأيون $[C_5H_3]^+$ المتكون من الجزئيات الثلاثة عند نقطة البداية أو عند مستويات الطاقة الأعلى هو التركيب الخطي وقد أمكن استخدام طريقة MNDO SCF النظرية لحساب حرارة التكوين لكل من الأيون الخطي والحلقي وتم كذلك مناقشة تأثير مجموعات الهيدروكسيل والأمين والسيانيد على طاقة التنشيط لتلك الأيونات وكذلك على طاقة التنشيط الزائدة. ولقد وجد المؤلفون أن طاقة التنشيط (ϵ) لتكوين الأيون $[C_5H_3]^+$ طبقاً للتفاعل:



هي ٨, ٧٤, ٨, ٦٠ الكترون فولت للأيون الناتج من الأمين البنزيلي، ٨, ٦٠, ٧, ٩٩ الكترون فولت للأيون الناتج من الكحول البنزيلي مقارنة بطاقة تنشيط أقل كثيراً (٧, ٩٩)

الالكترون فولت) في حالة الأيون الناتج من السيانيد البنزيلي. ووجد المؤلفون كذلك ان الطاقة الزائدة (ϵ_{exc}) المصاحبة لتكوين الأيون طبقاً للتفاعل السابق أيضاً تتناقص طبقاً للاتي: ١,٣٩ الالكترون فولت (الأمين البنزيلي) < ١,١٦ الالكترون فولت (الكحول البنزيلي) < ٠,٥٥ الالكترون فولت (السيانيد البنزيلي).