Kinetic Energy Release and Position of the Transition State for $[C_6H_7]^+$ Ions Produced from Isomeric C_7H_8O Precursors

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The energetic requirement and mechanisms for CHO$^\cdot$ loss from the molecular ions of isomeric C_7H_8O precursors have been reported. The heat of formation of $[C_6H_7]^+$ (protonated benzene) was determined and $\varepsilon_r^\ddagger$ evaluated. Measurement of the kinetic energy release T_B gives the energy-partitioning quotients $q = T_B/\varepsilon_r^\ddagger$ which range from 0.38 to 0.99. The energy available and T_B are small for the strongly endothermic reaction of benzyl alcohol but increase sharply in the case of the weakly endothermic reaction of anisole. All reactions have "late" transition states, the position $X_0^\ddagger$ of the transition state on the reaction coordinate varying from 0.64 to 0.93.

Introduction

In previous [1] investigations we have reported the appearance energies for $[C_6H_7]^+$ fragment ions produced from five isomeric molecules, namely 2-, 3- and 4-methylphenol, benzyl alcohol and anisole. Appearance energy measurements together with thermodynamical considerations indicate the formation of $[C_6H_7]^+$ ions (by CHO$^\cdot$ loss) with protonated benzene structure [1].

One important topic of research in the dynamics of elementary chemical reactions is the partitioning of the excess energy of an activated complex among the degrees of freedom of the reaction products. It appears that the investigation of the variation of the kinetic energy release T_B and the energy partitioning quotient $q = T_B/\varepsilon_r^\ddagger$ with structure change of the reactant ions gives some insight into fundamental properties of elementary reactions of organic ions, which will be useful in testing mechanistic models of organic chemistry and linking them more closely to physical theories of chemical reactions [2].

In the present paper the energy partitioning accompanying the elimination of CHO$^\cdot$ from the precursor molecules as well as the position $X_0^\ddagger$ of the transition states on the reaction coordinate are reported and discussed. For this purpose we have investigated metastable peaks associated with the reactions studied, which were used to determine the maximum value of T_B. Mechanisms for the formation of $[C_6H_7]^+$ ions from the precursor molecular ions are suggested.

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Experimental

Metastable peaks were measured using an Atlas CH-4 mass spectrometer. The maximum value of T_B during the fragmentation was determined [3] from the peak width at the base line after correcting [4] the width for the energy spread of the main ion beam. Each metastable peak was recorded several times and the reproducibility of T_B was always better than 7%. All the metastable peaks were checked for pressure dependence. The results indicate that non of the metastable peaks were pressure induced, i.e. they are due to unimolecular fragmentation.

Results and Discussion

Figure 1 shows the schematic reaction profile for the process $[M]^+ \rightarrow [C_6H_7]^+ + CHO^\cdot$ and defines energy data together with the symbols used.

The experimentally determined energy data for the loss of CHO$^\cdot$ from the five C_7H_8O precursors are reported in Table 1. The partitioning energy quotient $q = T_B/\varepsilon_r^\ddagger$, reaction enthalpy ΔH_R^+ and position $X_0^\ddagger$ of the transition state on the reaction coordinate derived from these data are also reported in Table 1. It should be emphasized that the ionization energy and appearance energy for the different precursors introduced in Table 1 were measured [1] at the same experimental

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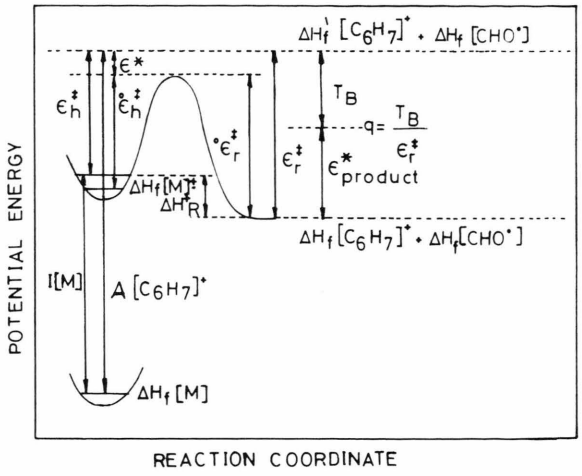


Fig. 1. Potential energy diagram for the process $[C_7H_8O]^+ \rightarrow [C_6H_7]^+ + CHO^{\cdot}$. $I[M]$ = ionization energy; $A[C_6H_7]^+$ = appearance energy of $[C_6H_7]^+$; ΔH_R^+ = reaction enthalpy; $\Delta H_f[M]^+$, $\Delta H_f[C_6H_7]^+$, $\Delta H_f[CHO^{\cdot}]$ = heat of formation of M^+, $C_6H_7^+$ and $CHO^{\cdot}$; $\Delta H_f'[C_6H_7]^+$ = apparent heat of formation of the ion; $\varepsilon_h^{\ddagger}$ = thermochemical activation energy of forward reaction; $\varepsilon_h^{\ddagger}$ = experimental activation energy of the forward reaction; ε^* = non fixed excess energy of the activated complex; $\varepsilon_r^{\ddagger}$ = thermochemical reverse activation energy, $\varepsilon_r^{\ddagger}$ = experimental reverse activation energy; T_B = maximum kinetic energy release.

conditions. This decreases systematic errors in the calculated $\varepsilon_h^{\ddagger}$ ($A[C_6H_7]^+ - I[M]$) values. The mechanisms suggested for the formation of the ions are reported in Schemes 1–3.

According to Miller's quantification [5] of the Hammond postulate [6] the position $X_0^{\ddagger}$ of the transition state of an elementary reaction on the reaction coordinate can be expressed by the barrier height $U^*(\varepsilon_h^{\ddagger})$ and potential energy of the reaction $U_f(\Delta H_R^+)$ according to

$$X_0^{\ddagger} = \frac{1}{2 - U_f/U^*} = \frac{1}{2 - \Delta H_R^+/\varepsilon_h^{\ddagger}} . \qquad (1)$$

X^* is the value of the reaction coordinate, X_0^* ($0 \leq X \leq 1$) corresponding to the position of the activated complex. The positions $X^* = 0$ and $X^* = 1$ represent the initial and final states of the reaction, respectively.

The crucial point in mass spectrometric investigations of the type discussed in this study is the knowledge of the structure of the reaction products and of their heats of formation [2]. The appearance energy $A[C_6H_7]^+$ does not correspond to the enthalpy of reaction ΔH_R^+ of a mass spectrometric fragmentation but to the potential energy of the transition state of

Table 1. Energy data[a] for the elimination of CHO from C_7H_8O precursors.

Molecule	Benzyl alcohol	2-Methyl-phenol	3-Methyl-phenol	4-Methyl-phenol	Anisole
$I[C_7H_8O]$	8.26 [b]	8.46 [c]	8.36 [c]	8.31 [c]	8.51 [d]
$A[C_6H_7]^+$ [e]	10.33	11.25	11.20	11.58	11.64
$\varepsilon_h^{\ddagger}$	2.07	2.79	2.84	3.27	3.13
$\Delta H_f[C_7H_8O]$ [f]	−1.04	−1.33	−1.37	−1.30	−0.75
$\Delta H_f[CHO^{\cdot}]$ [g]	0.38	0.38	0.38	0.38	0.38
$\Delta H_f'[C_6H_7]^+$	8.91	9.53	9.44	9.90	10.51
T_B	0.158	0.312	0.38	0.436	0.857
$\Delta H_f'[C_6H_7]^+ - T_B$	8.75	9.23	9.10	9.47	9.38
$\varepsilon_r^{\ddagger}$	0.16	0.78	0.70	1.15	1.76
$q = T_B/\varepsilon_r^{\ddagger}$	0.99	0.40	0.54	0.38	0.49
ΔH_R^+	1.91	2.01	2.14	2.12	1.37
$X_0^{\ddagger}$	0.93	0.78	0.80	0.74	0.64

[a] All values are in electron volt.
[b] Value from [13].
[c] Value from [14].
[d] Value from [1 b].
[e] Value from [1 c].
[f] Value from [15].
[g] Value from [16].

that reaction plus a small amount of non-fixed energy (kinetic shift) only. Thus, only "apparent" heats of formation $\Delta H_f'$ are obtained by using (1), including the activation energy of the reverse reaction $\varepsilon_r^{\ddagger}$. A part of the contribution of $\varepsilon_r^{\ddagger}$ can be corrected for by the amount released as the maximum kinetic energy T_B in the fragments according to (1). However, it is not known a priori whether the total $\varepsilon_r^{\ddagger}$ or only a part of it is released as T_B [2].

The energy data in Table 1 have been used to calculate the activation energy of the forward reaction $\varepsilon_h^{\ddagger}$, the apparent and corrected heats of formation of $[C_6H_7]^+$, $\Delta H_f'$ and $\Delta H_{f\,corr}'$, the reverse activation energy $\varepsilon_r^{\ddagger}$ and the enthalpy of the reaction ΔH_R^+ according to the equations

$$\Delta H_f'[C_6H_7]^+ = A[C_6H_7]^+ + \Delta H_f[M] - \Delta H_f[CHO] = \Delta H_f[C_6H_7]^+ + \varepsilon_r^{\ddagger} , \qquad (2)$$

$$\varepsilon_h^{\ddagger} = A[C_6H_7]^+ - I[M] , \qquad (3)$$

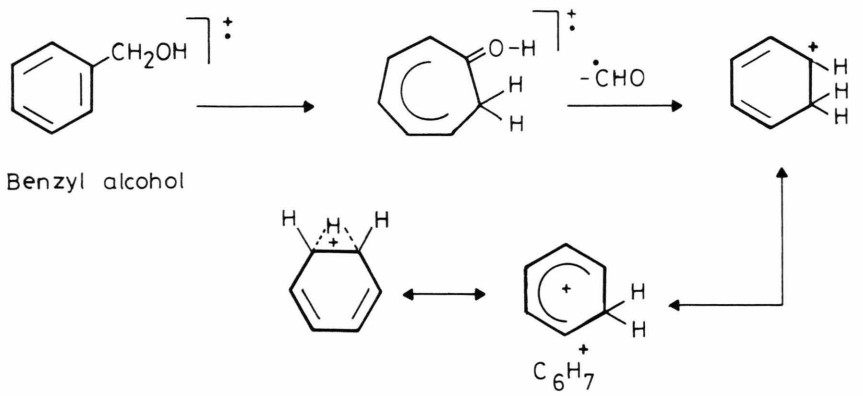
$$\Delta H_f'[C_6H_7]^+_{corr} = \Delta H_f'[C_6H_7]^+ - T_B \geq \Delta H_f[C_6H_7]^+ , \qquad (4)$$

$$\varepsilon_r^{\ddagger} = A[C_6H_7]^+ + \Delta H_f[M] - \Delta H_f[C_6H_7]^+ - \Delta H_f[CHO] = \varepsilon_h^{\ddagger} - \Delta H_R^+ , \qquad (5)$$

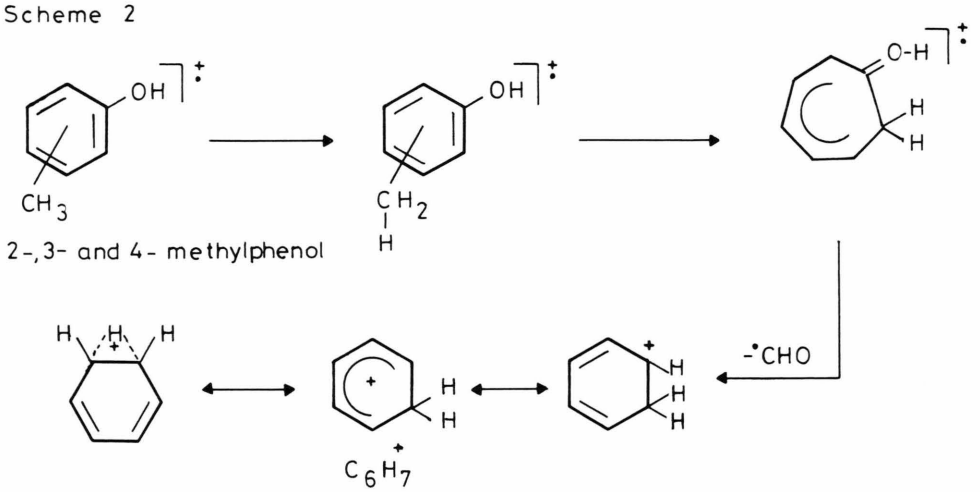
$$\Delta H_R^+ = \Delta H_f[C_6H_7]^+ + \Delta H_f[CHO] - I[M] - \Delta H_f[M] . \qquad (6)$$

The apparent heats of formation $\Delta H_f'[C_6H_7]^+$ of the $m/z = 79$ ions arising from the five precursors listed in Table 1 are not constant and considerably

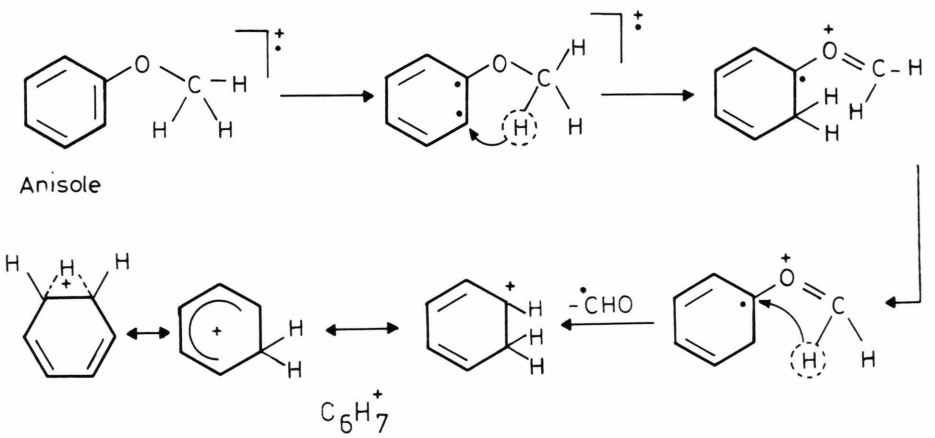
Scheme 1



Scheme 2



Scheme 3



Precursors	Intensity ratio
Benzyl alcohol	1.07
2-Methylphenol	0.26
3-Methylphenol	0.26
4-Methylphenol	0.26
Anisole	0.12

Table 2. Intensity ratio $I[C_6H_7]^+/I[M]^+$ in the mass spectra of C_7H_8O precursors at 14 eV (nominal).

Table 3. $T_{50\%}$, $\varepsilon_r^{\neq}$ and estimated $T_{50\%}/\varepsilon_r^{\neq}$ values for C_7H_8O reactions.

Molecule	$T_{50\%}$ (eV)*	$\varepsilon_r^{\neq}$ (eV)	$T_{50\%}/\varepsilon_r^{\neq}$
Benzyl alcohol	0.040	0.16	0.25
2-Methylphenol	0.116	0.78	0.15
3-Methylphenol	0.135	0.70	0.19
4-Methylphenol	0.156	1.15	0.14
Anisole	0.328	1.76	0.19

* Values from Ref. [1].

larger than those reported by Cassady et al. [7] and Lias et al. [8] for $[C_6H_7]^+$ (protonated benzene). This merely reflects the variation of the magnitude of the reverse activation energy $\varepsilon_r^{\neq}$ for the different precursors.

No constant value of $\Delta H_f'[C_6H_7]^+_{corr}$ is obtained (Table 1) after the correction of $\Delta H_f'[C_6H_7]^+$ by T_B, but $\Delta H_f'[C_6H_7]^+$ approaches the value 8.75 eV suggesting $\Delta H_f[C_6H_7]^+$ (protonated benzene) $\leq$ 8.75 eV. This agrees well with the $\Delta H_f[C_6H_7]^+$ value 8.70 eV for the protonated benzene structure obtained from the proton affinity of benzene and reported by Cassady et al. [7], and the value 8.85 eV reported by Lias et al. [8]. Hence $\Delta H_f[C_6H_7]^+ = 8.75$ eV has been used for the present calculations.

Applying (1) to the reactions corresponding to the formation of $[C_6H_7]^+$ from $[C_7H_8O]^+$ isomers shows that $X_0^{\neq}$ varies from 0.64 to 0.93 (Table 1), so that late transition states are involved. One may expect [2] that for this type of reactions most of the energy of the transition state is accumulated in the stretched bond and is released as kinetic energy of the product if the stretching of this bond proceeds toward dissociation. However, it is puzzling that the 2- and 4-methylphenol as well as anisole reactions do not follow the rule mentioned above. Although $X_0^{\neq}$ for these reactions ranges from 0.64 to 0.80, the ratio q ranges from 0.38 to 0.49 only, i.e. most of the available energy is not released as kinetic energy.

According to (1) the potential energy barrier varies continuously with the heat of the reaction. This corresponds to a change in the transition state configurations of the reacting molecular ions. This tendency is reflected by a parallel change in the abundance of $[C_6H_7]^+$ ions; one expects [9] low values for the abundance of the ions from all precursors since $X_0^{\neq} > 0.5$. All C_7H_8O reactions (Table 2) follow that trend exactly.

According to (5), $\varepsilon_r^{\neq}$ depends on the heat of the reaction, being smallest in case of the most endothermic and largest in case of the most exothermic reaction (assuming that $\varepsilon_h^{\neq}$ is constant or varies only slightly). Although the calculated $\varepsilon_h^{\neq}$ values are not constant and show significant variation, especially for the benzyl alcohol reaction, the calculated $\varepsilon_r^{\neq}$ values follow this rule. The smallest $\varepsilon_r^{\neq}$ (0.16 eV) is obtained for the most endothermic reaction of benzyl alcohol ($X_0^{\neq} = 0.93$), whereas the largest value (1.76 eV) is obtained for the weakly endothermic reaction of anisole ($X_0^{\neq} = 0.64$). The same trend is reflected in the values measured for T_B.

A correlation between the energy partitioning quotient q and $X_0^{\neq}$ makes it possible to obtain experimental information about the nature of the transition state produced in a mass-spectrometric fragmentation reaction, and thus provides more detailed data on these elementary reactions [9]. The formation of $[C_6H_7]^+$ from benzyl alcohol, with a strongly endothermic reaction ($X_0^{\neq} = 0.93$), takes place with the transformation of nearly all available energy into translational energy measured as the maximum kinetic energy T_B. This amount of energy is small (0.16 eV), as the available energy of the product-like transition state probably corresponds only to the freely fluctuating excess energy of the activated complex $\varepsilon^{\neq}$. The energy available and T_B increase sharply, however, in the case of the weakly endothermic reaction of $[C_6H_7]^+$ formation from anisole ($X_0^{\neq} = 0.64$). Also the energy available and T_B increase significantly (relative to the benzyl alcohol reaction) in the case of moderately endothermic reactions of methylphenols ($X_0^{\neq} = 0.74$ to 0.80), with the transformation of only 38 to 54% of all the available energy into translational energy.

Note that the mechanisms (Schemes 1 and 2) suggested for the reaction of benzyl alcohol and methylphenol isomers involve ring expansion followed by loss of CHO$^{\cdot}$ by simple cleavage while the mechanism (Scheme 3) suggested for the anisole reaction involves hydrogen transfer via a 4-membered cyclic transition

state. Beynon and his coworkers [10, 11] previously suggested that the value of the quotient $T_{50\%}/\varepsilon_r^{\ddagger}$ might provide an indication of the ring size involved in cyclic transition states. The values for the quotient $T_{50\%}/\varepsilon_r^{\ddagger}$ are estimated and reported in Table 3. According to Beynon's and his coworkers criterion [10, 11], these values suggest that all the reactions occur via a 4-membered cyclic activated complex. However, in case of the anisole reaction only the quotient value ≈ 0.19 agrees with the present proposal that hydrogen transfer occurs via a 4-membered cyclic activated complex. Finally, it is worth noting that the T values (Tables 1 and 3) for the reactions of benzyl alcohol and methylphenol isomers, which occur via the same ring expansion mechanism, are different, although the number of internal degrees of freedom for these reacting ions, which is known to influence the value of T [11, 12], are similar.

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