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 \(\text{CHO}^+\) 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 \(e^*\) evaluated. Measurement of the kinetic energy release \(T_B\) gives the energy-partitioning quotients \(q = T_B/e^*\) which range from 0.38 to 0.99. The energy available and \(T_n\) 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 \(X_q\) 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 \(\text{CHO}^+\) 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 \(q = T_B/e^*\) 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 \(\text{CHO}^+\) from the precursor molecules as well as the position \(X_q\) 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.

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 \([M]^+ \rightarrow [C_6H_7]^+ + \text{CHO}^+\) and defines energy data together with the symbols used.

The experimentally determined energy data for the loss of \(\text{CHO}^+\) from the five \(C_7H_8O\) precursors are reported in Table 1. The partitioning energy quotient \(q = T_B/e^*\), reaction enthalpy \(\Delta H^*_q\) and position \(X_q\) 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 conditions.

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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 $e^*$. A part of the contribution of $e^*_h$ 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 $e^*_h$ 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 $e^*_h$, the apparent and corrected heats of formation of $[C_6H_7]^+$, $\Delta H_f$ and $\Delta H_f^{\text{corr}}$, the reverse activation energy $e^*$ and the enthalpy of the reaction $\Delta H^\text{e}$ according to the equations

$$\Delta H_f'[C_6H_7]^+ = A[C_6H_7]^+ + \Delta H_f'[M] - \Delta H_f'[\text{CHO}]$$

(2)

$$e^*_h = A[C_6H_7]^+ - I[M],$$

(3)

$$\Delta H_f'[C_6H_7]^+/^{\text{corr}} = \Delta H_f'[C_6H_7]^+ - T_B$$

(4)

$$e^* = A[C_6H_7]^+ + \Delta H_f[M] - \Delta H_f[C_6H_7]^+ - \Delta H_f'[\text{CHO}]$$

(5)

$$\Delta H^\text{e} = \Delta H_f[C_6H_7]^+ + \Delta H_f'[\text{CHO}] - I[M] - \Delta H_f'[M].$$

(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

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**Table 1. Energy data** for the elimination of CHO from $C_7H_80$ precursors.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Benzyl alcohol</th>
<th>2-Methyl-</th>
<th>3-Methyl-</th>
<th>4-Methyl-</th>
<th>Anisole</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/C_7H_8O</td>
<td>8.26 b</td>
<td>8.46</td>
<td>8.36</td>
<td>8.31</td>
<td>8.51</td>
</tr>
<tr>
<td>A/C_7H_8+</td>
<td>10.33</td>
<td>11.25</td>
<td>11.20</td>
<td>11.58</td>
<td>11.64</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>2.07</td>
<td>2.79</td>
<td>2.84</td>
<td>3.27</td>
<td>3.13</td>
</tr>
<tr>
<td>$\Delta H_f'[C_6H_7]^+$</td>
<td>-1.04</td>
<td>-1.33</td>
<td>-1.37</td>
<td>-1.30</td>
<td>-0.75</td>
</tr>
<tr>
<td>$\Delta H_f'[\text{CHO}]$</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>$\Delta H_f'[C_6H_7]^+$</td>
<td>8.91</td>
<td>9.53</td>
<td>9.44</td>
<td>9.90</td>
<td>10.51</td>
</tr>
<tr>
<td>$T_B$</td>
<td>0.158</td>
<td>0.312</td>
<td>0.38</td>
<td>0.436</td>
<td>0.857</td>
</tr>
<tr>
<td>$e^*_h$</td>
<td>0.16</td>
<td>0.78</td>
<td>0.70</td>
<td>1.15</td>
<td>1.76</td>
</tr>
<tr>
<td>$q = T_B/c^*_h$</td>
<td>0.99</td>
<td>0.40</td>
<td>0.54</td>
<td>0.38</td>
<td>0.49</td>
</tr>
<tr>
<td>$\Delta H_f^{\text{corr}}$</td>
<td>1.91</td>
<td>2.01</td>
<td>2.14</td>
<td>2.12</td>
<td>1.37</td>
</tr>
<tr>
<td>$X^*_h$</td>
<td>0.93</td>
<td>0.78</td>
<td>0.80</td>
<td>0.74</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*a All values are in electron volt.  
* Value from [13].  
* Value from [14].  
* Value from [15].  
* Value from [16].
Scheme 1

Benzyl alcohol

Scheme 2

2-, 3- and 4- methyphenol

Scheme 3

Anisole
Table 2. Intensity ratio \( \frac{[C_6H_7]^+}{[M]^+} \) in the mass spectra of C\(_7\)H\(_8\)O precursors at 14 eV (nominal).

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol</td>
<td>1.07</td>
</tr>
<tr>
<td>2-Methylphenol</td>
<td>0.26</td>
</tr>
<tr>
<td>3-Methylphenol</td>
<td>0.26</td>
</tr>
<tr>
<td>4-Methylphenol</td>
<td>0.26</td>
</tr>
<tr>
<td>Anisole</td>
<td>0.12</td>
</tr>
</tbody>
</table>

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\(_6\)H\(_7\)]\(^+\) ions; one expects [9] low values for the abundance of the ions from all precursors since \( X_0^* > 0.5 \). All C\(_7\)H\(_8\)O reactions (Table 2) follow that trend exactly.

According to (5), \( e_r^* \) 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 \( e_h^* \) is constant or varies only slightly). Although the calculated \( e_h^* \) values are not constant and show significant variation, especially for the benzyl alcohol reaction, the calculated \( e_r^* \) values follow this rule. The smallest \( e_r^* \) (0.16 eV) is obtained for the most endothermic reaction of benzyl alcohol \( (X_0^* = 0.93) \), whereas the largest value (1.76 eV) is obtained for the weakly endothermic reaction of anisole \( (X_0^* = 0.64) \). The same trend is reflected in the values measured for \( T_B \).

A correlation between the energy partitioning quotient \( q \) and \( X_0^* \) 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\(_6\)H\(_7\)]\(^+\) from benzyl alcohol, with a strongly endothermic reaction \( (X_0^* = 0.93) \), 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 \( e^* \). The energy available and \( T_B \) increase sharply, however, in the case of the weakly endothermic reaction \( (X_0^* = 0.64) \), 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\(^-\) by simple cleavage while the mechanism (Scheme 3) suggested for the anisole reaction involves hydrogen transfer via a 4-membered cyclic transition...
Beynon and his coworkers [10, 11] previously suggested that the value of the quotient $T_{q\phi}/e_0^*$ might provide an indication of the ring size involved in cyclic transition states. The values for the quotient $T_{q\phi}/e_0^*$ 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 $\approx 0.19$ 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.

References: