Mass Spectrometric Observation of Persistent Ion-Molecule Complexes of Acrylonitrile and of Benzene

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Two persistent collision complexes between an ion and a neutral molecule have been observed in a mass spectrometer. C₆H₅N₂⁺ (primary ion C₆H₆N⁺) is formed in acrylonitrile, C₁₂H₁₁⁺ (primary ion C₆H₅⁺) in benzene. The formation of both complexes very strongly decreases with increasing kinetic energy of the ions. This is explained by the decrease in lifetime due to the increased internal energy of the activated complexes. Some decomposition products of the complexes have also been observed. The results are compared to Pottie and Hamill's theory of complex formation.

The theory of chemical rate processes postulates the formation of an activated complex in a bimolecular reaction which then dissociates into the reaction products. In conventional chemical reactions there exists no chance of observing such intermediate complexes because of their short lifetimes. Complexes formed in a mass spectrometer between an ion and a neutral gas molecule can be detected if their lifetimes are higher than the time of 10⁻⁸ sec required for the flight through the spectrometer. Although a great number of ion-molecule reactions has been observed, only a few persistent activated complexes have been detected. Pottie and Hamill reported the first examples of such complexes formed by reaction of molecular halide ions with neutral halides, i.e., C₄H₁₀I₂⁺, C₄H₁₀Br₂⁺ and C₆H₁₄I₂⁺.

Several decomposition products of such complexes have also been found. We have observed complexes in acrylonitrile and in benzene as well as secondary ions resulting from the loss of H-atoms from these complexes. The complex C₄H₆N₂⁺ in acrylonitrile is formed by the reaction of the parent ion with a neutral molecule as in Pottie and Hamill's reactions. The complex C₁₂H₁₁⁺ in benzene is attributed to the addition of the C₆H₅⁺ fragment ion to a molecule of benzene.

Table 1 shows the data on these reactions and some additional processes which lead to other ions of the C₆⁻series in acrylonitrile. The ratio of the secondary and primary ion currents is compared with that of the reaction H₂O⁺ + H₂O → H₂O⁺ + OH⁻ in the last column of the table. The experimental de-

<table>
<thead>
<tr>
<th>No.</th>
<th>Secondary ion</th>
<th>Mass</th>
<th>Reaction</th>
<th>iₙ/iₚ</th>
<th>relative iₙ/iₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>H₃O⁺</td>
<td>19</td>
<td>reference reaction in water</td>
<td>2.4 • 10⁻²</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O⁺ + H₂O → H₂O⁺ + OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>C₄H₆N⁺</td>
<td>106</td>
<td>acrylonitrile</td>
<td>4.0 • 10⁻⁴</td>
<td>0.018</td>
</tr>
<tr>
<td>III</td>
<td>C₄H₆N⁺</td>
<td>105</td>
<td></td>
<td>2.0 • 10⁻⁴</td>
<td>0.009</td>
</tr>
<tr>
<td>IV</td>
<td>C₄H₆N⁺</td>
<td>103</td>
<td></td>
<td>4.0 • 10⁻⁴</td>
<td>0.018</td>
</tr>
<tr>
<td>V</td>
<td>C₄H₆N⁺</td>
<td>102</td>
<td></td>
<td>2.4 • 10⁻⁴</td>
<td>0.10</td>
</tr>
<tr>
<td>VI</td>
<td>C₄H₆N⁺</td>
<td>101</td>
<td>benzene</td>
<td>1.2 • 10⁻²</td>
<td>0.48</td>
</tr>
<tr>
<td>VII</td>
<td>C₁₂H₁₁⁺</td>
<td>155</td>
<td></td>
<td>2.4 • 10⁻³</td>
<td>0.10</td>
</tr>
<tr>
<td>VIII</td>
<td>C₁₂H₁₁⁺</td>
<td>154</td>
<td></td>
<td>3.3 • 10⁻³</td>
<td>0.14</td>
</tr>
<tr>
<td>IX</td>
<td>C₁₂H₁₀⁺</td>
<td>153</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* at 500 μ of pressure in the reservoir of the gas inlet system. Repeller field strength: 3.84 volts/cm.

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3 R. F. Pottie, R. Barker and W. H. Hamill, Radiation Res. 10, 644 [1959].
tails of these investigations have been described in the preceding communication 4 and in a former paper 5.

**Acrylonitrile**

The mass spectrum of acrylonitrile contains secondary ions at the mass numbers 101 – 106. The intensity of the ion at $m = 104$ was very low, no efforts have therefore been made to investigate its formation. Exact mass determinations occurred by using cyclopentylchloride as mass marker (parent ion peaks at $m = 104$ and 106). The parent ion $C_3H_3N^+$ is the precursor of $C_6H_6N_2^+$ and $C_6H_5N_2^+$ as can be seen from the comparison of the ionization efficiency curves in Fig. 1. The curves of $C_3H_3N^+$ are the precursors of $C_6H_6N_2^+$ and $C_6HN_2^+$, respectively. The curve of $C_6H_2N_2^+$ is in between the curves of $C_3N^+$ and $C_3HN^+$. Probably, both ions contribute to its formation.

![Fig. 1. Ionization efficiency curves of $C_3H_3N^+$ and two secondary ions in acrylonitrile. Normalization of the curves carried out for 40 volts of electron accelerating voltage.](image1)

![Fig. 2. Ionization efficiency curves of some primary and secondary ions of acrylonitrile in the $C_3^-$ and $C_6^-$-range, respectively.](image2)

![Fig. 3. Dependence of the current ratio $i_s/i_p$ of ion-molecule reactions in acrylonitrile on the repeller field strength. The reference reactions $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ and $Ar^* + H_2 \rightarrow ArH^+ + H$ are included for comparison.](image3)

The dependence of the current ratio $i_s/i_p$ of these reactions on the repeller field strength is shown by Fig. 3. The results can be described by the equation

$$i_s/i_p \propto \varepsilon^a$$

for $\varepsilon > 5$ volts/cm. The exponent $a$ has higher negative values for all reactions than the value of $-0.5$ expected for complex formation according to the polarization theory of ion-molecule reactions 6,7.

The strongest decrease of $i_s/i_p$ with increasing $\varepsilon$ is shown by reaction II (Table 1) of the complex formation. POTTIE and HAMILL also reported a strong dependence on the repeller field strength for their

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complexes. However, the exponent \( a \) for reaction II is even higher \( (a = -1.22) \) than their value of \( a = -1.0 \). As mentioned in the theoretical part of the preceding paper, part of the relative kinetic energy of the collision partners will be transferred into internal energy of the complex. Its lifetime will therefore decrease with increasing repeller field strength.

**Benzene**

The mass spectrum of benzene contains secondary ions at the mass numbers 150—156. The most intense ion in this range occurs at \( m = 155 \), \( m = 156 \) being just an isotope peak. Exact mass determination has been carried out by using diphenyl (parent ion at \( m = 154 \)) and ethyl iodide (parent ion at \( m = 156 \)) as mass markers. The \( \text{C}_6\text{H}_5^+ \) ion is the precursor of \( \text{C}_{12}\text{H}_{11}^+ \), \( \text{C}_{12}\text{H}_{10}^+ \) and \( \text{C}_{12}\text{H}_9^+ \) as can be seen from the identical form of the ionization efficiency curves in Fig. 4. Reactions VIII—X have therefore been formulated in Table 1. Fig. 5 shows that the complex formation again is most sensitive to the repeller field strength. The exponent \( a \) in equation (1) here amounts to \( -1.4 \). The higher the repeller field strength the smaller becomes the intensity of the complex ion with respect to the intensities of the \( \text{C}_{12}\text{H}_{10}^+ \) and \( \text{C}_{12}\text{H}_9^+ \) ions resulting from its dissociation.

Most interesting is the high current ratio \( i_i/i_p \) of reaction VIII at low repeller field strength. This ratio is of the same order as that of the reference reaction I (Table 1) which occurs with a cross section of more than \( 8 \times 100 \text{ Å}^2 \). The complex \( \text{C}_{12}\text{H}_{11}^+ \) must therefore be extremely stable, i.e. its lifetime is longer than the \( 10^{-6} \) seconds required for its flight through the mass spectrometer.

![Fig. 4. Ionization efficiency curves of \( \text{C}_6\text{H}_5^+ \), \( \text{C}_6\text{H}_4^+ \) and three secondary ions in benzene.](image)

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![Fig. 5. Dependence of the current ratio \( i_i/i_p \) of some ion-molecule reactions in benzene on the repeller field strength.](image)

Fig. 5. Dependence of the current ratio \( i_i/i_p \) of some ion-molecule reactions in benzene on the repeller field strength.

POTTIE and HAMIL1,2 have pointed out that the lifetime of a complex is very sensitive to its internal energy. The lifetime is considered to change discontinuously to zero at a critical value of the translational energy of the primary ion. There is a corresponding limit of the length of the track \( (l_t) \) of the primary ion (measured from the electron beam towards the exit slit) along which a viable complex can be formed. Since \( l_t \) is proportional to the reciprocal of the repeller field strength \( \varepsilon \), \( i_i/i_p \) will be proportional to \( \varepsilon^{-1.0} \) regardless of the functional dependence of the cross section on \( \varepsilon \). Since \( l_t \) is only a small portion of the total distance \( l \) between electron beam and exit slit, the ratio \( i_i/i_p \) of such short lived complexes must always be considerably lower than that of normal ion-molecules which can occur along the whole path \( l \) of the primary ion. The complex formed in acrylonitrile shows a small value of \( i_i/i_p \) (Table 1). Apart from the exponent \( a = -1.22 \), POTTIE and HAMIL1's theory therefore proves correct in this case. However, the complex in benzene shows such a high ratio of \( i_i/i_p \) that formation of the complex along the whole path \( l \) must be postulated. The observed dependence of \( i_i/i_p \) on \( \varepsilon \) therefore must be regarded here as representative of the true functional dependence of the cross section (plus lifetime) on the relative kinetic energy of the collision partners.

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