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

By Arnim Henglein

Radiation Research Laboratories, Mellon Institute, Pittsburgh, Pa., USA
and Hahn–Meitner-Institut für Kernforschung, Berlin-Wannsee, Germany

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Two persistent collision complexes between an ion and a neutral molecule have been observed in a mass spectrometer. $C_6H_6N_2^+$ (primary ion $C_3H_3N^+$) is formed in acrylonitrile, $C_{12}H_{11}^+$ (primary ion $C_6H_5^+$) 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 [1] 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^{-6} 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 [2] reported the first examples of such complexes formed by reaction of molecular halide ions with neutral halides, i. e., $C_4H_{10}I_2^+$, $C_4H_{10}Br_2^+$ and $C_6H_{14}I_2^+$. Several decomposition products of such complexes have also been found [3]. 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 $C_6H_6N_2^+$ in acrylonitrile is formed by the reaction of the parent ion with a neutral molecule as in Pottie and Hamill's reactions. The complex $C_{12}H_{11}^+$ in benzene is attributed to the addition of the $C_6H_5^+$ 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 C_6-series in acrylonitrile. The ratio of the secondary and primary ion currents is compared with that of the reaction $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ in the last column of the table. The experimental de-

No.	Secondary ion	Mass	Reaction	i_s/i_p [a]	relative i_s/i_p
			reference reaction in water		
I	H_3O^+	19	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	$2.4 \cdot 10^{-2}$	1.0
			acrylonitrile		
II	$C_6H_6N_2^+$	106	$C_3H_3N^+ + C_3H_3N \rightarrow C_6H_6N_2^+$	$4.0 \cdot 10^{-4}$	0.018
III	$C_6H_5N_2^+$	105	$C_3H_3N^+ + C_3H_3N \rightarrow C_6H_5N_2^+ + H$	$2.0 \cdot 10^{-4}$	0.009
IV	$C_6H_3N_2^+$	103	$C_3HN^+ + C_3H_3N \rightarrow C_6H_3N_2^+ + H$	$4.0 \cdot 10^{-4}$	0.018
V	$C_6H_2N_2^+$	102	$C_3N^+ + C_3H_3N \rightarrow C_6H_2N_2^+ + H$		
VI	$C_6H_2N_2^+$	102	$C_3HN^+ + C_3H_3N \rightarrow C_6H_2N_2^+ + H_2$		
VII	$C_6HN_2^+$	101	$C_3N^+ + C_3H_3N \rightarrow C_6HN_2^+ + H_2$	$2.4 \cdot 10^{-4}$	0.10
			benzene		
VIII	$C_{12}H_{11}^+$	155	$C_6H_5^+ + C_6H_6 \rightarrow C_{12}H_{11}^+$	$1.2 \cdot 10^{-2}$	0.48
IX	$C_{12}H_{10}^+$	154	$C_6H_5^+ + C_6H_6 \rightarrow C_{12}H_{10}^+ + H$	$2.4 \cdot 10^{-3}$	0.10
X	$C_{12}H_9^+$	153	$C_6H_5^+ + C_6H_6 \rightarrow C_{12}H_9^+ + H_2$	$3.3 \cdot 10^{-3}$	0.14

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

Table 1. Ion-molecule reactions in acrylonitrile and in benzene.

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1 S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York 1941.

2 R. F. Pottie and W. H. Hamill, J. Phys. Chem. **63**, 877 [1959].

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 $C_3H_3N^+$

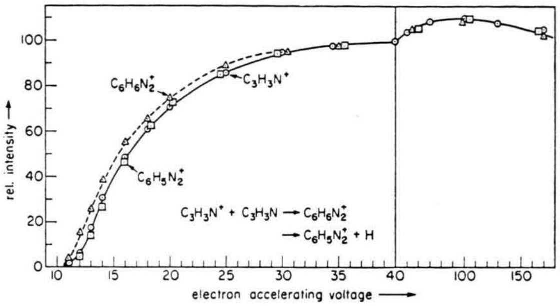

Fig. 1. Ionization efficiency curves of $C_3H_3N^+$ and two secondary ions in acrylonitrile. Normalization of the curves carried out for 40 volts of electron accelerating voltage.

and $C_6H_5N_2^+$ are identical. The complex $C_6H_6N_2^+$ has the same appearance potential. Its ionization efficiency curve, however, increases more steeply than that of $C_3H_3N^+$ especially at low voltages above the appearance potential. Although the difference between the two curves is not very great, they are believed to be real since they were reproducible. The explanation of the phenomenon may be derived from Fig. 1 in the preceding paper. A long living activated complex is only formed by the acrylonitrile ion in its ground state. If an ion with excess energy enters the reaction, the complex possesses too much internal energy and will decompose before finishing its flight in the mass spectrometer.

Fig. 2 shows the ionization efficiency curves of the other primary ions in the C_3-range and those of the ions of mass 101 – 103. C_3HN^+ and C_3N^+ apparently are the precursors of $C_6H_3N_2^+$ 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.

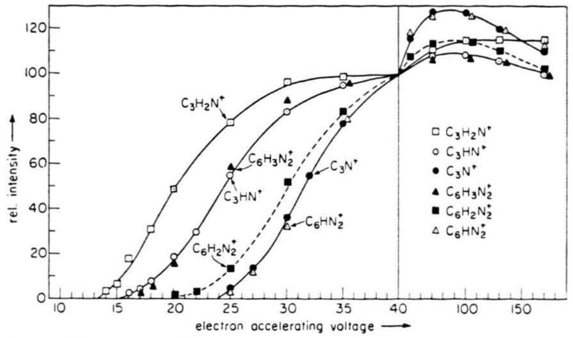

Fig. 2. Ionization efficiency curves of some primary and secondary ions of acrylonitrile in the C_3- and C_6-range, respectively.

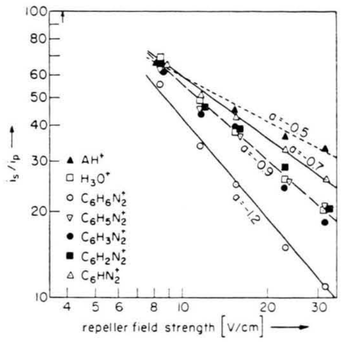

Fig. 3. Dependence of the current ratio i_s/i_p of ion-molecule reactions in acrylonitrile on the repeller field strength. The reference reactions $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ and $Ar^+ + H_2 \rightarrow ArH^+ + H$ are included for comparison.

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

$$i_s/i_p \propto \varepsilon^a \qquad (1)$$

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 ε 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

[4] A. HENGLEIN, Z. Naturforschg. **17 a**, 37 [1962], preceding paper.

[5] A. HENGLEIN and G. A. MUCCINI, Z. Naturforschg. **15 a**, 584 [1960].

[6] D. P. STEVENSON and D. O. SCHISSLER, J. Chem. Phys. **29**, 282 [1958].

[7] A. GIOUMOUSIS and D. P. STEVENSON, J. Chem. Phys. **29**, 294 [1958].

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 $C_6H_5^+$ ion is the precursor of $C_{12}H_{11}^+$, $C_{12}H_{10}^+$ and $C_{12}H_9^+$ 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 $C_{12}H_{10}^+$ and $C_{12}H_9^+$ ions resulting from its dissociation.

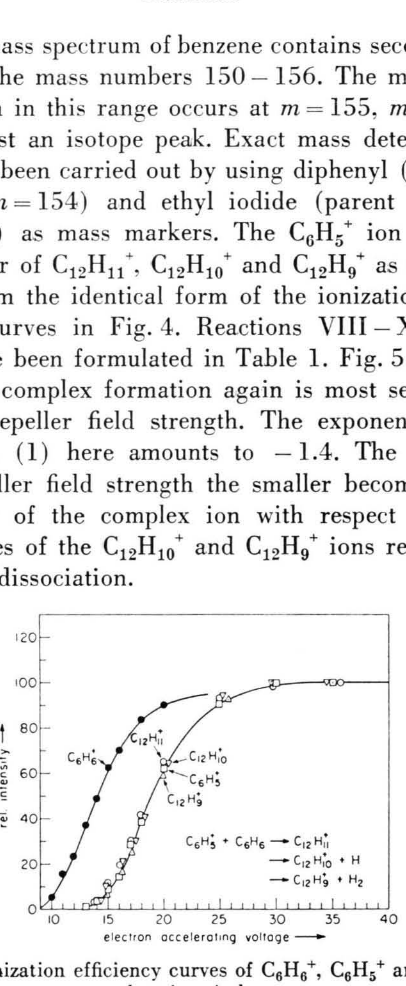

Fig. 4. Ionization efficiency curves of $C_6H_6^+$, $C_6H_5^+$ and three secondary ions in benzene.

Most interesting is the high current ratio i_s/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] 100 Å². The complex $C_{12}H_{11}^+$ must therefore be extremely stable, i. e. its lifetime is longer than the 10^{-6} seconds required for its flight through the mass spectrometer.

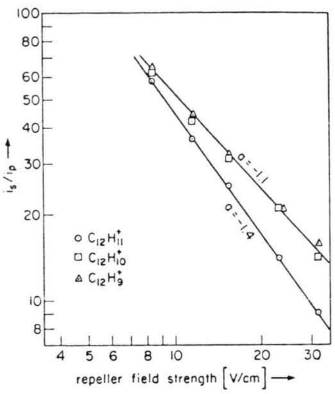

Fig. 5. Dependence of the current ratio i_s/i_p of some ion-molecule reactions in benzene on the repeller field strength.

Pottie and Hamill [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_1) of the primary ion (measured from the electron beam towards the exit slit) along which a viable complex can be formed. Since l_1 is proportional to the reciprocal of the repeller field strength ε, i_s/i_p will be proportional to $\varepsilon^{-1.0}$ regardless of the functional dependence of the cross section on ε. Since l_1 is only a small portion of the total distance l between electron beam and exit slit, the ratio i_s/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_s/i_p (Table 1). Apart from the exponent $a = -1.22$, Pottie and Hamill's theory therefore proves correct in this case. However, the complex in benzene shows such a high ratio of i_s/i_p that formation of the complex along the whole path l must be postulated. The observed dependence of i_s/i_p on ε 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.

The author wishes to thank Mr. G. K. Buzzard for his assistance in carrying out the experiments reported here.

[8] F. W. Lampe, F. H. Field and J. L. Franklin, J. Amer. Chem. Soc. 79, 6132 [1957].