DYNAMICS OF THE ION–MOLECULE REACTION $D_2O^+(NH_3, NH_2)$ HD_2O^+ FROM CROSSED-BEAM SCATTERING EXPERIMENTS

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

Dynamics of the HD_2O^+ formation in the reaction of D_2O^+ and NH_3 was investigated in a crossed-beam scattering experiment. At $T = 1.5$ eV (c.m.) the product is formed simultaneously by two different collision mechanisms, by a direct H-atom transfer and by the decomposition of an intermediate complex $(D_2O.NH_3)^+$; the probabilities of the two mechanisms are about equal at this collision energy. The scattering makes it possible to suggest that in the critical configuration the intermediate complex is a prolate, near-linear species $D_2OH^+.NH_2$.

Ion-molecule chemical reactions in which a proton or H-atom transfer takes place represent a large group of elementary ion processes. Detailed investigation of their dynamics shows that very often, together with a direct transfer of H^+ and/or H another collision mechanism is involved which leads to the formation (and subsequent decomposition) of an intermediate persistent complex. In our studies we showed[1,2] that this was the case in the system $CH_4^+ + CH_4$ and $H_2O^+ + H_2O$ (and its isotopic variants[3]). The existence and structure of these intermediate species is of interest[4-6].

In this communication we report on a crossed-beam investigation of reaction (A)

$$D_2O^+ + NH_3 \rightarrow HD_2O^+ + NH_2 \qquad (-\Delta H_R) = 1.70 \text{ eV} \qquad (A)$$

in the hyperthermal collision energy region $1-3$ eV (c.m.) $(1 \text{ eV} = 96.4868 \text{ kJ} . \text{ mol}^{-1})$. Experimental results revealed that at these energies the product is formed by two distinct mechanisms, a direct H-atom transfer, and via a decomposition of an intermediate persistent complex $(D_2O.NH_3)^+$. From the scattering data important conclusions concerning the characteristics of the complex should be made.

EXPERIMENTAL

The crossed-beam apparatus EVA II was used in these experiments. The schematics of the experimental arrangement is shown in Fig. 1. Briefly, molecular ions D_2O^+ were formed by impact of 110 eV electrons on D_2O in the ionization chamber (pressure of several Pa), the ions

were extracted and formed into a beam, mass selected at an energy of about 100 eV, and decelerated to the desired laboratory energy (2—6 eV) by a multielement electrostatic lens. The D_2O^+ beam was crossed at right angles by a beam of target molecules NH_3 of thermal energy, emerging from a multichannel jet. The ion beam had an angular spread of 1° (full-width-at-half-maximum, FWHM) and an energy spread of 0·25 eV (FWHM), the neutral beam had an angular spread of 12° (FWHM). Reaction products formed in the intersection of the two beams were detected by the detection slit, 2·5 cm from the reaction zone, subjected to the energy analysis, and registered by the multiplier of the detection mass spectrometer. To remove problems of ion collisions with background gas molecules, the reactant neutral beam was modulated by a rotating chopper and only locked-in AC signals of the ion product, originating from the reaction zone, were registered. Angular distributions were measured by pivoting the two beams about the beam intersection.

Angular distribution of the reactant and product ion, and energy profiles of the product ion at a series of eight laboratory scattering angles were measured 3—7 times. The data were treated using standard procedures[7,8] to yield product ion HD_2O^+ scattering diagrams (contours of the Cartesian probability of HD_2O^+). From those, relative differential cross sections and relative translational energy distributions were obtained in the usual way[8]. In order to obtain the relative differential cross section for the intermediate complex formation, the Cartesian probability profiles for the c.m. angles 0—90° were deconvoluted using a simple fitting procedure to provide components pertinent to the intermediate complex formation and the direct H-atom stripping, respectively.

Internal state population of D_2O^+ ions in the reactant ion beam may be estimated in the following way: the ions were formed by a 110 eV electron impact and to a good approximation
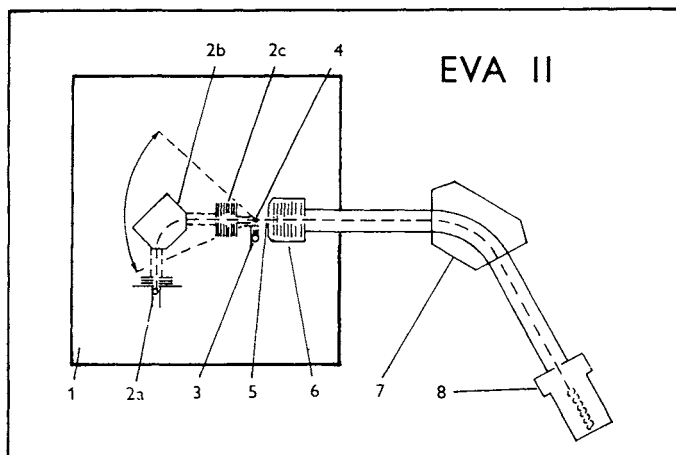

FIG. 1

Schematic diagram of the crossed-beam apparatus EVA II: **1** scattering chamber, **2a** ionization chamber, **2b** ion beam analyzing magnet, **2c** deceleration lens, **3** neutral beam source, **4** scattering zone, **5** detection slit, **6** energy analyzer, **7** detection mass spectrometer, **8** electron multiplier

the population of internal states (electronic and vibrational) may be assumed to be similar to that from photoionization experiments. Photoelectron spectra of D_2O show[9] that about 40% of the ions are primarily produced in the vibrationally ground state of the electronic ground state X^2B_2. Electronically excited states formed in the ionization event are likely to be quenched by collisions at our source pressures[10], or by radiative transitions[11] during the passage from the ion source to the reaction zone. Though the radiative transitions may increase somewhat the population of higher vibrational states of the electronic ground state, we may conclude that the beam of reactant ions in our experiments consisted of D_2O^+ mostly in the vibrationally ground state of the electronic ground state X^2B_2.

Thus we are dealing with a convenient situation, where in the total energy balance of the insulated reactive collision event, E_{TOT},

$$E_{TOT} = T + V + R + (-\Delta H_R) = T' + V' + R' \tag{1}$$

the leading quantities in the entrance channel are T (1—3 eV) and $(-\Delta H_R)$ (1·7 eV), while V and R are small or negligible. In Eq. (1) T, V, R and T', V', R' are the translational, vibrational, and rotational energies of the reactants and products, respectively: $\Delta H_R = \sum(\Delta H_f)' - \sum(\Delta H_f)$ is the reaction enthalpy; primed quantities refer to products.

RESULTS AND DISCUSSION

A scattering diagram of the ion product HD_2O^+ from reaction (A) at the collision energy of 1·5 eV (c.m.) is shown in Fig. 2. The relevant Newton diagram based on the most probable velocities of the reactants is given in the lower part of the figure. The scattering diagram shows three distinct peaks in the distribution of the product ion: the most intense, forward peak occurs at the product ion c.m. velocity expected for a direct transfer of H from NH_3 to D_2O^+ with basic features of the stripping mechanism (labelled S.S. in Fig. 2). With the increasing scattering angle the peak sharply decreases in intensity and forms a separate ridge in the forward hemisphere.

The other prominent feature in the scattering diagram are twin peaks symmetrically located on the relative velocity forward and backward with respect to the tip of the center-of-mass velocity vector. The peaks are lower in intensity than the stripping peak (maximum 30% backward and 56% forward, the latter, however, with an underlying contribution of the stripping peak tail). They occur at a lower c.m. velocity of HD_2O^+ than the stripping peak and they develop into a ridge at the c.m. scattering angles between 0° and 180°. This type of scattering is a clear manifestation that the respective part of the product ion HD_2O^+ was formed by decomposition of an intermediate complex $(D_2O.NH_3)^+$ whose lifetime was longer than several rotations of this collision species.

Thus the scattering results show that the product ion is formed at this collision energy simultaneously by two different mechanisms, by the direct stripping-type H-atom transfer, and by decomposition of an intermediate persistent complex.

The two mechanisms give rise to a doubly-peaked product translational energy distribution, $P(T')$ (Fig. 3). The peak at lower energies $(T' = 0.47$ eV) indicates

a strongly inelastic process which leaves most of the energy available $(E_{TOT} = 3 \cdot 2 \text{ eV})$ as the internal energy of the products (85% at the peak of the distribution). The peaking occurs at T' predicted by the analysis of the distribution of translational energy of products of a loose complex decomposition which includes exit centrifugal barrier considerations[12]. The second peak of the $P(T')$ curve in Fig. 3 occurs close to the position expected for a spectator stripping process (arrow denoted S.S. in Fig. 3). The shift of this peak toward lower T' is at least partly due to the underlying tail of the distribution connected with the first maximum. The product translational energy distribution curve in Fig. 3 can be used to estimate the relative weight of the two collision mechanisms: at $T = 1 \cdot 5 \text{ eV}$ the two mechanisms are about equally probable.

Fig. 4 shows the relative differential cross-section $P(\vartheta)$ obtained from the scattering diagram in Fig. 2. Open circles give the results of integration over the entire scattering diagram, full circles over the part of the scattering diagram which corresponds to the intermediate complex formation. The stripping process is thus the difference
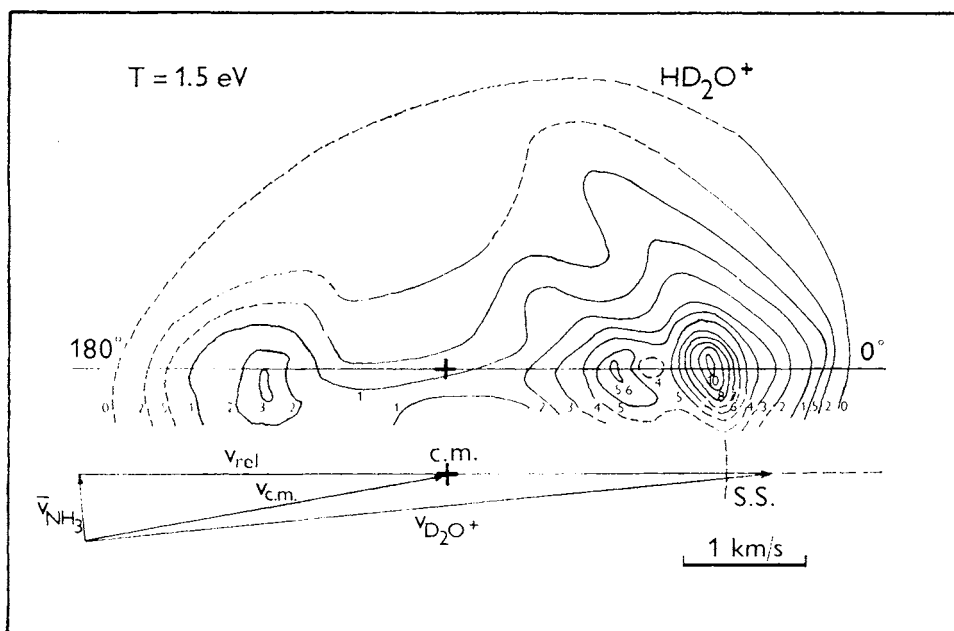

FIG. 2

Scattering diagram of HD_2O^+ from reaction (A) at $T = 1 \cdot 5 \text{ eV}$. The basic Newton diagram is shown in the lower part of the figure, SS — expected spectator stripping peak position

of the two: a sharply forward-peaked distribution with the maximum at $\vartheta = 0°$. The $P(\vartheta)$ pertinent to the complex formation is shown enlarged in Fig. 5. It shows a fairly flat part between 40° and about 140° and very sharp peaking at 0° and 180°. For comparison, the simple function $1/\sin \vartheta$ is shown in the figure by a dashed line
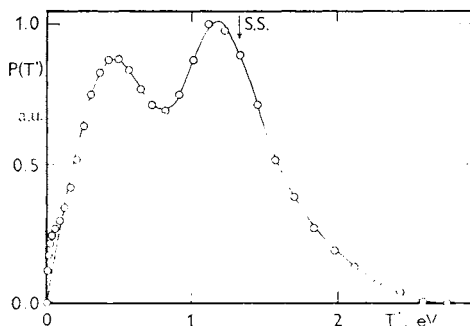

FIG. 3

Relative translational energy distribution of products of reaction (A) at $T = 1·5$ eV. SS — energy of products expected from the ideal spectator stripping model
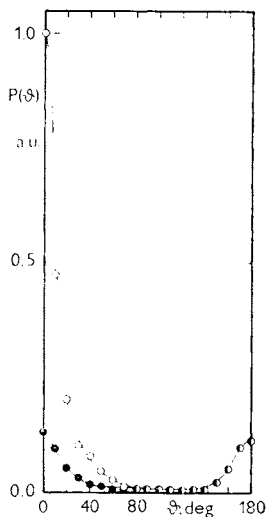

FIG. 4

Relative differential cross section of HD_2O^+ from reaction (A) at $T = 1·5$ eV. Open points — integration over the entire scattering diagram in Fig. 2, full points — integration over the part corresponding to the complex formation (see text)
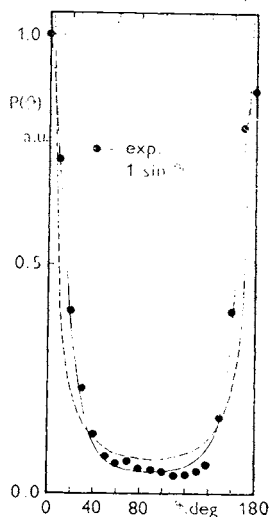

FIG. 5

Relative differential cross section of HD_2O^+ formed by the decomposition of the intermediate complex. Full points — experiment (data from Fig. 4 with the ordinate scale expanded), dashed line — function $1/\sin \vartheta$

(the two curves are normalized to the same total cross section). It can be seen that the two curves agree reasonably well in the flat area in the middle and in the sharp peaking at 0° and 180°.

It follows from the classical analysis of the intermediate complex decomposition[13] that such a sharp peaking may be expected for a rather special case of an intermediate complex dynamics. First, the total angular momentum of the complex, K_{tot}, must come mostly from the orbital angular momentum of the reactants, L, and should result mostly in the orbital angular momentum of the products, L' (the case $K_{tot} \approx L = L'$, with $J = J' \approx 0$, J, J' being rotational momenta of reactants and products, respectively[13]. Second, the complex in the critical configuration can be regarded as a very prolate top, i.e. it is expected to be practically linear. In our case, the orbital angular momenta involved in the formation of the complex from the reactants may be expected to be of the order of 100 $h/2\pi$, much larger than the thermal rotational momenta of the reactants. The scattering results imply dissociation of the critical configuration of the complex along the axis of the bonds O—H—N lying in line with a fairly large separation between the two heavy atoms. The structure of the critical configuration ought to be then $[D_2O\text{–}H\ldots NH_2]^+$. The reaction path on the potential energy hypersurface which leads to the product formation via the intermediate complex ought to be characterized by a well extending substantially into the product valley so that the intermediate species behaves still like a loose complex for interatomic separations between O and N of about 3 Å. The depth of the well which the complex experiences on the reaction hypersurface may be roughly estimated, too: because the forward-backward symmetry of the scattering pattern is fully developed even at $T = 1 \cdot 5$ eV, one may assume that the mean lifetime of the intermediate complex is larger than several rotations, and a simple RRKM estimation leads to the well depth of about 1 eV with respect to dissociation to the products.

These rough characteristics of the intermediate species will have to be further corroborated by the analysis of scattering data at a series of different collision energies. The work is in progress. Reaction (A) appears to be an interesting target for theoretical investigation of the geometry and energetics of the possible intermediate species, potential energy surfaces involved and reaction dynamics calculations.

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