REACTIONS OF IONS WITH ATOMIC AND

MOLECULAR FREE RADICALS

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MASTER

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Abstract

During the preceding contract year we have made a very detailed study of the microscopic dynamics of the reaction

over the range of relative kinetic energy from 0.001 eV to 25 eV. At very low collision energy, we find the total reaction cross section to be governed by long-range forces - principally the charge-quadrupole interaction, which favors reactions on Π -type potential energy surfaces in the covalent interaction region. At high collision energies, we observe a clear transition to reactions on a strongly repulsive potential energy surface. The change in reaction dynamics is evident from the shape of the energy dependence of the total reaction cross section, and from a shift in the product angular distribution from 0° toward 180° in the center-of-mass coordinate system.

I. RESEARCH DESCRIPTION

Our research effort during the preceding contract year has focussed on the reaction

which has not been investigated (or even observed) prior to our merged-beam studies. Previously, we had completed studies of the systems¹⁻⁴

In addition to yielding other information concerning the reaction dynamics in these previously unstudied systems, our data indicates that large fractions of the low-energy reactive collisions in these cases are electronically nonadiabatic. The electronic structure of the $H_2^+ + F$ system differs in several respects from those of the $H_2^+ + O, N, C$ systems, making a comparison of the reaction dynamics especially useful. First, the order of the energies of both the reactant and product charge states is opposite in FH_2^+ from that in XH_2^+ ($X=O, N, C$). The reactants $F^+(^3P_g) + H_2$ lie 1.99 eV above $F(^2P_u) + H_2^+$ and the products $FH^+(^2\Pi) + H$ lie 2.42 eV above $FH(^1\Sigma^+) + H^+$. In each of the other systems the lowest energy reactant and product charge states are $X^+ + H_2$ and $XH^+ + H$, respectively. The large probabilities observed^{1,2} (in violation of predictions based on the correlation diagrams) for the reactions

could be interpreted as a tendency of the reactive system to seek the lowest energy electronic state of the products even in the presence of symmetry and angular momentum constraints. In the $D_2^+ + F$ system such a tendency would

produce $DF + H^+$ products, resulting in a small probability for reaction to give the FD^+ product. Another difference in the systems is that the ground state reaction $D_2^+ + F(^2P_u) \rightarrow FD^+(^2\Pi) + D$ is only 0.79 eV exothermic. The reaction dynamics should therefore be less dominated by the exoergicity of the reaction than in the other cases studied. Finally, the interpretation of the experimental results in the $D_2^+ + F$ system is simplified because it is unnecessary to consider the possible influence of electronically excited states in the neutral atom beam. The first excited state of F lies 12.7 eV above the ground state and will therefore be produced with negligible probability in the charge exchange process.

Figure 1 shows the correlation diagram for the low-lying electronic states of FH_2^+ . In collinear approaches the reactants $F(^2P_u) + H_2^+(^2\Sigma_g^+)$ correlate through $^1\Pi$ and $^3\Pi^+$ states with the observed products $HF^+(^2\Pi) + H$, and through $^1\Sigma^+$ and $^3\Sigma^+$ states with the endothermic product channel $HF^+(^2\Sigma) + H$. The $^1\Sigma^+$ surface, however, has an avoided crossing with a $^1\Sigma^+$ surface connecting the product ground state $HF(^1\Sigma) + H^+$ with $F(^1S) + 2H^+$ at very high energy. This avoided crossing forces the $^1\Sigma^+$ intermediate to connect instead to $HF(^1\Sigma) + H^+$. Isosceles approaches of $F(^2P_u)$ to $H_2^+(^2\Sigma_g^+)$ yield $^1,^3A$, $^1,^3B$, and $^1,^3B_2$ intermediates. Through an avoided crossing the reactants correlate to the ground 1A_1 state of HFH^+ which lies 8.5 eV below the reactants in energy - an extremely deep intermediate potential well which would be expected to influence the reaction dynamics profoundly. This state correlates with $HF(^1\Sigma) + H^+$ products, however, so reactions proceeding along this path will not be observed experimentally. The $^1,^3B_1$ and $^1,^3B_2$ intermediate states are probably much higher in energy than the reactants (although the energies are not known quantitatively).

Fig. 2. Energy dependence of the total reaction cross section.

the charge-induced dipole and charge-quadrupole interactions. The electronic state correlations indicate no significant potential barrier for Π approaches, and there is also no long-range charge-quadrupole barrier. The product angular distribution at low kinetic energies shows strong forward scattering, i.e. the FD^+ emerges in the same direction as the incident F atom in c.m. coordinates. This is also consistent with reaction on a purely attractive potential surface.⁶

At high kinetic energies, an unusual feature appears in the reaction cross section for the $D_2^+ + F(^2P)$ system. The high-energy cross sections

for all of the other systems which we have examined exhibit a simple monotonic decay which is due to the onset of three-body dissociation, when the incipient product molecular ion is formed with too large an internal energy to remain bound. The cross section for the $D_2^+ + F(^2P)$ reaction, however, exhibits an inflection at a kinetic energy of about 5 eV, which appears to be due to the onset of an additional high-energy process yielding $FH^+ + H$ products. This increase in the total reaction cross section is accompanied by a shift in the product angular distribution toward a c.m. scattering angle of 180° . Both of these observations support the conclusion that, at high kinetic energies, reaction begins to occur on one or more of the repulsive potential energy surfaces which are represented schematically in Fig. 1. The three-body dissociation channel is less probable for a repulsive interaction, because much of the kinetic energy of the incident reactants is consumed in climbing the repulsive barrier, and therefore less is available to be distributed as internal energy in the very impulsive short-range part of the interaction. Backward scattering is expected for strongly repulsive interactions because of the additional centrifugal barrier which accompanies large impact parameter collisions.

The kinetic energies associated with this part of the reaction cross section are sufficiently large to permit either the $HF^+(^2\Pi)$ ground state or the $FH^+(^2\Sigma)$ first excited state to be formed. We are presently analyzing the data on the product kinetic energy distributions, which may allow us to distinguish between these two possibilities on the basis of the stability of the HF^+ product with respect to dissociation at the observed value of internal energy.

II. REFERENCES

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III. PERSONNEL

The principal investigator, W.R. Gentry, has devoted 25% time to work on this contract and will continue to contribute this same fractional effort for the remainder of the present contract period. A graduate research assistant, George Schuette, has devoted 50% time to this project since June 15, 1975, and will continue to devote 50% time to this project for the remainder of the contract period. Dr. Gregory Bearman, a postdoctoral research specialist, has devoted 100% time to this project until October 9, 1979.

IV. CONTRACT COMPLIANCE

The contractor has complied with all the administrative and scientific requirements of contract EY-76-S-02-2640.A002.