MASTER

REACTIONS OF IONS WITH ATOMIC AND

MOLECULAR FREE RADICALS

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Reactions of Ions with Atomic and Molecular Free Radicals

Abstract

A program of research has been undertaken to study the dynamics of the reactions of ions with atomic and molecular free radicals, using a merged molecular beam technique. The objectives of this research are (1) to obtain fundamental information on reaction mechanisms in reactions of species having open-shell electronic configurations, and (2) to investigate the importance of electronic nonadiabaticity in chemical reactions. During the present contract year we worked on completing our studies of the reaction

and of the complementary reactions

We also carried out some experiments on the reaction

to complement our previous work on the opposite initial charge state of the system,

Finally, as an aid in interpreting our merged-beam data at kinetic energies as low as 0.002 eV, we have performed a theoretical analysis of the differential cross sections for ion-dipole capture collisions followed by direct-mode reactions. The results indicate that shifts in the product angular distribution with a change in the reactant kinetic energy do not necessarily imply a change in the short-range reaction mechanism.

I. RESEARCH DESCRIPTION

On May 1, 1975, a DOE-sponsored program of research was begun which focuses on the reactions of ions with atomic and molecular free radicals, in order to investigate the role which the electronically adiabatic state correlations of the reactants, intermediates and products play in determining the reaction dynamics. In systems of this type the reactants approach each other on several asymptotically discrete potential energy surfaces which in general correlate with different product electronic states. By measuring the energy dependence of the total reaction cross section and the product energy and angular distributions one can, in favorable cases, obtain information on the product state distribution, the reaction probability per collision, and certain features of the effective potential energy surface on which reactions to give the observed products occur. Any inconsistency of these data with predictions based on the adiabatic state correlations indicates that nonadiabatic effects are important.

The apparatus used in this work¹ is a merged-beam instrument constructed at the University of Minnesota which enables the determination of absolute total reaction cross sections to an accuracy of ~5% over the range of relative kinetic energy from ~0.002 eV to > 20 eV. Product laboratory energy distributions may be measured with an energy resolution of 0.04% to 0.88%, yielding directly the distribution of product velocity vector components along the beam axis. A deconvolution-projection technique² can then be used to deduce from the energy distribution data several moments of the product energy and angle distributions in center of mass (c.m.) coordinates.

We have now completed our studies of the reactions

which have been described in several published reports,²⁻⁴ and in two recent review articles.^{5,6}

An important part of the data analysis for P-state atoms, such as $O(^3P)$ and $C(^3P)$, was our discovery that the atomic quadrupole moment plays an important role in determining the energy dependence of the reaction cross section at very low kinetic energies.⁷ The charge-quadrupole interaction enables one to distinguish between reactions on Σ -type potential energy surfaces and Π -type potential energy surfaces.^{3,4} During the last year we have made a considerable effort to complete the series of reactions

where X is a first-row atom, by studying the reaction

Although we had succeeded previously in obtaining some data on this reaction, we were not satisfied with the quality of the data, because the limited resolution in our Wien filter mass spectrometer did not permit complete separation of F^+ from the HF^+ contaminant in the ion beam from source A. We finally decided to solve this problem once and for all by rebuilding the Wien filter. After this was done, the resolution was more

than sufficient for these experiments. We now anticipate that the $F(^2P)$ experiments will be completed by the end of this contract year, with the data having quality comparable to our experiments with the C, N and O reactions.

In the meantime, taking advantage of the fact that our ion source produced copious amounts of HF^+ , we performed some experiments on reactions of D_2^+ with HF, which is the first system we have studied with the merged beam technique in which the neutral species has a large dipole moment. We observed three reaction channels for this system:

By far the most probable process was production of FHD^+ , which corresponds to abstraction of D^+ by HF. Qualitatively, this reaction obeys stripping dynamics, and the FHD^+ product is preferentially scattered in the direction of the incident HF reactant, even at very low kinetic energies. The strong and long-range (R^{-2}) charge-dipole potential does not result in formation of long-lived intermediate complexes, even at an energy of only 0.25 eV. It is perhaps surprising that the next most probable reaction channel is not FD_2^+ formation, which could be viewed as an abstraction of F by D_2^+ , but rather the substitution reaction which produces FD^+ .

Another reaction was investigated during the last year in order to complement our previous study of the reaction

We had observed that this reaction occurs by a direct mechanism at all kinetic energies, with the CD^+ product scattered preferentially in the direction of the C atom reactant. On the other hand, both Koski and co-workers,^{8,9} and Mahan and coworkers¹⁰ had observed that the reaction

shows a tendency toward symmetric angular distributions as the kinetic energy is lowered. The merged beam technique is capable of much lower relative kinetic energy than the methods used by Mahan and Koski, so we decided to test whether the evidence for complex formation in this system would persist if the kinetic energy were lowered even further. What we found is that even at much lower kinetic energies, the merged beam data on the reaction

continued to exhibit preferential forward-scattering of the CD^+ product. The difference between the merged-beam data and the crossed-beam data for this system may be caused by the difference in the vibrational energy of the D_2 reactant.¹¹ In the merged beam experiments, D_2 is produced by charge-exchange neutralization of D_2^+ , a process which results in considerable vibrational excitation. The crossed beam experiments were done with H_2 in the ground vibrational state. It is not surprising that vibrational excitation might result in a shorter-lived intermediate, and a more anisotropic angular distribution. We observed similar vibrational energy effects in a previous study of the endoergic reaction

in which the vibrational energy of the H_3^+ was varied by changing the ion source pressure.⁵

Consideration of the angular distributions to be expected from direct-mode ion-molecule reactions at extremely low relative kinetic energies also led us, during the last year, to a theoretical study of the influence of long-range interaction potentials on the differential cross sections for several simple models of direct chemical reactions.¹² The purpose of this study was to examine how much information about the nature of the short-range reaction dynamics can be obtained by measurements of the differential reaction cross section in the energy regime where the total reaction cross section is governed by the long-range interaction potential. The problem may be posed as follows: We know that in the absence of the long-range forces, the angular distribution of the reaction products will yield valuable microscopic information about the reaction dynamics. Simple models which have been proposed to describe extreme cases for a reaction of the type $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ are: (a) the stripping model, in which the reactant A abstracts an atom or group of atoms B from the other reactant without momentum transfer to the remaining C fragment, (b) the rebound model, in which A makes a head-on approach to BC and the AB product recoils from C in the opposite direction, and (c) the complex model, in which the ABC intermediate lives for at least several rotational periods, and decays with a statistical angular distribution. These three cases are distinguished by an AB angular distribution sharply peaked at 0° (relative to the initial A atom velocity vector) for the stripping model, an angular distribution broadly peaked at 180° for the rebound model, and an angular distribution symmetric about 90° for the complex model.

The effect of adding strongly attractive long-range forces, for collisions of low-energy reactants, is that the trajectories are deflected by significant angles even at distances too large for reaction to occur. An extreme example is the orbiting trajectory itself, which undergoes an arbitrarily large angular deflection. If one pictures the direct mechanisms (a) and (b) operating in the short-range part of the interaction, then certainly the effect of an attractive long-range force will be to blur out sharp peaks in the angular distribution. Such effects seem likely to become important whenever the potential energy well depth is much greater than the initial kinetic energy of the reactants. Indeed, it has sometimes been implied that a deep potential well is a sufficient condition for the complex mechanism (c) to hold. In this study, we asked the question: how low can one go in kinetic energy before the angular distribution information characteristic of the short-range part of the interaction is lost? To answer this question we calculated the classical cross sections for close collisions on several model potential functions, which we designed to mimick direct reactive encounters in simplistic ways. All of these potentials have a long-range behavior proportional to r^{-4} , but they differ in the short-range part. Since we wished to mimick only reactive encounters, we included contributions to the differential cross section only from impact parameters $b < b_0$.

Two of the model potential functions for which the differential cross sections were calculated are shown in Figs. 1 and 2. Fig. 1 shows a hard-core potential function, for which one may assume either (a) specular reflection from the core, or (b) reflection perpendicular to the core. This potential simulates rebound scattering. Fig. 2 shows the opposite case, a transparent-core potential which simulates stripping dynamics.

Fig. 1. Hard-core scattering models.

- (a) elastic scattering (specular reflection) from the hard-core. (b) reflection perpendicular to the hard-core surface. (c) plot of the hard-core potential function.

Fig. 2. Transparent-core scattering models.

- (a) elastic scattering trajectory. (b) straight-line trajectory leaving the constant-potential core. (c) plot of the transparent-core potential function.

Although the collision models which we considered in this study are extremely oversimplified as models of actual reactive scattering events, we believe that two valid conclusions may be drawn from the results: (1) Even at collision energies much less than the potential well depth, information on the dynamics of the short-range part of the interaction may persist in the product angular distribution despite the influence of a strong, long-range attractive potential. (2) However, it is possible for the long-range attraction to distort the angular distribution which would arise from the short-range part of the interaction alone, to the extent that a qualitative shift in the angular distribution as the kinetic energy is lowered should not necessarily be taken as evidence for a change in the reaction mechanism. If, in the case of a particular reaction, the anisotropy of the product angular distribution remains qualitatively the same as the kinetic energy is lowered into the orbiting regime, it appears to be a reasonably safe conclusion that the qualitative nature of the short-range reaction dynamics has not changed. However, when a qualitative change in the angular distribution does occur, there may be explanations for this behavior other than a change in the reaction mechanism. The most commonly observed of such changes in the product angular distribution is a shift from a highly asymmetric distribution at high energies, toward a symmetric distribution at low energies, as was the case for the crossed-beam data on $C^+ + H_2 \rightarrow CH^+ + H$ mentioned above. This is the sort of behavior which one expects if there is a strong tendency of the system in the short-range part of the potential surface to form a statistically-coupled complex, having a lifetime which increases with a decrease in the total energy of the system. Such a complex may occur in a real chemical system if there are many strongly-coupled

degrees of freedom in which the kinetic energy of the system can be dissipated temporarily. Our results demonstrate that such a complex will not occur simply because the well depth is much larger than the initial kinetic energy. Conversely, the observation of a symmetric product angular distribution does not necessarily imply either a long-lived intermediate complex, or a deep intermediate potential energy well.

It appears that one should be particularly careful about interpreting trends in the product angular distribution as a function of kinetic energy. If a symmetric distribution is observed over a large range of kinetic energy, then the evidence for a long-lived intermediate complex is relatively good. However, large qualitative changes in the angular distribution can also be caused by the influence of the long-range forces, without a change in the short-range reaction dynamics. In particular, with a decrease in the kinetic energy of collision over a limited energy range, it is possible to get a shift either away from a symmetric angular distribution (as in the case of a hard-core potential) or toward a symmetric distribution (as in the case of a transparent-core potential).

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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 since Aug. 1, 1978, and will continue to devote 100% time to this project for the remainder of the current contract period.

IV. CONTRACT COMPLIANCE

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