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**LOW ENERGY ION-MOLECULE REACTIONS
AND
CHEMIIONIZATION KINETICS**

Progress Report

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Research Accomplishments February 1, 1991 - October 1, 1991**Research Overview**

Our research program is devoted to understanding the dynamics of elementary ionic collisions at the level of the underlying potential surface by measuring energy and angular distributions of reactively scattered products with crossed beam methods over the relative center-of-mass energy range from 0.3 to several eV.

During the grant period beginning February 1, 1991, we have performed reactive and non-reactive scattering studies on the proton and hydrogen atom transfer systems listed below:

In both of these systems, the reactions are hypothesized to occur on potential energy surfaces having two minima.^{1,2} The first minimum corresponds to the formation of an electrostatically bound complex, e.g., $\text{O}^-(\text{H}_2\text{O})$, followed by an intramolecular hydrogen atom/proton transfer to yield OH^-OH , which may then form the products by cleavage of the complex.

Our work has focused on both reactive and non-reactive collisions. We have observed that non-reactive decay of the $\text{O}^-\text{H}_2\text{O}$ collision complex is the dominant channel, easily inferred from the bimodal O^- kinetic energy distributions in which the high energy component corresponds to "direct" elastic and inelastic scattering, while the low energy component corresponds to O^- ejected from the collision complex with a substantial fraction of the incident kinetic energy transferred to internal degrees of freedom of the H_2O

collision partner. We are currently comparing the kinetic energy distributions extracted from these data with the predictions of statistical phase space theory calculations.³

The reactive scattering fluxes show a very interesting energy-dependent behavior. The proton transfer reaction is endothermic, and near threshold the differential cross sections are backward-scattered, consistent with the small impact parameters expected for reaction. At slightly higher collision energies, the angular distributions are bimodal, with both a forward and backward scattered component, and increasing kinetic energy results in a strong forward scattered peak, consistent with earlier high energy collision studies by Cross and co-workers.⁴ We are currently extracting product recoil energy distributions from these data for comparison with the predictions of dynamical models.

The $\text{O}^\cdot + \text{NH}_3$ system is quite similar to the $\text{O}^\cdot + \text{H}_2\text{O}$ system in that the dominant scattering process is non-reactive decay of the $\text{O}^\cdot\text{NH}_3$ collision complex. However, the reactive scattering fluxes are quite different. We observe even at the lowest collision energies that the reactive scattering process is direct, yielding forward scattered OH products. This result is quite surprising, since the reaction is only mildly exothermic, and thus we would expect the intermediate complex to live sufficiently long to yield a significant cross section over a wide angular range. We are continuing to examine this question.

We expect the knowledge base we are acquiring on these translationally driven reactions to assist us with future experiments in which we place significant vibrational excitation into internal modes of the neutral reagent via laser excitation.

References

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3. W. J. Chesnavich and M. T. Bowers, *J. Chem. Phys.* **66**, 2306 (1977).
4. M. P. Karnett and R. J. Cross, Jr., *Chem. Phys. Lett.* **82**, 277 (1981).

Publications, February 1, 1991-January 31, 1992

J.M. Farrar, "Crossed Beam Studies of Ion-Molecule Complexes: Collisions and Clusters", in *Dynamics of Ion-Molecule Complexes*, edited by W.L. Hase, in press.

D.F. Varley, D.J. Levandier, and J.M. Farrar, "Dynamics of the Reaction of O⁻ with NH₃: Reactive and Nonreactive Decay of Collision Complexes," in preparation

D.F. Varley, D.J. Levandier, and J.M. Farrar, "Product Quantum State-Resolved Reactive Scattering in the O⁻ + H₂O system," in preparation.

Statement of Unexpended Funds

No unexpended funds are anticipated for the grant, "Low Energy Ion-Molecule Reactions and Chemiionization Kinetics", DE-FG02-88ER13849, for the period February 1, 1991 through January 31, 1992.

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