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DE-FG02-88ER13849

DOE/ER/13849-A6

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

Progress Report

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February 1, 1991- January 31, 1994

**Prepared for the U. S. Department of Energy
under Grant No. DE-FG02-88ER13849**

Date submitted: July 26, 1993

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Research Overview

Our research program is devoted to understanding the dynamics of elementary ionic collisions at the level of the underlying potential surface. We measure 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 to make the connection between energy disposal and the potential energy surface. Our work during the past three years of grant support has been directed toward understanding the dynamics elementary gas phase proton transfer reactions, particularly those of the O^- ion. Such reactions are of importance in understanding the ion chemistry of flames, but equally importantly, the dynamical insight that such studies yield with respect to correlating energy disposal pathways with potential energy surface topology are important for all reactions. Our published work over the past 30 month period has been concerned with dynamics of reactions of O^- with H_2O , NH_3 , and HF . Our accomplishments, outlined in detail below, are enumerated here.

1. We have carried out both reactive and nonreactive probes of these systems, probing both the entrance and exit channels for these systems, allowing us to assess the role of intermediate complexes in these systems.
2. Collecting both reactive and nonreactive fluxes has allowed us to apply a classical inversion algorithm to extract deflection functions for reactive and nonreactive scattering as well as opacity functions for chemical reaction. Our data are the first for which the method can be tested extensively, both over a range of collision energies and with a variety of systems.
3. These proton transfer reactions show very rapid variations in dynamical signature, *i.e.*, transitions from rebound/complex collisions to impulsive reactions, over very narrow kinetic energy ranges, as narrow as 0.2 eV. We believe such variations provide evidence for a significant resonant scattering contribution to the reactive cross sections.

4. We have provided definitive evidence for the participation of a hydrogen bonded O^-HF intermediate in the $\text{O}^- + \text{HF}$ system. The participation of such complexes has only been inferred from earlier studies that measure only product state distributions.
5. We have observed vibrationally state-resolved product differential cross sections in the $\text{O}^- + \text{HF}$ system, extending the laser based measurements of Leone and collaborators to higher energies, and allowing us to probe the nature of "induced repulsive energy release" on a potential energy surface with a deep potential energy well. This detection of product state resolved cross sections using high resolution kinetic energy measurements is a long-standing goal of ours, and has finally been met in this favorable system.

O^- Proton Transfer Reactions

The experiments reported on below have been performed using crossed ion and molecular beams, detecting the reaction products as a function of lab scattering angle and energy. The present studies represent our first attempts to examine negative ion reactions at low kinetic energies. The dynamical diversity exhibited by these systems suggests that systematic studies over a wide range of incident kinetic energies hold promise for establishing useful correlations of potential surface topology with energy disposal.

We first studied reactive and nonreactive collisions between O^- and H_2O over the collision energy range from 0.67 to 1.07 eV. The reaction between O^- and H_2O ,

is an example of an endothermic reaction in which reasonably firm evidence for an intermediate collision complex comes from ion beam-collision cell measurements of total cross sections over the collision energy range from 0.17 to 3.5 eV.¹ In our experiments,

Figure 1
Nonreactive scattering fluxes, 1.07 eV

kinetic energy analysis of the O^- scattered nonreactively from H_2O shows two components: the first arises from direct scattering and is nearly quasielastic, while the second occurs at significantly lower barycentric energies and corresponds to O^- ejected without reaction from electrostatically bound $O^- \cdot H_2O$ complexes formed by approaching reagents.

Representative data are shown in Figure 1.

This nonreactive flux is significantly more intense than the reactive OH^- flux. The

kinetic energy distributions for the low energy O^- nonreactive flux are in qualitative agreement with statistical phase space theory, although recoil distributions that model the exit channel by an r^{-4} potential underestimate the kinetic energy release.

The reactive flux distributions show a strong energy dependence. Flux distributions for OH^- production over the collision energy range from 0.67 to 1.07 eV are shown in Figure 2.

At the lowest collision energy, the OH^- is produced through two pathways, the first involving the participation of a complex living a fraction of a rotational period, the second producing OH^- strongly backward scattered and with a much broader kinetic energy distribution. With increasing collision energy, the complex contribution to the scattering falls off rapidly, and

product formation moves from the backward hemisphere to the forward direction. The

Figure 2

3D plots of polar flux intensity for $O^- + H_2O$ scattering at 0.67, 1.07 eV.

angular distribution asymmetries at the lowest collision energies can be interpreted in terms of the osculating model for chemical reactions² taking place in a fraction of a rotational period of the intermediate complex. This model suggests that the complex lifetime is ~ 250 fs at collision energies between 0.7 and 0.8 eV, a result in good agreement with RRKM calculations. The kinetic energy distributions at these energies are in good agreement with statistical phase space theory calculations.³ At the highest collision energies, still below the

threshold for impulsive stripping collisions, the OH^- product is scattered sharply forward with a broad kinetic energy distribution peaking near 0.3 eV.

The rapid change in the reaction dynamics that we observe over a relatively small collision energy change of 0.4 eV provides important insight into the nature of the potential energy surface governing this process. The endothermicity for the reaction is 0.34 eV, and the behavior we observe 0.3 eV above the reaction threshold indicates that small impact parameters yield products preferentially scattered in the backward direction. The $O^- + H_2O$ system is isoelectronic with $F + HF$, and the related $Cl + HCl$ system, extensively investigated in a number of theoretical studies, provides several interesting points for

comparison.^{4,5,6} The similar heavy-light-heavy mass combinations and the fact that hydrogen atom transfer is endothermic for both systems result in potential energy surfaces with similar exit channel characteristics and skewing angles, although the ionic system has an attractive well. A recent theoretical calculation on the $\text{Cl} + \text{HCl}$ system⁷ is particularly interesting in light of the observation that the thresholds for scattering through barycentric angles smaller than 180° increase with decreasing scattering angle. Thus, as the collision energy increases, the reactive system is able to surmount the higher barriers to yield more forward scattered products. In fact, this system demonstrates a significant broadening of the predominately backward peaked angular distribution as well as the development of a forward-scattered peak as the collision energy increases over an energy increment of only 0.2 eV. This comparison suggests that in large part, the energy dependence of the reaction dynamics is characteristic of the mass combination and concomitant potential surface skewing angle, as well as the exit channel barrier. Furthermore, the mass combination is particularly favorable for resonance contributions to the cross section,⁵ and the rapid variation in cross section may provide some initial evidence for this effect. This work, performed as part of the the Ph.D. dissertation of David Varley, now a postdoc with Paul Dagdigian at Johns Hopkins, and Dale Levandier, now a postdoc with Phil Johnson at Stony Brook, has been published in *The Journal of Chemical Physics*, **96**, 8806 (1992).

The behavior of the $\text{O}^- + \text{NH}_3$ system, studied at relative collision energies of 0.65 and 1.24 eV, presents some similarities in the nonreactive scattering, but some significant differences in the reactive scattering. We observed a significant contribution to the collision dynamics from nonreactive encounters between the reagents. In addition to elastic scattering,

we observed a direct contribution to this nonreactive scattering with a very strong angular dependence of energy transfer on scattering angle. A third contribution to nonreactive scattering arose from O^-NH_3 collision complexes that regenerate the reactants. In these collisions, approximately 80% of the incident translational energy is transformed into vibrational-rotational excitation of the NH_3 reagent. The kinetic energy distribution is in reasonable agreement with statistical phase space theory calculations.

We also observed reactive collisions in this system. The hydrogen atom transfer process to yield $\text{OH}^\cdot$ is exothermic by 0.11 eV and exhibits direct dynamics at all collision energies. Proton transfer to form NH_2^+ , endothermic by 0.9 eV, was studied as its deuterium analog and was observed only at the higher collision energy, and took place with very small cross section. The product kinetic energy distributions for the hydrogen atom transfer reaction approach a Gaussian form at the higher collision energy, and we ascribe that behavior to the impulsive nature of reactive collisions in which the ground state vibrational wavefunction of the N-H bond to be broken is reflected onto product translational energy states through the "corner" of the potential energy surface. Such a Franck-Condon picture of the reaction is a consequence of the highly skewed potential energy surface associated with the heavy-light-heavy mass combination. This work was also performed by Varley and Levandier, and has appeared in *The Journal of Chemical Physics*, **97**, 4008 (1992).

State-Resolved Proton Transfer Reaction Dynamics

The field of chemical reaction dynamics has clearly defined its dominant direction toward laser-based determinations of product state distributions and state-to-state chemistry.

While these technologies and others have had some impact on the study of ions, particularly positive ions, negative ion reaction dynamics remain an area where little is known about reactivity and energy disposal. Low signal levels often preclude the application of laser based detection schemes to such systems, although Leone and collaborators have applied laser induced fluorescence (LIF) to a selected number of systems that produce OH.⁸ Although the observation of product states provides significant dynamical detail, the absence of angular information limits the ability of the data to illuminate the role of transient complexes in the collision process.

In our study of this system, we present the angular and kinetic energy distributions for the products of the proton transfer reaction

$\text{O}^- + \text{HF} \rightarrow \text{OH} + \text{F}^-$ at a center of mass collision energy of 40.5 kJ mol^{-1} (0.42 eV).

The angular distribution shows clear forward-backward symmetry for the formation of products, indicating that the reaction proceeds through a transient $[\text{OHF}]^-$ complex living several rotational periods. This is the first direct experimental evidence for the participation of a complex in this reaction. The experimental data of Figure 3 show clear structure associated with the formation of OH with quantum numbers

Figure 3
 F^- fluxes from $\text{O}^- + \text{HF}$ reaction, showing structure from OH in $v'=0, 1$, and 2.

$v'=0, 1$, and 2. The flux map shown in Figure 4 shows reasonable symmetry about $\pi/2$, providing direct evidence for complex participation. Approximately 40% of the OH reaction products are formed in $v'=1$. This value is consistent with drift tube studies at lower collision energies in which increasing reagent translational energy transforms preferentially into product vibration. Such energy partitioning is consistent with the argument that mixed energy release in the **Heavy + Light-Heavy** mass combination is induced by the strong electrostatic attraction of the reactants. This work, performed with David Varley, Dale Levandier, and Mike Carpenter, has appeared recently in *The Journal of Chemical Physics*, 99, 148 (1993).

More recent experiments at higher collision energy (0.61 eV, 59 kJ mol⁻¹) demonstrate conclusively that incremental translational energy begins to partition into product *translation* as the system is able to access the repulsive wall of the potential surface. This work, done by graduate student Mike Carpenter and undergraduate Martin Zanni, demonstrates that product formation in this system still proceeds through a long-lived collision complex, but that the forward scattered component has a significant contribution from stripping-like collisions. The data show clearly that the OH

Figure 4
F⁻ 3D flux distribution, O⁻ + HF at 0.42 eV

product rotational excitation, evidenced by the widths of the individual vibrational state cross section contributions, is much lower for these stripping collisions than for products formed by a long-lived complex that disposes larger amounts of angular momentum.

In Figure 5, we compare the population of $v'=1$ in OH as a function of the energy in excess of the $v'=1$ threshold for the hyperthermal LIF experiments of Leone *et al.* and our

Figure 5

Population in OH($v'=1$) vs. total energy in excess of $v'=1$ threshold.

(○) Data of Ref. 8. (●) This work.

experiments conducted at higher kinetic energies. The LIF experiments fit a straight line, consistent with partitioning excess translation in product vibration, as expected from mixed energy release. In contrast, our higher energy experiments show that incremental translation begins to move out of this state, consistent with the concept of induced repulsive energy release as the system begins to access new regions of the potential surface, in this case the low energy

repulsive wall. This work is being prepared for publication in a special issue of *The Canadian Journal of Chemistry* in honor of John Polanyi's 65th birthday.

These experiments represent the first from our lab in which we have been able to perform product state resolved differential cross section measurements. The complementarity of these measurements with other experimental techniques makes the $O^- + HF$ system one of the best-studied anion-neutral systems and provides both a bench mark and a challenge to

theory. A significant part of the work we propose for the next grant period will be concerned with state-resolved measurements of this sort.

Classical Inversion of Reactive Collision Data

From a classical point of view, a particularly useful representation of chemical reaction dynamics comes from correlating reactivity with impact parameter and scattering angle. The so-called "opacity function" for chemical reaction, $P(b)$, represents the reaction probability as a function of impact parameter b . The optical model for collisions extracts an opacity function by analyzing both reactive and nonreactive collisions, and attributing the deficit in wide angle scattering to chemical reaction. This model has been used extensively, most recently in the context of Penning and associative ionization reactions. An example of particular significance for us is the collisional ionization work on $\text{Ne}^+ + \text{HCl}$, yielding $\text{HCl}^+ + \text{Ne}$ and $\text{NeH}^+ + \text{Cl}$ through chemical reaction occurring in a nascent NeHCl^+ complex formed by associative ionization. We have been involved with these studies through a NATO Collaborative Research Grant with Professor Franco Vecchiocattivi of the University of Perugia in Italy. In this work, a local complex optical potential of the form

$$V(R) = U(R) - \frac{1}{2} i \Gamma(R)$$

has been used to describe both nonreactive and reactive scattering, and the parameters of the potential have been fitted through the partial wave expansion to the experimental data.⁹

In our own work, we have used another approach developed by Gilbert¹⁰ that does not involve any assumptions about the interaction potential. The method exploits the fact that for

each collision system, we measure a complete set of cross sections for nonreactive (elastic and inelastic) and reactive scattering. The classical differential cross section for a realistic potential with both attractive long range and repulsive short range behavior is expressed as follows:

$$I(\theta) = \sum_{i=1}^3 \frac{b_i P(b_i)}{\sin \theta} \left| \frac{d\theta}{db} \right|^{-1}$$

where b_i is the impact parameter for a given branch, $P(b_i)$ is the opacity for that impact parameter, and $d\theta/db$ is the derivative of the classical deflection function $\Theta(b)$.

For a single branch deflection function $\Theta(b)$, this expression reduces to a single term and the opacity function $P(b)$ can be extracted from the differential cross section uniquely. In the Gilbert method, one relies on the unitarity of the sum of inelastic and reactive scattering. When only two channels are open the fraction of flux that is nonreactive scattering must be $(1 - I_{\text{reactive}})$. This condition gives two separate expressions for the reactive opacity functions, one related to reactive cross sections and one related to nonreactive cross sections. These expressions are summarized below:

$$P_{\alpha}(b) = \frac{d\sigma_{\alpha}}{d\omega} \frac{\sin |\theta| \left| d\Theta_{\alpha}/db \right|^{-1}}{b}$$

$$P'_{\alpha}(b) = 1 - P_{00}(b) \frac{d\sigma_{00}}{d\omega} \frac{\sin |\theta| \left| d\Theta_{00}/db \right|^{-1}}{b}$$

The index "0r" refers to reactive scattering, while the index "00" refers to the inelastic channels. By choosing suitable parametric forms of the deflection function, the standard deviation D between P'_{0r} and P'_{00} can be minimized by a pointwise nonlinear least squares

$$D = \sum_k |P_{\alpha}(b_k) - P'_{\alpha}(b_k)|^2$$

algorithm. We have used the general parametric form shown below for Θ_{0c} to construct the reactive ($c=r$) and inelastic ($c=0$) opacity functions that minimize D .

$$\theta_{0c}(b) = \pi e^{-\alpha b} \frac{\cos(\beta b + \gamma)}{\cos \gamma}$$

Figure 6

Reactive and nonreactive single-branch deflection functions and opacity for high energy $O^- + H_2O$

The direct minimization relies on the existence of a one-to-one correspondence between impact parameter and scattering angle. This direct minimization worked exceptionally well for systems that were not thought to proceed through a long lived collision complex, e.g., $O^- + NH_3$ and $O^- + H_2O$ at the two highest collision energies. In Figure 6, we show the results of the inversion on the $O^- + H_2O$ system at a collision energy of 0.94 eV, where the scattering is dominated by stripping collisions. The deflection

functions for both nonreactive and reactive scattering show single branches, while the

opacity function falls off beyond $1.5 \text{ \AA}$, indicative of the range of the potential for stripping collisions.

When more than one impact parameter contributes to the scattering at any angle, the

problem becomes more complex. We have begun to investigate inversion methods using multi-branched deflection functions. The approach we follow involves choice of analytical functional forms for both the deflection and opacity functions, the latter described as follows:

$$P(b) = \frac{1}{1 + \exp [-(b - b_c) / \zeta]}$$

This function has the appearance of a Fermi distribution, with the falloff of the distribution from its maximum occurring over a range of width ζ about the impact parameter b_c . The method allows for a maximum of three impact parameters to contribute to the scattering at any one angle and is equivalent to a nonlinear least squares fitting routine with the parametric forms of the opacity and deflection functions varied to minimize the quantity D :

$$D = \frac{1}{n} \sum_{0,r} \sum_j^n | I(\theta_n)_{\text{exp}} - I(\theta_n)_{\text{calc}} |^2$$

We note that the calculated reactive cross section is given as follows:

$$I(\theta_j)_{\text{calc}} = \sum_{i=1}^3 b_{ij} P(b_{ij}) \left| \frac{d\theta_{\alpha}(b_{ij})}{db} \right|^{-1}$$

Results for the $O^- + H_2O$ system at the lowest collision energy, 0.67 eV, are shown below:

Recall that at the lowest energies, the reaction has both complex and low impact parameter rebound components, while the latter channel disappears at the higher collision energy.

Comparison of Figure 7 with Figure 6 shows that the inversion recovers that phenomenon.

The inversion work is in a very preliminary stage. Our motivation in pursuing this approach arises from the fact that we have the unique ability to probe both reactive and nonreactive collisions over essentially the full range of scattering angles and recoil speeds. In

Figure 7

Reactive and nonreactive deflection functions, and opacity functions for the $O^- + H_2O$ systems

applying these inversion methods to our data, we are subjecting the model to extensive testing

because our data exemplify both complex and direct dynamics, showing clear transitions from one regime to the other. In addition, the data

show evidence for nonreactive scattering that proceeds through a complex, while the reactive collisions appear to proceed as direct processes.

We need to introduce more flexible forms for the deflection and opacity functions. We also need to account for orbiting collisions more correctly,

allowing deflection functions to have attractive branches extending beyond π . At present, our

models apply only to the angular distributions, and we must develop methods to extend inversions methods to the energy-resolved data of our experiments. There are no literature precedents for such procedures, and our initial attempts will be phenomenological.

Summary

The experimental work we have performed represents the highest resolution studies of chemical reaction of anions with molecular collision partners performed to date. The experiments have shown a wide variety of dynamical signatures from low impact rebound collisions at low kinetic energies, through complex formation, and then finally through

stripping collisions that sample the repulsive wall of the potential surface. Product state-resolved work in the $O^- + HF$ system has yielded cross sections for which comparison with detailed quantum scattering theory computed on realistic potential surfaces should be possible. Nonreactive scattering studies have probed the entrance channels and collision complex regions of the potential surface. The studies represent a comprehensive probe of potential energy surfaces over a wide collision energy range and complement spectroscopic approaches to reaction dynamics at thermal energies. Finally, the application and development of a classical inversion technique, uniquely applicable to our simultaneous measurements of reactive and nonreactive scattering, holds great promise for extracting information on reaction opacities, refining our picture of what parts of the potential surface are important in governing reactivity.

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