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LOW ENERGY ION-MOLECULE REACTION DYNAMICS
AND
CHEMIIONIZATION KINETICS

Progress Report

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Abstract

A crossed molecular beam apparatus for the study of low energy ion-molecule reactions and free-radical chemiionization kinetics has been constructed and its initial work has been in the study of reactions of $\text{H}_2^+ + \text{CO}$, N_2 , and Ar at energies between 5 and 10 eV. The preliminary results we have obtained indicate that in the energy range studied, the reactions proceed via impulsive, direct collisions. The molecular ion products are scattered in the backward direction with respect to the incoming H_2^+ projectile with translational energy in excess of that predicted by spectator stripping.

We have also completed construction of a discharge ion-source with a sample vaporization compartment, allowing solids and liquids to be used as source materials. This source will be used to prepare HCO^+ beams for studies of reactions such as

considered important in hydrocarbon flames.

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Introduction

Since the initiation of our contract with the Department of Energy in February, 1978 we have focused attention on molecular collision studies, with emphasis on the proton-transfer reactions of H_2^+ with CO, N_2 , and Ar. Aside from the teaching responsibilities associated with the Principal Investigator's appointment in the Department of Chemistry at the University of Rochester, the research supported by DOE in this contract occupies the full effort of the Principal Investigator. The same commitment of time will hold for the remainder of the contract year terminating January 31, 1978. A reasonable estimate of the percentage of the Principle Investigator's time which is expended in carrying out the research is 75%.

Our initial proposal to DOE outlined a program in ion-molecule chemistry and chemiionization kinetics of atomic and free-radical species. Our intent has been to establish an active program in ion-molecule chemistry in which the operating parameters of our crossed molecular beam apparatus are well-established and we have an opportunity to study the reaction dynamics of a class of proton-transfer reactions not studied before by beam techniques. The ion-molecule chemistry which we are studying involves proton-transfer reactions, some of which will provide a prelude to studies of model systems considered important in combustion systems. We shall discuss these systems later in some detail.

The chemiionization systems which we proposed to study involve

reactions of CH radicals, with particular emphasis on the reactions

The rather complicated chemistry associated with production of CH radicals is still in an unsatisfactory state and consequently, we proposed to use ionic precursors for generating CH radicals. Because of the small number of bound states of molecular anions, coupled with the recent work of Lineberger¹ on CH^- , we proposed a scheme in which photodetachment of the electron from CH^- was used to prepare electronically state-selected beams of CH. By use of a laser operating near 7000 Å, $CH(^2\Pi)$ can be produced, whereas photodetachment with the 4880 Å line of an argon ion laser generates a beam of $CH(^2\Pi) + CH(^4\Sigma^-)$. The technique then should allow a measurement of the associative ionization cross sections of $O+CH$ as desired, as a function of the electronic state of CH. Such experiments will answer long-standing questions regarding the necessity of electronically excited CH in promoting the well-known reaction of $O+CH$.

In addition to developing an apparatus with ultimate capabilities to produce intense beams of CH^- for preparation of CH, we have also initiated our experimental program in ion-molecule chemistry with the idea in mind that ion-molecule reactions are inherently interesting to study because they provide excellent systems for examining molecular collision dynamics involving several strongly-coupled potential energy surfaces. In addition to this fundamental reason for examining ion-molecule reactions, we are also aware of

interesting ionic processes which occur in hydrocarbon flames. We can study these processes under well-controlled circumstances in the laboratory.

It is well-known that the primary chemion in hydrocarbon flames is the HCO^+ species² and the reaction $\text{O} + \text{CH}$ has been hypothesized to account for its presence.³ Another well-known fact is that the primary ion in hydrocarbon flames is H_3O^+ and its presence is hypothesized to involve the proton transfer reaction⁴

In the multiple context that ion-molecule reactions are valuable probes of the multisurface problem in chemical kinetics, are important in hydrocarbon flames, and the technology for studying them provides an important precursor for some free-radical chemiionization reactions, we have embarked on a program of study in this area of chemical kinetics.

Many previous studies of ion-molecule reactions have involved reactions of the type $\text{X}^+ + \text{H}_2 \rightarrow \text{HX}^+ + \text{H}$ and much has been learned from these studies.^{5,6} With the exception of ICR studies of charge-exchanged reactants, $\text{X} + \text{H}_2^+$, and several beam studies of the reaction $\text{H}_2^+ + \text{He}$ ^{7,8}, little has been done on the systems $\text{X} + \text{H}_2^+$, where X is an atom or a diatomic molecule.

With these facts in mind, we fabricated a general purpose beam apparatus with capabilities of delivering 10^{-9} amp of H_2^+ ions at energies as low as 1 eV. The apparatus is equipped with

a doubly-differentially pumped supersonic neutral beam source which is appropriate for producing "seeded beams" of heavy atoms or molecules. Because proton transfer reactions from H_2^+ to heavier atoms and molecules involve a kinematic situation in which the centroid of the system points near the neutral beam direction with a speed comparable to the neutral beam molecule, one must use accelerated beams of neutral species. In essence, the laboratory energy of products "follows" the centroid speed and a thermal beam of neutrals leads to thermal energy ions.

This problem has been overcome to a large extent through the use of a "seeded beam", in which atoms or molecules of the desired neutral species are mixed with a great excess of a light carrier gas such as H_2 or He. All species attain the same terminal velocity which is governed by the average mass of the mixture and is generally close to the mass of the light diluent gas.

In addition to beam sources ideally suited for the production of ionic and neutral species for chemical reaction studies, the apparatus is equipped with a rotatable lid on which an electrostatic energy analyzer-quadrupole mass spectrometer detection train is mounted. Product detection can thus be performed as a function of mass, energy, and scattering angle.

A significant part of our experimental effort in the last several months has been focused upon interfacing this device to our lab minicomputer. With the signal averaging capabilities afforded by this system, our apparatus is capable of single particle detec-

tion in the energy range from 0.5 eV to ~100 eV.

We have made progress recently in studying the reactions $\text{H}_2^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}$, $\text{H}_2^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$, and $\text{H}_2^+ + \text{Ar}$ in the energy region between 5 and 10 eV. In these studies, a unifying feature of the reactive scattering has appeared which leads to some rather interesting questions. In the cases of the three reactions which have been studied over a fairly narrow energy range, we find that the reactions are all ultra-direct, with collision times lasting a very small fraction of a rotational period.

A common observation in ion-molecule systems in which direct reactions are found is the so-called "spectator stripping" mechanism. This mechanism suggests that when an atom is transferred from reactant to product, the atom or molecular fragment which remains after the transfer has the same barycentric velocity as its precursor reactant molecule. In the case of H_2^+ scattering, the "spectator" is a hydrogen atom and a stripping mechanism indicates that reaction products should be formed in the backward hemisphere with respect to the incoming H_2^+ projectile.

In fact, we do observe that the reaction involves a stripping mechanism, but that the product molecular ion is formed with translational energy much in excess of the spectator stripping limit. This result is rather unusual because, in general, spectator stripping represents a limit such that as collision energies are raised, the internal energy of the molecular product eventually exceeds a dissociation limit and the product is unstable.

However, another interesting factor in the formation of these highly translationally excited fragments may involve the rather high vibrational excitation of H_2^+ produced by electron impact. Franck-Condon factors suggest that a substantial fraction of H_2^+ ions produced by electron impact are in high vibrational states with $v \geq 3$. Vibrational motion of H_2^+ may effectively become motion of relative translation of the products. Consequently, the role of reactant excitation must be elucidated; we have proposed the use of a method⁹ for quenching $\text{H}_2^+(v \geq 2)$ which will give us an assessment of this effect in the reaction dynamics. This study plus others, particularly at lower collision energies, will be a major focus of our work in the coming year.

The observation and detailed study of reactive scattering in H_2^+ systems is significant because it marks the first crossed molecular beam experiments (with the exception of $\text{H}_2^+ + \text{H}_2$ and He) in which reactive scattering measurements have been made with the simplest molecular ion. Such studies will hopefully become "benchmark" studies to which theoreticians will make comparisons in their attempts to improve models of chemically reactive systems, particularly in multistate systems.

The reactions of HCO^+ with neutral species, particularly H_2O , are postulated to be of importance in hydrocarbon flames. We have, within the past few months, completed a discharge ion source with a heatable reservoir which will allow us to produce HCO^+ beams by discharge ionization of H_2CO . With this source and our neutral

source for the production of H_2O beams, we will be able to study the proton transfer reaction of HCO^+ with H_2O .

In summary, our research has begun in the direction of ion-molecule reaction dynamics. The characteristics of our apparatus have been well-established and we have begun fruitful work on H_2^+ reactions, with initial efforts toward HCO^+ studies as well. The apparatus functions as we have hoped and its use in chemiionization studies and related problems is assured.

The work described in this progress report is not yet complete. Because of this, no publications have yet been prepared. We expect that our data, as well as data to be collected in the next few months to be in publishable form within the next contract year.

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