Studies in Radiation and Hot Atom Chemistry

Progress Report

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Abstract

The ion-molecule reactions of $F^+(^3P)$ and $F^+(^1D)$ with H_2 , D_2 and HD were studied over an energy range from a few eV to 40 - 100 eV in the laboratory system. Likewise the charge transfer reactions of $F^+(Ne,F)Ne^+$ were examined for the two electronic states of F^+ . The exoergicity of the $F^+(D_2,D)FD^+$ reaction was determined. The charge distribution of ^{13}N ions arising from the reaction $^{12}C(d,n)^{13}N$ was measured for deuteron energies of 8, 10 and 14 MeV. With $30 \mu g/cm^2$ carbon foils essentially an equilibrium charge distribution was observed. Departures from equilibrium were observed with foils of $16.3 \mu g/cm^2$ thickness and 10 MeV deuterons.

Beam attenuation studies of B^+ produced by electron fragmentation of boron trihalides showed that when BF_3 was used as a target molecule 35% ^3P state and 65% ^1S state was produced. BI_3 , on the other hand, gave only ground state B^+ . The results were consistent with reactions of B^+ with N_2O .

Pair production was observed in the electron fragmentation of CF_4 and evidence for F^{--} as a product was found in fragmentation of CF_3Cl .

Progress Report

Introduction

This report is a summary of progress made in radiation and hot atom chemistry program in the Department of Chemistry at The Johns Hopkins University for the research period 1973-74, under contract AT(11-1)-3283. Under the category of hot atom and their precursor reactions we have made progress in measuring the cross section and isotope effect of F^+ with molecular hydrogen. Some reactions of the ground and first excited states of F^+ were studied. In addition, preliminary studies of the distribution of the charge states of ^{13}N produced from the reaction $^{12}C(d,n)^{13}N$. Under the radiation chemistry studies the electron fragmentation of the boron trihalides, of CF_4 and some highly preliminary studies of CF_3Cl are reported. Of course, it is realized there is no sharp line of demarcation between these two categories and a considerable amount of overlap exists.

I. Hot Atom Studies

The relevance behind these hot atom studies is the fact that associated with chemical reactions immediately following nuclear transformation, either an ion is directly involved or is a precursor to the neutral hot species that leads to the final chemical product. In order to get a better insight into the nature of such processes the reactions of ions with molecules are being studied in a systematic way. Since many hot atom studies in the past have involved fluorine we are examining reactions of F^+ with simple molecules. In addition, attention was given to the role played by excited states and reactions of F^+ in the ground state (^3P) and in the first excited state (^1D) were examined.

The composition of the F^+ ion beam was determined by examining its attenuation in Ne as a function of the gas pressure. In addition to cross section measurement the kinematics and the angular and energy distribution of the ionic fragments were measured.

Over the years the hot atom chemistry of ^{13}N produced by $^{12}C(d,n)^{13}N$ reaction has been studied in a number of laboratories. At this time we are making a report on the charge distribution of the ^{13}N recoils using 8, 10 and 14 MeV deuterons.

a. Cross Section and Isotope Effect in the Reaction of F^+ with Molecular Hydrogen.

The ion-molecule reactions of $F^+(^3P)$ and $F^+(^1D)$ with H_2 , D_2 and HD were studied over an energy range from a few eV to 40-100 eV in the laboratory system. The charge transfer reactions of $F^+(Ne,F)Ne^+$ were also examined for the two states. The cross section behavior and isotope effects were similar to those reported for the much studied reaction $Ar^+(H_2,H)ArH^+$. The cross sectional behavior of this reaction in the higher energy region indicated that the reaction proceeded by a direct mechanism. No unambiguous conclusions could be drawn about reaction mechanism in the region below about 6 eV in the laboratory system. The published results of this study will appear in the Journal of Chemical Physics in the near future.

b. Kinematics of the Reaction $F^+(D_2,D)FD^+$.

In studying the cross section of a reaction as a function of ion kinetic energy one gets no information on the internal energy residing in the product ion or of the kinetic energy possessed by the products. Since the fate of these products in radiation chemical and hot atom

chemical processes is frequently decided by such factors we have examined the kinematics of the $F^+(D_2,D)FD^+$ reaction. In this study the kinetic energy is measured at zero degrees to the projectile ion beam. From these measurements one then could compute Q , the exoergicity (difference between kinetic energy of reactants and products). For ground state reactants and products this reaction, i.e. $F^+(D_2,D)FD^+$ is exothermic by 3 eV and the values of Q indicate that a significant amount of the heat of the reaction goes into translational energy of the products. At 2 eV laboratory energy the value of Q corresponds to what would be expected if the reaction was going through complex formation. At higher energies, i.e. 5 eV the reaction appears to be going by some direct mechanism.

c. Dynamics of the $F^+(D_2,D)FD^+$ Reaction.

In this investigation we studied the angular and energy distribution of the FD^+ products. At 1 eV and 2 eV the FD^+ product showed a high degree of symmetry about the center of mass indicating complex formation. At 5 eV the FD^+ distribution was well forward of the center of mass indicating a direct mechanism. A few more measurements will have to be made on this reaction and the spin, symmetry and molecular orbital correlations, which will be valuable in interpreting the results, will be made and these results coupled with the kinematic results will be submitted for publication.

d. Charge States of ^{13}N from the $^{12}C(d,n)^{13}N$ Reaction.

In our studies of the hot atom chemistry of ^{13}N produced from the reaction $^{12}C(d,n)^{13}N$ we found that when the recoils were permitted to interact with a organic molecule such as CH_4 the main products formed

were HCN and CH_3CN . At the time of nuclear transformation one would expect that the ^{13}N is formed as a multiple positive ion and it was of interest to us to determine what this charge distribution was. Two types of charge distribution should be considered. The non-equilibrium charge distribution can only be expected when thin enough target foils are used so that the charge distribution is characteristic of the nuclear reaction and the initial charge distribution is not altered by electron pick-up etc. from the target atoms. The equilibrium charge distribution is one that is expected if the recoils make a number of collisions with the target atoms and equilibrium charged distribution of the recoils characteristic of type of foil, energy of recoils, thickness of foil is produced.

In our experimental set up deuterons from the U.S. Army Edgewood Arsenal tandem accelerators were permitted to impinge on self supporting graphite foils. The resulting ^{13}N recoils were collimated and deflected in a magnetic field and then caught on a tantulum catcher foil the activity of which was determined by scanning with a Geiger counter. Peaks of activity on the foil could readily be assigned to ^{13}N of various charges. Unfortunately the work was not completed since the Army closed down the accelerator. However, measurements were realized at 8, 10 and 14 MeV deuterons and are tabulated below.

<u>Deuteron Energy</u>	<u>^{13}N Charge</u>	<u>Fi 30 $\mu\text{g}/\text{cm}^2$ foil (Y)</u>	<u>Equilibrium Charge Distribution</u>	<u>Fi 16.3 $\mu\text{g}/\text{cm}^2$(A)</u>
8	2	.190	.115	
	3	.397	.432	
	4	.330	.383	
	5	.083	.069	
10	2	.083	.045	.094
	3	.317	.322	.193
	4	.439	.494	.385
	5	.162	.140	.328
14	3	.176	.151	
	4	.462	.523	
	5	.362	.326	

Fi is the fractional charge distribution. The equilibrium charge distribution was obtained from published results in which charged ^{14}N particles passed through graphite foils of varying thicknesses and the resulting charge distribution was measured. Y designates foils obtained from an Israeli source and A represents foils obtained from an Arizona source. It is clear our 30 $\mu\text{g}/\text{cm}^2$ foils give essentially an equilibrium distribution of charges. It was not until we reached a foil thickness of 16.3 $\mu\text{g}/\text{cm}^2$ that departures from equilibrium 10 MeV deuterons began to appear. It would have been desirable to go to smaller thickness foils, however, the shut down of the accelerator terminated the experiments. Difficulty was being experienced with the signal to noise level since as the foil thickness was decreased less activity was produced. Very likely to go to thinner foils a revamping of the experimental arrangement

would be necessary.

II. Radiation Chemical Studies

When high energy radiation interacts with matter, electrons and photons are emitted by various mechanisms. As these electrons are slowed down they lead to a variety of chemical reactions and excitation through electron attachment, dissociative electron attachment and ion pair processes. The study of these elementary steps and the chemical intermediates involved is pertinent to an understanding of radiation chemistry. In general, when electrons interact with molecules to produce positive ions, excited as well as ground state ions are produced. A considerable amount of interest has been exhibited by radiation chemists in the role played by excited states although very little work has been done in this area. We are therefore attempting to compare reactions of ground state ions and those in excited states that arise from electron bombarding processes.

a. Electronic States of B^+ Produced by Electron Bombardment of Boron Trihalides.

Beam attenuation studies of B^+ as a function of attenuating gas pressure shows that the beam has a composition of 35% ^3P and 65% ^1S when produced by 70 eV electrons from BF_3 . As one proceeds in the series from BF_3 to BI_3 , the amount of excited state varies in a regular manner and B^+ ions are completely in the ground state when BI_3 is used as a target. The composition of the beam could also be varied by varying the electron energy.

The results of the attenuation studies were also confirmed by studying the cross section vs. beam energy curves for the $B^+(^1S)$ and $B^+(^3P)$ reactions with N_2O .

This material has been published in the Journal of Chemical Physics and a reprint is enclosed.

b. Electron Fragmentation of CF_4 .

Theoretical considerations in our laboratory indicate that when CF_4 is irradiated with low energy electrons there is extensive decomposition into neutrals i.e., CF_3 , F, etc. Furthermore it has been reported that light emission occurs from the CF_3 indicating that at least some of the CF_3 radicals are in excited states. These indications are supported by the fact that we observe a small number of CF_3^+ ions on electron bombardment of CF_4 using electron energies as low as 8.5 eV. Since ionization potential of the ground state of CF_3 is greater than this, excited states of the neutral are indicated. Another problem concerning CF_4 is the question of pair formation. Ion pairs have been detected in CF_3Cl , CF_3Br , CF_3I , but over the years no report has been made of pair formation in CF_4 . Using an apparatus where we could detect coincidences between positive and negative ions we have been able to detect CF_3^+ and F^- formation in coincidence. The threshold was about 12.5 eV. These experimental results and the supporting theoretical material is now being prepared for publication.

c. Electron Fragmentation of CF_3Cl .

We have been examining the electron fragmentation of CF_3Cl and in addition to the usual positive and negative ions, a mass peak corresponding to a negative ion at 9.5 was observed. This has been interpreted as arising from F^{--} . This material has been published in Nature and a reprint is enclosed.

List of Publications

- C00-3283-5   Photoelectron Spectrum of Pentaborane, R. W. Jones and W. S. Koski, J. Chem. Phys. 59, 1228 (1973).
- C00-3283-6   Evidence for Doubly Charged Negative Fluorine Ions From Electron Bombardment of CF_3Cl , J. E. Ahnell and W. S. Koski, Nature, 245, 30 (1973).
- C00-3283-7   Electronic States of B^+ Produced by Electron Bombardment of Boron Trihalides: Some Ion-Molecule Reactions of B^+ , K. C. Lin, R. J. Cotter and W. S. Koski, J. Chem. Phys. 60, 3412 (1974).

Publications in Press

1. Scattering of Positive Ions, an invited chapter in MOLECULAR BEAMS, a book published by Wiley-Interscience and edited by K. P. Lawley.
2. Cross Section and Isotope Effect in Reactions of F^+ with Molecular Hydrogen, with K. C. Lin and R. J. Cotter, J. Chem. Phys.
3. Reactions of Electronically Excited Positive Ions, an invited lecture presented at the NATO Advanced Study Institute on Ion-Molecule Reactions (June, 1974), to be published by Plenum Publishing Corp.
4. Formation and Behavior of Excited Cations, W. S. Koski, Int. J. Radiat. Phys. Chem.

Items of Interest

K. C. Lin received his Ph.D. degree in June 1974.

Dr. W. S. Koski presented an invited lecture on "Reactions of Electronically Excited Positive Ions" at the NATO Advanced Study Institute on Ion-Molecule Reactions in June, 1974, at Biarritz, France. He also presented papers at the national meetings of The American Chemical Society at Los Angeles and The American Physical Society in Washington.

Dr. Joyce J. Kaufman presented an invited lecture on "Theoretical Considerations of Potential Energy Surfaces for Ion-Molecule Reactions" at the NATO Advanced Study Institute at Biarritz, France.

She also has presented papers at the national meetings of The American Chemical Society (Los Angeles) and The American Physical Society (Washington).

Dr. Kaufman was awarded The American Chemical Society's Garvan Medal for 1973. She has also been named by The American Chemical Society as a Legislative Counselor to Congressman Clarence Long.

Dr. Kaufman is also serving on The National Academy of Science Committee on Nuclear Science, Ad Hoc Panel on Heavy Ion Sources.

The following personnel participated in the research effort covered by this contract:

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