427
Should be
Attached to
TOP OF THIS
REPORT

Studies in Hot Atom and Radiation Chemistry

Progress Report

September, 1975

Energy Research and Development Administration

E(11-1)-3283

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

W. S. Koski, Contract Director

Department of Chemistry

The Johns Hopkins University

Baltimore, Maryland 21218

UNCLASSIFIED

MASTER

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

pg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Abstract

The cross sections of the ion-molecule reactions of $F^+(^3P)$ and $F^+(^1D)$ with molecular hydrogen and its stable isotopic variants were measured using a tandem mass spectrometer.

The kinematics and differential cross sections for the reaction of $F^+(^3P)$ with D_2 were studied. The study of the exoergicity as a function of projectile ion energy showed that the bulk of the exothermicity of the reaction was converted into vibrational energy of the product ion. This data also indicated that at low energies (<2 eV) that the FD^+ product was produced in its ground state ($^2\Pi$) and at higher projectile energies the product was in the $^2\Sigma^+$ state. The energy and angular distribution of the ionic products in this reaction showed that at low energies the distribution showed a high degree of symmetry relative to $\pm 90^\circ$ although some forward peaking was detectable. At higher energies the distribution was asymmetric relative to $\pm 90^\circ$ indicating the presence of a direct mechanism. Failure to observe the reaction $F^+(D_2, FD)D^+$ was attributed to a violation of spin and symmetry conservation rules.

Bombardment of CF_4 with near monochromatic electrons coupled with the use of coincidence mass spectrometer permitted the detection of the ion pair process $CF_4 + e \rightarrow CF_3^+ + F + e$ for the first time. In addition a low level CF_3^+ ion was observed below the ionization potential of CF_3 . This was attributed to the ionization of excited CF_3 radicals.

The electronic states of C^+ produced by electron (100 eV) bombardment of halogenated methanes showed that in CH_4 14% of the C^+ product was in the first excited state (4P) whereas in CF_4 33% of the C^+ was in this state. For other methane derivatives (CCl_4 , CBr_4 , CI_4 , and $CHBr_3$) only ground state C^+ was produced.

Progress Report

Introduction

This report is a summary of progress made in the radiation and hot atom chemistry program in the Department of Chemistry at The Johns Hopkins University for the research period December 1, 1974 to November 30, 1975, under contract E(11-1)-3283.

For purposes of this report we divide the work into three categories (1) reactions of energetic species which includes what are sometimes referred to as hot atom reactions and (2) production of reactive species by electron bombardment. Under the first category the reactions of the ground state and first excited state of F^+ with molecular hydrogen are covered and in addition results for the reactive scattering of the ground state of F^+ with D_2 is reported since it gives insight on the distribution of energy in the product FD^+ ion. Under the second category some results are presented on ion pair formation (CF_3^+ and F^-) on electron bombardment of CF_4 as well as some preliminary measurements on the electronic states of C^+ produced by electron bombardment of various compounds. Finally (3) some very preliminary work is presented on bombardment of solid targets by ions.

1. Reactions of Energetic Ions

Studies of reactions of energetic ions are relevant to a wide range of energy producing processes. In chemical reactions immediately following many nuclear transformations an ion is directly involved or is a precursor to a neutral hot species that leads to a final chemical product so such studies are relevant to production of energy by fission reactors.

However, relevance of the reactions of energetic species is not solely limited to fission reactors, but is pertinent to a wide variety of processes in thermonuclear production of energy, plasma chemistry and in many combustion processes.

(a) Reactions of F^+ With Molecular Hydrogen

When one is dealing with monoatomic ions as reactants the excitation can take on two forms i.e., translational energy and internal energy in the form of electronic excitation. In the reactions of F^+ with molecular hydrogen the role of both these forms of excitation were studied when the cross section measurements were made for the reaction F^+ with molecular hydrogen and its various stable isotopic variants as a function of projectile ion energies for F^+ in its ground state (3P) and in its first excited state (1D). In many instances the role that translational energy plays in the rate of reaction is modified by the thermodynamics of the process. Generally, a reaction cross section falls with increasing projectile energy for an exothermic process except in special situations where details of the potential energy surfaces may alter the cross section behavior. For endothermic reactions the cross section curve starts at some threshold rises to a maximum and then falls with projectile kinetic energy. Electronic excitation tends to increase reaction cross sections as a general rule however again details of the potential energy surfaces can have a marked influence on this behavior. Likewise, spin and symmetry conservation can play an important role in these reactions for example, the reaction $F^+(D_2,D)FD^+$ the atom abstraction process proceeds in the expected manner and is observed with moderate cross sections. On the other hand $F^+(D_2,D^+)FD$, the hydride ion abstraction process has

a cross section too small to be observed by our instruments. This was attributed to violation of spin and orbital symmetry conservation. These observations are discussed in two publications, "Cross Sections and Isotope Effects in Reactions of F^+ With Molecular Hydrogen," published in Journal of Chemical Physics and in "Reactions of Electronically Excited Positive Ions," published in Interactions of Ions and Molecules, Plenum Publishing Corporation. Reprints of both are included with this report.

(b) Kinematics and Reactive Scattering of the $F^+(D_2,D)FD^+$ Reaction

We have also studied the reactive scattering of $F^+(^3P)$ with D_2 in the energy range 0.7 - 12.5 eV in the laboratory system. The angular and energy measurements show that the reaction proceeds by a direct impulsive mechanism. At the lowest energies studied the contour maps showed a high degree of symmetry indicating considerable amount of interaction between the projectile and both atoms of the target molecule. Energetic considerations and measurements of the exoergicity of the reaction showed that in our low energy domain the product ions, i.e., FD^+ were formed on the ground state whereas in the higher energies at which measurements were made to FD^+ ions were produced in the first excited state. Using angular momentum conservation considerations and the measured cross section values it was possible to say that although the FD^+ product was in part rotationally excited that the bulk of the internal energy was in the form of vibrational excitation in FD^+ . The results were reminiscent of results reported in the corresponding neutral-neutral reaction $F(D_2,D)FD$ where again the internal excitation was in the form of vibrations with an inversion of the vibration energy level populations.

2. Electron Bombardment of Molecules

a. Ion Pair Production in CF_4

In the second phase of this work we have completed some work on the

electronic bombardment of CF_4 with particular emphasis on the ion pair, CF_3^+ , F^- formation. This material was published in the Journal of Chemical Physics and a reprint is enclosed. Ion pairs yielding F^- have been reported for related molecules such as CF_3Cl , CF_3Br , and CF_3I but in spite of many searches no ion pair process has been detected for CF_4 . In our laboratory a careful search has been made for the ion pair process $\text{CF}_4 + e \rightarrow \text{CF}_3^+ + \text{F}^- + e$ in the electron bombardment of CF_4 using a coincidence mass spectrometer with near monochromatic electrons. A weak but easily detectable ion pair process was observed. Its threshold was measured. In addition, a low level of CF_3^+ ions was observed below the ionization potential of CF_3 . This was attributed to the ionization of excited CF_3 radicals. A reprint is enclosed.

b. Excited State Production

In the reactions of energetic species the role of excitation energy is an important factor deciding whether an actual reaction will take place and how fast. At least three factors appear to determine whether excited states occur. These are the electron energy, pressure of the target gas, and the chemical nature of the target molecule. We have given some attention to all three of these factors and during the current research period additional studies have been made on the states of the C^+ ion produced by electron bombardment of several compounds. In a previous study we found that in a study of the states of B^+ produced from electron bombardment of the boron trihalides that there was a systematic variation in the amount of B^+ produced in the first excited state for 100 eV electrons as one proceeded through the series BF_3 to BI_3 . The composition of the beam was determined by studying the attenuation of the beam as a function of pressure of a suitable attenuating gas, N_2 is the case of C^+ beams.

The following results were obtained for the bombardment of various substituted methanes.

Source of C^+	Gas Pressure(u)	Electron Energy (eV)	% Excited State
CF_4	22	96	0
	0.5	96	33
	0.5	37	0
CH_4	23	96	0
	0.5	96	14
	0.5	35	0
CCl_4	12	96	0
	0.55	96	0
CBr_4	22	96	0
	0.60	96	0
CI_4	20	96	0
	0.5	96	0
$CHBr_3$	22	96	0
	0.5	96	0

The results appear to be consistent with the observations on the boron trihalides that if the carbon is bonded to an element in the low end of the Periodic Table some excited state C^+ ions are produced whereas if it is bonded to an element high in the Periodic Table no excited state C^+ ions are produced. Work is continuing in this area.

3. Ion Bombardment of Solids

Some very preliminary work on the bombarding of solids with ions has been carried out during the research period. The objectives of this experiment was to determine if one could study the reactions of ions and neutral projectiles by permitting them to bombard a solid target and then to take the material off the target and process it by means of gas

chromotography and mass spectrometry (GCMS) to find out the nature of the newly formed chemical compound. We had previously carried out such experiments successfully with radioactive Br^+ ion beams bombarding benzene. However, in the current experiments we are attempting to circumvent the disadvantages of using radioactive materials of rather high activity. If one permitted a μ ampere of ions to bombard a target for one hour and if one assumes that about one ion in a thousand forms the desired product about 3×10^{-11} moles of material might be expected. The limits of detection using a modern GCMS system is about 10^{-11} gm. or 10^{-13} moles for a material of molecular weight of a 100. It would therefore appear that success may be feasible in favorable cases. An apparatus was assembled consisting of an ion source, a quadrupole mass filter coupled to a suitable target. Preliminary experiments on the bombardment of solid pentaborane with N_2^+ , a system known to have a high reactive cross section to form $\text{B}_5\text{H}_8\text{N}^+$, were unsuccessful.

Items of Interest

Dr. W. S. Koski presented papers at the national meeting of the American Chemical Society in Philadelphia, IX International Conference on the Physics of Electronic and Atomic Collisions and at the Washington-Baltimore Colloquium on Atomic and Molecular Collisions.

Dr. Joyce J. Kaufman presented papers at the national meeting of the American Chemical Society in Chicago and the IX International Conference on the Physics of Electronic and Atomic Collisions. She was the distinguished graduate lecturer at the University of Florida and the Lucy Pickett Lecturer at Mount Holyoke.

Dr. Kaufman was awarded the 1974 Maryland Chemist Award as the outstanding chemist in the Maryland Section of the American Chemical Society. She is serving on the Organizing Committee for the International Conference on Heavy Ion Sources to be held in Gatlinburg, Tenn., in October 1975 as well as on the American Chemical Society Council Committee on Program Review.

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

L. Frees

C. A. Jones

J. J. Kaufman

W. S. Koski

K. W. Wendell

List of Publications

- C00-3283-9 Cross Section and Isotope Effect in the Reaction of F^+ with Molecular Hydrogen. K. C. Lin, R. J. Cotter, and W. S. Koski, J. Chem. Phys. 61, 905 (1974).
- C00-3283-12 Reactions of Electronically Excited Positive Ions. W. S. Koski in "Interactions Between Ions and Molecules," p. 215, Plenum Press, New York, (1975).
- C00-3283-14 Ion Pair Formation in CF_4 . J. E. Ahnelt and W. S. Koski. J. Chem. Phys. 62, 4474 (1975).
- C00-3283-15 Dynamics of the Reaction of F^+ with D_2 . K. Wendell, C. A. Jones, Joyce J. Kaufman, and W. S. Koski. J. Chem. Phys. 63, 750 (1975).
- C00-3283-16 Theoretical Considerations of Potential Energy Surfaces For Ion-Molecule Reactions. Joyce J. Kaufman in "Interactions Between Ions and Molecules," p. 185, Plenum Press, New York, (1975).

Publications in Press

1. Scattering of Positive Ions, an invited chapter in Molecular Beams, published by Wiley-Interscience and edited by K. P. Lawley.
2. Formation and Behavior of Excited Cations, W. S. Koski, Int. J. Radiat. Phys. Chem.