Studies in Radiation and Hot Atom Chemistry

Progress Report

September, 1973

Atomic Energy Commission Contract

AT(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 Atomic Energy Commission, 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 IS UNLIMITED

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.

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 1972-73, under contract AT(11-1)-3283.

I. Hot Atom Studies

In many problems associated with the chemical reactions immediately following nuclear transformation, either an ion is directly involved or is a precursor to the reaction hot species that eventually leads to the final chemical product. In order to get a better understanding of the elementary processes taking place, we have been investigating the reactions of ions with molecules. This year we have initiated a study of the reactions of F^+ since there have been many fluorine hot atom studies by several groups in this country and abroad but none of these groups considered the reactions of this active species. Our efforts this year and in this area have been concentrated on producing F^+ ions in a known electronic state and examining its reactions with the simplest molecule namely molecular hydrogen. When positive ions are produced by electron bombardment of a suitable target molecule in general the positive ion is produced in more than one electronic state. In our studies two different molecules have been used as targets i.e., BF_3 and CF_4 . Both produced F^+ in the ground (3P) state and in the first excited state (1D). This was determined by studying the attenuation of F^+ ion beam in Ne gas. Of these two target gases BF_3 was very corrosive and contaminated the ion source more rapidly than CF_4 , consequently

the latter was chosen as the working target molecule. In using CF_4 as a source of F^+ it was found that the amount of excited state in the ion beam was a function of electron energy and by lowering the electron energy one could produce an F^+ ion beam which was predominantly in the ground state, however, concomitant with the lowering of the electron energy there was a rapid reduction in the F^+ ion beam total intensity. The reduction was sufficiently large so that the resultant F^+ beam was awkward to work with, consequently it was desirable to find some other method of removing the ^1D state and retaining the ^3P state. In view of the fact that the transition from the ^1D to the ^3P is a forbidden singlet-triplet transition it was decided to try to realize this deactivation by introduction of a paramagnetic material (NO) in the ion source. It was assumed that the paramagnetic gas (NO) would form a loose complex with the excited F^+ permitting a spin exchange and in this way one would be left with only the ground state F^+ . The mechanism of this process was not investigated but attenuation studies of F^+ in Ne showed that if a 30% NO-CF_4 mixture was irradiated with 70 eV electrons only F^+ (^3P) was produced. We do not intend to ignore the reactions of the first excited state of F^+ especially since radiation chemists are showing growing interest in such reactions (the writer has been asked to write an article for a radiation physics journal on reactions of excited states). In these initial studies it was decided to study reactions of the ground state of F^+ .

The first reaction that was studied was the charge transfer reaction with Ne since this process was probably the most significant one as far as the attenuation of F^+ was concerned.

This reaction is endothermic for both state of F^+ and its cross section as a function of increasing ion energy rose and went through a broad maximum and then fell. The reaction with $\text{F}(^1\text{D})$ had a significantly higher cross section at the maximum than that of $\text{F}(^3\text{P})$ and the apparent threshold was lower in energy. Indicating as might be expected in this reaction that the electronic excitation energy was contributing considerably to the reaction cross section. On the other hand in the reactions of F^+ with H_2 and D_2 there wasn't any large differences in the reaction cross sections between ^3P and ^1D fluorine ions. The reactions were exothermic and thus the cross sections fell as a function of projectile ion kinetic energy.

Finally the isotope effect in the reaction

was studied. It was found that at low ion kinetic energies that the ratio of the cross sections $\frac{\sigma_{\text{FH}^+}}{\sigma_{\text{FD}^+}}$ was less than unity but as the kinetic energy rose the ratio increased and at 50 eV it exceeded 4.0. This behavior was reminiscent of the much studied reaction

This behavior was interpreted as meaning that at low energy where the isotope effect was less than unity complex formation was taking place

and at higher energy the reaction was proceeding by some direct mechanism. There is some question about this interpretation so it is hazardous to extend the same conclusion to the F^+ reaction.

Measurements and calculations on these reactions are being completed and at that time the material will be submitted for publication probably in the Journal of Chemical Physics.

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 very pertinent to an understanding of radiation chemistry as a whole. In this category we have a number of items to report.

a. Electron Fragmentation of the Boron Trihalides

When we first examined the use of BF_3 as a possible molecular target gas for the production of F^+ examination of the appearance potential of various ions including B^+ suggested that the B^+ was not in its ground state. This indication was also present in some of our earlier work on the boron trihalides. Since we had samples of all four of the trihalides in the laboratory it was decided to examine the B^+ electronic states produced from electron bombardment of these compounds. The attenuation of B^+ in an appropriate gas was used as a diagnostic tool to determine the B^+ ion beam composition. It was found that the amount of the excited state (3P) in the B^+ ion beam varied in a systematic

way as one varied the target molecule from BF_3 to BCl_3 , BBr_3 and finally BI_3 . The percentage of the excited state decreased as one proceeded in this series and BI_3 gave the B^+ ion completely in the ground electronic state (^1S). Preliminary examination of some ion molecule involving both states of B^+ confirmed the conclusions reached from the attenuation studies. This material is now being prepared for publication. A preliminary preprint is enclosed.

b. Electron Fragmentation of CF_4

Our study of the electron bombardment of CF_4 has continued in spite of instrumental and personnel problems. There is considerable interest in this problem since it will be recalled that no parent ion, CF_4^+ is formed and there is no satisfactory explanation of this fact to date. We have made two interesting observations which are very pertinent to an explanation of the behavior of CF_4 under electron bombardment. First, and electron pair process, $\text{CF}_4 + e \rightarrow \text{CF}_3^+ + \text{F}^- + e$ has been observed in our coincidence mass spectrometer. This process has a threshold of about 13.5 eV. The value of this appearance potential suggests that the CF_3^+ is produced in an excited state and/or the ionic products have considerable amounts of kinetic energy. Both of these facts are supported by our quantum chemical calculations on this system.

A second observation which will help in the overall interpretation of these results is the fact that a small amount (50 counts/min.) of CF_3^+ is observed down to a bombarding electron energy of about 8.5 eV. Our quantum chemical calculations indicate that there are many repulsive electron states of CF_4 just about the attractive ground electronic state consequently one would expect to get extensive decomposition of CF_4 into

neutral fragments such as CF_3 , F etc. This suggests that this small yield of CF_3^+ at the low appearance potential arises from the ionization of neutral fragments such as CF_3 . The fact that this appearance potential is below the reported ionization potential of the ground state of the free radical CF_3 indicates that our neutral CF_3 's formed by electron dissociation are in excited states. Qualitative molecular orbital considerations indicate that this is reasonable.

We have had considerable instrumental malfunction of our coincidence mass spectrometer that was used in this study. As soon as this difficulty is corrected the measurements on this molecule will be completed and a combined theoretical and experimental paper will be published on our findings.

c. Photoelectron Spectrum of Pentaborane

This study may be peripheral to our main objectives, however in some of our work such as the CF_4 study we have been using empirical quantum chemical calculations to help us in the interpretation of the physical results obtained from experiments. The question repeatedly arises as to how reliable are such empirical calculations and if they disagree with the true results do they deviate in some systematic manner so that at least qualitative allowance can be made for such deviations. If the system is simple enough a rigorous ab-initio calculation can be performed however in most of our cases either the system is too complex or the amount of computer time for an ab-initio study is prohibitive so an answer to these questions as to how reliable the empirical calculations were was desirable. We therefore measured the photoelectron spectrum of B_5H_9 , a molecule with which we had considerable

experience, and for which an SCF ab-initio calculation existed in the literature. Using programs available in our laboratory we carried out the empirical INDO, CNDO and Extended Hückel calculations on the molecule and a comparison was made with the molecular orbital results. The results will appear in the Journal of Chemical Physics. A preprint of the results is enclosed.

d. Electron Fragmentation of CF_3Cl

We have been examining the electron fragmentation of CF_3Cl and in addition to the usually expected ionic species from a molecule such as this we have consistently observed a mass peak at 9.5 corresponding to the doubly charged negative ion F^{--} . This ion was not observed using the same equipment when CF_4 was used as a target gas. The yield of the ion rose as the electron bombarding energy was raised from 30 eV to 100 eV. These observations suggest that the F^{--} arises from a secondary process. Multiply charged negative ions are of considerable interest to nuclear accelerator scientists and we plan to publish this observation as a Letter to the Editor in the near future.

e. Light Emission from Irradiated H_2O

We had observed light emission from H_2O vapour irradiated with 3 M eV deuterons or protons. The Balmer lines plus a number of unidentified lines were observed. As more observations were made there was considerable variation in the results, although the Balmer lines were present in all cases. A study of the situation revealed that the bulk of the observed lines were due to small amounts of N_2 present in the gas phase. This was consistent with the recent observations of the H_2O^+ ion emission

spectrum produced by an electrical discharge in H_2O vapour. The intensity of the emitted light was extremely low and required long time observations using a computer averaging techniques to detect the emitted light. This low intensity emission would not have been detected under our experimental conditions.

Likewise the irradiation of liquid water has failed to give information of interest to radiation chemistry. These experiments were performed on a tandem accelerator using 14 M eV protons as projectiles and triply distilled water as a target. A Bausch and Lomb monochrometer and a photo multiplier was used as a dispersive and detecting system. Either recordings or oscilloscope displays were used depending on whether single accelerator pulse emission spectra were under study or the average effect of many pulses were used. Examination of the average spectra resulting from many accelerator pulses and after correcting photomultiplier sensitivity showed that the observed light emission was constant over the range $3000 \text{ \AA}^0$ to $7500 \text{ \AA}^0$. No lines were present. In the pulsed experiments (.2.Nanosecond pulses) the light emission pulse from the water was only slightly wider than the accelerator pulse. Since Cerenkov radiation is not expected to be a factor under our conditions there is no satisfactory explanation for the light emission observed, however, it is possible that the light may originate from bremsstrahlung. At any rate it does not appear likely that the light arises from excited species derived from H_2O . This conclusion is reminiscent of the work of Czapski and Katakis (J. Phys. Chem. 1966).

In addition to ionic species such as H_2O^+ one would expect species such as H_3O^+ since the ion molecule reaction $\text{H}_2\text{O}^+(\text{H}_2\text{O}, \text{OH})\text{H}_3\text{O}^+$ has a high cross section. This reaction is expected to proceed by two mechanisms

In one case proton transfer takes place from the projectile to the target and a singlet state is expected. In the second case atom transfer takes place from target to the projectile to form H_3O^+ and a triplet state would be expected. During this research period evidence for the two mechanisms was obtained by performing a deuterium tracer study using the reactions $\text{H}_2\text{O}^+(\text{D}_2\text{O}, \text{OH})\text{HD}_2\text{O}^+$ and $\text{H}_2\text{O}^+(\text{D}_2\text{O}, \text{OD})\text{H}_2\text{DO}^+$. The cross section for the first reaction falls with decreasing energy whereas the second one rises with decreasing energy. This suggests that at thermal energies one would have a considerable excess of triplet state so one might expect light emission (phosphorescence) corresponding to the forbidden triplet-singlet transitions. In studying the reactivity of the excited states of H_3O^+ one also obtained evidence for vibronic excitation in this species so light emission should also be present from vibronic transitions. In summary one might expect light emission from proton irradiated H_2O , however, our difficulty in observing discrete spectra of excited species derived from H_2O may arise from the very low intensity of the light emitted.

f. Charge States of Fast Nitrogen Ions

In this phase of our research only preliminary observations on the charge states of fast nitrogen ions produced by the reaction $\text{C}^{12}(\text{d}, \text{n})\text{N}^{13}$

have been made because of personnel problems and because of malfunction of our electrostatic generator. By permitting 3 MeV deuterons to impinge on thin graphite targets and by collimating the product, N^{13} , through a slit arrangement and passing the resulting beam through magnetic field and then catching the N^{13} on aluminum foils we were able to detect the presence of N^0 and N^+ in the N^{13} product. This probably represents equilibration of the charged nitrogens in the graphite target and not the charge distribution present at the instant of nuclear transportation. To realize the latter we will have to go to higher deuteron energies and to thinner targets. To do this we will have to get some time on an accelerator other than ours and this point is being looked into.