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Annual Progress Report

RESEARCH ON HIGH-ENERGY CHEMICAL REACTIONS

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Abstract

The research performed under the A.E.C. contract covers five areas:

- 1) studies of hot tritium reactions using nuclear recoil techniques, 2) measurements of the energy dependence of hot tritium reactions using molecular beams, 3) the determination of the structure of the benzene ion, 4) studies of ion-molecule reactions, 5) calculations on the reactions of the H_3^+ system.

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Professor Cross took over the direction of this contract last June on the sudden death of Professor Richard Wolfgang. The research proposed in Wolfgang's last proposal has been continued with only minor changes, but several areas of research will be dropped at the end of the summer when the relevant students and postdoctoral fellows leave. The support for study of ion-molecule reactions on EVA will be shifted entirely to the NASA contract; the beam study of hot tritium reactions will be continued under AEC sponsorship; other projects will be dropped. This summer, then marks a major turning point in the contract. My next annual report will contain a summary of all the work done under Professor Wolfgang, a complete bibliography, and a list of all students and postdoctoral fellows who worked on the contract.

1. Studies of Hot Tritium Reactions using Nuclear Recoil Techniques:

We have examined several aspects of the kinetic theory of hot reactions. The basic Wolfgang-Estrup theory of hot reactions has been modified to take account of hot reactions with the radical scavengers present in the system. The corrections to α (the slowing down parameter) and $I = \int [p(E)/E] dE$ are large enough to require correction and reinterpretation of much existing data. The theory has been tested using stochastic calculations. A reasonable choice is made for α and the energy dependence of $p(E)$, the probability for reaction. A computer program was written to examine the fate of a number of hot tritium atoms as they collide and react randomly. We have also tested the theory experimentally by measuring the yields of hot products as a function of scavenger concentration. We are now reinterpreting some old data and remeasuring parameters for the $T + CH_4$ and $T + CD_4$ systems.

We have also found that the relative yields for hydrogen abstraction and displacement depend on the type of moderator used (even at the same f/α) in contradiction to the theory. The most likely explanation is that much of the HT formed has a high translational and vibrational energy and may dissociate on subsequent collisions with the moderator. The probability for dissociation will, of course, depend on the type of moderator.

2. Measurements of the Energy Dependence of Hot Tritium Reactions Using Molecular Beams:

The molecular beam machine ADAM was originally constructed to study the reactions of hot tritium reactions with a solid target. We have

modified it to measure the reaction cross sections for gas-phase reactions as a function of energy. T^+ ions are formed in a plasma, are accelerated, focused, and mass selected. The ion beam is then bent by 90° (to remove neutrals), neutralized in a crossed beam of CO_2 . The ions are removed electrostatically, and the resulting T beam passes through a separately pumped chamber into the reaction chamber which contains the reactant, a rare gas moderator, usually helium (the major constituent), and a small amount of a radical scavenger. The T atoms lose energy on collision with the helium and react. The products of the reaction effuse through the entrance hole in the reaction chamber and are pumped by a 4 in. diffusion pump attached to the separately pumped chamber. The products are then trapped in a molecular sieve at $77^\circ K$. After the run the products are analyzed by gas chromatography and flow-counting. Since we know the T-He potential, we can calculate the energy distribution of the reacting T atoms. By varying the initial beam energy we can vary this distribution. Thus we can obtain the reaction cross section as a function of energy. We have done preliminary runs and are now investigating a scavenger system (C_2H_4). We hope to have preliminary results shortly. This project will be continued under AEC sponsorship.

3. Determination of the Structure of the Benzene Ion:

The beam machine CAIN was constructed to form a mass selected beam of ions and to neutralize them on a solid surface. If the beam energy is low enough and the excess energy of the final neutral molecule is drawn off fast enough, the structure of the final neutral species will be the same as that of the ion. There is some evidence that benzene and 1,3-hexadien-5-yne have the same ion (the mass spectra are almost identical). We have made beams of $C_6H_5T^+$ ions from both tritiated benzene and tritiated hexadienyne. We find that benzene gives exclusively benzene and hexadienyne gives a mixture of benzene and hexadienyne. Thus there are two ions. Benzene does not open up on ionization, but hexadienyne may isomerize on ionization (the isomerization could be in the ion source or on the target).

4. Studies of Ion-Molecule Reactions:

Using the crossed beam machine EVA we can measure the energy, angular, and mass distributions of products of ion-molecule reactions as a function of initial ion energy. We have measured such distributions for

and other isotopic permutations. The product distributions present a rich variety: some are nearly isotropic, some are peaked forward, some backward, and one is sideways peaked. It is obvious that the results cannot be explained by a simple model such as spectator stripping. The interesting feature of the results is that they can be explained by an ab initio theory (see below).

We have also investigated several organic ion-molecule reactions. We have found, using deuterium labels that the reaction

proceeds via the intermediate hypervalent carbonium ion,

We have also looked at the reactions

At the lowest energies there is complete scrambling of hydrogens. As the energy is raised, the lifetime of the C_2H_7^+ intermediate decreases, and the scrambling is no longer random. We have explained our results in terms of a simple competition between protons jumping from carbon to carbon and the splitting off of H_2 from the C_2H_7^+ intermediate. This work is partially supported by N.A.S.A. grant NGL-07-004-043. N.A.S.A. will assume the full support next year.

5. Calculations on the Reactions of the H_3^+ System:

We have calculated many of the various cross sections for reaction (1) by a completely ab initio method. Only two electrons are involved so the potential energy surfaces are not difficult. Unlike many reactions, there are two intersecting surfaces. The system can jump from one to the other. We have used the semiclassical Trajectory Surface Hopping model to calculate the probability of the jump. Apart from the jumping, classical mechanics is used to treat the motions of the system on each surface. The results obtained agree quite well with experiment. This marks the first substantial agreement between an ab initio theory and a molecular beam experiment.

Bibliography of Published Work

Below are listed ten new publications which have been written during the past year. Reprints and preprints have been sent under separate cover.

- AEC 1-316 As in previous reports.
- AEC 317 The Temperature Dependence of Simple Hot Atom Reactions. Homer Chang and Richard Wolfgang. J. Chem. Phys. 75, 3042 (1971).
- AEC 318 The Production of Acetylene by Laser-Generated Atomic Carbon. D. Blaxell, R. Peterson, D.J. Malcolme-Lawes and R. Wolfgang. J. of the Chem. Commun., 110 (1972).
- AEC 319 Limits of the Validity of the Kinetic Theory of Hot-Atom Reactions. D.J. Malcolme-Lawes. J. Chem. Phys. 56, 3442 (1972).
- AEC 320 The Effect of Scavenger Competition on Hot Atom Chemistry. Part I. D.J. Malcolme-Lawes. J. Chem. Phys.
- AEC 321 The Effect of Scavenger Competition on Hot Atom Chemistry. Part II. D.J. Malcolme-Lawes. J. Chem. Phys., to be published.
- AEC 322 High Energy Reaction Kinetics Using a Hard-Sphere Model. Part I. D. J. Malcolme-Lawes. J.C.S. Faraday 2., to be published.
- AEC 323 High Energy Reaction Kinetics Using a Hard-Sphere Model. Part II. D.J. Malcolme-Lawes. J.C.S. Faraday 2., to be published.
- AEC 324 Computer Simulation of Some Reactions of Energetic Hydrogen Atoms. D.J. Malcolme-Lawes. J. Phys. Chem., to be published.
- AEC 325 The Accuracy of Hot Atom Kinetic Theory Parameters. G.A. Press, Abigale Freedman and Roy Carlson and D.J. Malcolme-Lawes. Radiochimica Acta., to be published.
- AEC 326 Plateau Shifting Effects in Gas Flow Proportional Counters During Tritium Analysis. Radiochem. Radioanal. Letts. 7, 101 (1972).