EXPERIMENTAL CHEMICAL KINETICS
5
A STUDY OF CHEMICAL REACTIONS BY MEANS OF
MOLECULAR BEAM TECHNIQUES

Progress Report
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ABSTRACT

The exchange of translational with internal energy ΔE in collisions of CsI with Ar and Xe is studied at initial kinetic energies in the thermal range. Differential cross sections are integrated over scattering angles to get total cross sections for various ΔE . There is evidence that a short-lived complex is formed at low energies.

Beams of electrons can influence the motion of neutral atoms and molecules by concentrating them near the electronic beam. This effect, which has been studied in detail for beams of KCl and K and for the residual gas in a vacuum system, is insignificant for pressures higher than 1.3×10^{-2} Pa but can increase densities of neutrals by large factors ($10^2 - 10^4$) at lower pressures.

Classical calculations are made for the interaction of hard spheres with rigid surfaces having one-dimensional periodicity of various symmetries and amplitudes.

The chemical effects on molecules of colliding with a wall at kinetic energies up to 10^2 kJ mol⁻¹ are studied by collecting the products for analysis by gas chromatography. The molecule studied is ethyl iodide which is accelerated by being seeded into a jet of hot H₂ flowing into a vacuum.

The work supported by ERDA Contract No. AT(11-1)3129 since October 1975 has progressed as follows:

1. Publications

- a. W. D. Armstrong, R.J. Conley, R.P. Creaser, E.F. Greene and R.B. Hall.

The elastic and inelastic scattering of diatomic molecules by atoms: CsI + Ar, CsCl + Ar, CsI + Xe. J. Chem. Phys. 63, 3349 (1975).

Reprints have become available and are enclosed.

- b. E. F. Greene, R. B. Hall, and N. A. Sondergaard. The elastic and inelastic scattering of CsI by Ar and Xe.

Submitted to the Journal of Chemical Physics. A preprint is enclosed together with 6 copies of the Abstract.

- c. N. A. Sondergaard. Energy transfer in diatom-atom collisions: the elastic and inelastic scattering of cesium iodide by argon and xenon, Ph.D. Thesis Brown University, 1976. Copies of the Abstract are enclosed.

2. Status of current research

Work on the several projects being studied has progressed as follows:

- a. The inelastic and elastic scattering of alkali halides by rare gases. The second part of this work is complete and a manuscript has been submitted for publication (see Section 1b).

Copies of the Abstract and a preprint are submitted with this report.

- b. The control of the motion of neutral molecules by a beam of electrons.

There has been substantial progress since the publication of the first results of this work (J. Chem. Phys. 62, 190 (1975)), but some parts of the new work have not been tested sufficiently as yet to justify the writing of a second paper now.

Particular effort has been put into the study of the interaction of beams of electrons with coaxial beams of molecules from an oven loaded with KCl. The temperature dependence of the current of a detector set on the axis of the beams is shown in Fig. 1. At high temperatures of the KCl source there is a slight reduction in the detector signal I_N in the presence of the electrons compared to that in its absence I_P . As the temperature drops I_N begins to exceed I_P . The latter falls in proportion to the vapor pressure of KCl in the source as is expected. I_N , however, stays nearly constant and only begins to drop when it is approximately 10^8 times I_P .

This signal is so large that even the collection by the electronic beam of all the KCl effusing from the oven would not account for all of I_N . Apparently an impurity to which the detector is sensitive must be present in the KCl. KOH produced by hydrolysis of the KCl by atmospheric H_2O is a reasonable candidate. Another possibility, that the beam molecules are being desorbed from some surface instead of coming from the source, is ruled out because a shutter only wide enough to block the hole in the source shuts off the beam. The experiment shows remarkably efficient collection of these molecules by the electronic beam. To test the suggestion that KOH may be contributing to the signal from the KCl source similar experiments have been done with K replacing the KCl. These are unaffected by the presence of KOH because its vapor pressure is much lower than that of K. For beams of K there is no "excess" collection, but the actual efficiency may be somewhat lower than was reported earlier. These results need checking.

In other, related experiments a rotatable electronic beam is set up in a vacuum chamber separated by a small hole or slit from a second chamber containing a mass spectrometer. The size and shape of the electronic beam can be observed from the light emitted when it hits a fluorescent screen. When the beam is focussed sharply and then rotated from the screen to aim at the slit between the two chambers, an increase in signal is observed in the mass spectrometer. This increase is 5% of the background recorded in the chamber containing the mass spectrometer, when the latter records total pressure. When it is set for masses 2, 14, and 18 amu, the signals increase to 3.3, 1.05 and 1.20 times their background values respectively. Adjustment of the position of the slit between the two chambers shows that the increases in signal caused by the electronic beam are in the form of a beam, not a diffuse cloud, of molecules pumped by the electrons into the adjoining chamber. As in the experiments with beams of KCl the pumping efficiency of the electronic beam falls as the background pressure rises. The absolute increase is constant at about 5% of the background pressure in the mass spectrometer when the pressure P_1 in the chamber containing the electronic beam is increased from 3×10^{-5} to 3×10^{-4} Pa but drops to half this when P_1 is increased to 1.3×10^{-2} Pa ($1 \text{ torr} = 1.3 \times 10^2 \text{ Pa}$). These effects seem to be real ones and of a significant magnitude. Nevertheless, more information about the mass dependence and better reproducibility of the signals are needed.

c. The scattering of hard spheres from a rigid surface.

Calculations have been started of the angular distribution of hard spheres scattered from a surface periodic in one-dimension. The calculations show how the angular dependence of the scattered particles is affected by changes in the amplitude, symmetry and spacing of the structure of the surface as well as by the size of the incident particle and the ratio of the incident energy to the energy of attraction of the particle for the surface. These classical calculations, which pertain necessarily to elastic scattering, may be reasonable representations of the actual elastic scattering of real atoms from real surfaces if only that fraction (perhaps a very small one) of scattered atoms having their final energy within a small range of their initial energy can be observed without interference from the inelastic scattering. If this "elastic" scattering can be observed experimentally, its features may be interpretable in terms of the structure of the surface and thus be useful in helping to show how to fit scattering data to more realistic forms of the potential.

d. Reactions of molecules caused by energetic collisions.

When heavy molecules such as CCl_4 are seeded into streams of lighter molecules such as He in large excess, the speed of the CCl_4 molecules approaches that of the He. With such seeded beams CCl_4 flowing from a source into an evacuated chamber has been speeded up to have a laboratory velocity of $1.8 \times 10^3 \text{ ms}^{-1}$ corresponding to an energy of 112 kJ mol^{-1} (J. Chem. Phys. 54, 3054 (1971)). When these CCl_4 molecules hit a stationary wall, they are subject to violent collisions which may cause chemical reactions. In this earlier work a gray-white deposit of a complicated mixture of solids collected on the wall which had had prolonged exposure to the fast CCl_4 beam.

These experiments have been resumed in an effort to study the nature of the decomposition which results and to compare it with that produced by normal pyrolysis. The first compound selected for study is $\text{C}_2\text{H}_5\text{I}$. It is seeded into a beam of H_2 heated to ca 500K which then can strike a wall which is either at room temperature or cooled by liquid nitrogen. After a running time of about 1 hr. the flow is

stopped, the vacuum chamber is isolated from the pumps, and the product recovered for analysis by gas chromatography and mass spectroscopy.

Preliminary results show that I_2 as well as small amounts of C_2 and C_4 hydrocarbons are formed.

e. Other reactions on surfaces.

No progress has been made in the past year on the study of ionization at surfaces or the reaction of $LiCl + H$ on a Re surface.

3. Personnel

The people who have worked on projects supported by the contract during the past year are listed here. The numbers after each name indicate the projects with which they have been associated.

Dr. Graham Staker (2a, 2c) joined this group in June 1976 after completing the work for his Ph.D. at the University of Adelaide.

Dr. N.A. Sondergaard (1b, 1c, 2a, 2d) finished the work for his Ph.D. at Brown in August 1976 and will stay for a few months as a research associate.

Mr. H.D. Lambropoulos (2b) is a graduate student who has nearly completed the work for his Ph.D. He has just started a leave of absence, so the completion of his thesis will probably be delayed.

Mr. M. Pickering (2a, 2c) is a new graduate student who worked during the past summer.

Mr. J. Bading (2b) is currently a graduate student in Physics at Brown. He worked as a research assistant for several months but is now devoting all his time to finishing his thesis. He is expected to be a research associate working in this group when his thesis is done.

Mr. W. Molber (2b) who has just received his Sc.B. in Physics did his undergraduate research in this group.

Mr. C. Parks (2d) is a junior chemistry major who worked during the summer.

Professor E.A. Mason (2c) and Professor T.H. Morton (2d) have collaborated in projects and contributed to the work supported by the contract.

Professor E.F. Greene, the principal investigator, has spent 50% of his time on work supported by the contract since the start of the current term. This fraction will either stay the same or increase for the rest of the term. From September 1976 to June 1977 he is on sabbatical leave from Brown. He

is spending this time working in Dr. H. Hagstrum's Department of Surface Physics at the Bell Laboratories in Murray Hill, New Jersey where he is associated most closely with Dr. M.J. Cardillo studying the interaction of molecular beams with surfaces. This provides him with an excellent opportunity to learn about the work of a leading laboratory in this field. He also has at least half his time available for work on the projects supported by the contract. In his absence from Brown, Professor Mason has kindly agreed to supervise the work of the group there.

Fig. 1. Logarithm of detector current I versus reciprocal temperature of source for beams of molecules in presence I_N (O) and absence I_P (+) of a coaxial beam of electrons. Source contains KCl with possible impurities KOH and $(KOH)_2$. Dashed lines show vapor pressures (ordinate on right) and $I(A)$ expected for complete collection of material leaving oven for material at equilibrium at T . (ordinate on left).