EXPERIMENTAL CHEMICAL KINETICS
A STUDY OF CHEMICAL REACTIONS BY MEANS OF MOLECULAR
BEAM AND SHOCK WAVE TECHNIQUES

Progress Report

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Abstract

The rate of dissociation of HBr and Br₂ in shock waves, the ionization of Ar in molecular beams, the physical interpretation of oscillations in glory scattering, and the estimation of the interaction potential of I atoms and Kr from scattering measurements are described in publications. The inelastic scattering of CsI by Ar with velocity selection and analysis at E, relative kinetic energies, of 1 to 2 kcal mole⁻¹ shows the inelastic cross section is large but the amount of vibrational energy transferred is not as large as is found at higher energies. The ratio of the yield of negative to positive ions produced from CsI or CsCl beams incident on a hot Nb or Re surface is independent of energy in the range 3 to about 50 kcal mole⁻¹. One scattering apparatus is being improved by the addition of a nozzle beam to give better resolved differential cross sections for scattering of various molecules from rare gases.

The progress which has been made on AEC Contract AT(11-1)3129 since October 1971 is as follows.

1. Publications

- a. R. H. Hammond, J.M.S. Henis, E.F. Greene and J. Ross, J. Chem. Phys. 55, 3506 (1971). Kinetic energies of ionization products from collisions of Ar-Ar, He-He below 150eV c.m. energy. Reprints have become available and are enclosed.
- b. K. Westberg and E. F. Greene, J. Chem. Phys. 56, 2713 (1972). Dissociation of HBr and Br₂ in shock waves. Reprints are enclosed.
- c. E. F. Greene and E. A. Mason, J. Chem. Phys. 57, 2065 (1972). Physical interpretation of glory oscillations in scattering cross sections. Reprints are enclosed.
- d. M. S. Chou, Ph.D. Thesis, Brown University, June, 1972. Crossed molecular beam study of the scattering of CCl₄ by Kr and by iso-octane and of CH₂Cl₂ by iso-octane. Copy of abstract attached.
- e. M. J. Cardillo, M. S. Chou, and E. F. Greene, paper 77 before the Division of Physical Chemistry of the American Chemical Society, Boston, Mass., 9-14 April 1972. The scattering of I atoms by Kr. Copy of abstract attached.

2. Manuscripts in preparation

a. R. P. Creaser, R.P. English (MIT), and J.L. Kinsey (MIT). Unfolding differential cross section data using an iterative linearized least square/spline function approach. This manuscript, mentioned in the previous progress report, has been revised to make it shorter and more directed toward molecular beam than computer workers. It will be submitted for publication soon.

b. E. A. Mason and E. F. Greene. An expansion of the slope of the deflection function at zero scattering angle has been worked out and used to estimate the amplitude of the glory oscillations of the total cross section for atom-atom scattering. The results are applied to several potentials of the Lennard-Jones (n,6) form and to the square well potential.

3. Status of current research.

a. Two manuscripts are in preparation. See 2a,b.

b. The work, described in previous progress reports, on the velocity analysis of the scattering of Cs and CsI by Ar is continuing although not as rapidly as had been expected. Improvements in the apparatus made during the past year now permit in-plane scattering with a noise level ($\sim 10^{-17}$ A) about ten times lower than previously. Experiments with Cs + Ar and CsI + Ar have been made at three initial kinetic

energies in the range 1-2 kcal mole⁻¹. Because the angular resolution is not as good for the in-plane as for the out-of-plane configuration some check runs with the latter configuration will be repeated before the results are prepared for publication. There is no clear evidence of a complex formed between Ar and CsI. The cross section for inelastic scattering is large but there is not the extreme transfer of energy which is reported for this system at higher energies (Loesch and Herschbach, J. Chem. Phys. 57, 2038 (1972)).

c. Preliminary results for the scattering of I atoms by Kr and Xe have been reported. See 1e. However, two complications have arisen. The first, an experimental one, is that the Kr or Xe beams were not as well collimated or as nearly monoenergetic as is desirable for obtaining good differential cross sections. The cross beam is now being redesigned to provide a nozzle source with two more stages of differential pumping. This source is expected to be working soon and should permit much improved measurements. The second complication is in the theoretical interpretation. The mixing of the several m_j states of I ($^2P_{3/2}$) in collision with Kr (1S) make the

interpretation of the differential cross sections in terms of the interaction energies for I and Kr both more interesting and more complicated than is the case for the scattering of singlet atoms.

d. Beams of CsCl, CsI and CH_3I have been directed to hot surfaces of Nb and Re where the beams produce currents of positive (I_+) or negative (I_-) ions depending on the bias of the filament. The variation of these currents and of the current of electrons (I_e) with the filament temperature permit a measurement of the work function of the metal under operating conditions and some test of the mechanism of ion formation at the surface. The simple model for the efficiency of ion formation (Equations 4 and 5, Persky, Greene and Kuppermann, J. Chem. Phys. 49, 2347 (1968)) seems to fit the results well up to a temperature of about 1800°K although the apparent work function is approximately 0.5eV higher than literature values for both metals. Above about 1800°K the ion yield of negative ions decreases and shows that some unknown process is making a substantial change in the mechanism of ion formation. Measurements with beams of CsCl and CsI over a range of initial kinetic energy E of the beam in the range $1 < E \text{ (kcal mole}^{-1}\text{)} < 100$ show that the ratio I_-/I_+ is constant, independent of energy.

Because I_+ for the Cs compounds is likely to be independent of E in this range, so apparently I_- is also. This is in contrast to a report (G. P. Koennen, FOM Institute, Amsterdam, private communication) which shows a linear rise of I_- with E to nearly 20% ionization efficiency at higher energies ($E = 20\text{eV}$) for beams of KCl on thoriated tungsten surfaces. The results with CH_3I are much less precise than those with CsI and CsCl but I_-/I_+ seems again not to be dependent on E . This is inconsistent with results reported for CH_3I on $\text{Re}(\text{O}_2)$ for which I_+ apparently rises sharply with E in the range near 10 kcal mole^{-1} (Gersh and Bernstein, J. Chem. Phys. 56, 6131 (1972)).

g. Because of the demands of the other work two projects proposed previously have not as yet received the attention they were expected to receive. One of these is the scattering of tetracyanoethylene by cyclopentadiene where there is the possibility of a Diels-Alder condensation. The other project is the improvement of methods of data collection for the two apparatus. The better signal-to-noise ratio now available in the two rotor apparatus makes this second need less urgent, but attention should be devoted to both projects.

4. Personnel

The projects supported by the contract with which the various people have been concerned is indicated by the symbols in parentheses which refer to sections of this report.

Dr. M.S. Chou (1d,1e) received his Ph.D. in June, 1972 and is now a postdoctoral research associate working with Professor George Fisk at Cornell University.

Dr. S.M. Bobbio (3c,3d) is completing his first year as a postdoctoral research associate after receiving his degree in physics from the College of William and Mary.

Dr. S.E. Johnson has recently started an appointment as a research associate.

Mr. W. D. Armstrong (3b) is in his third year of graduate work.

Miss Veronica Vaida and Mr. Steve McInnes are undergraduates who have just started on molecular beam projects.

Mr. Richard Hall will arrive in October to start a year's appointment as a research associate.

There continues to be profitable collaboration with Professor J. Kinesey's group at MIT (2a) and with Professor E.A. Mason (1c,2b).

The principal investigator, Professor E.F. Greene has

spent and expects to continue to spend 50% of his
time on the work supported by the contract.

ABSTRACT

CROSSED MOLECULAR BEAM STUDY OF THE SCATTERING OF CCl_4 BY Kr AND BY ISOCTANE AND OF CH_2Cl_2 BY ISOCTANE

Mau-Song Chou, Ph.D.
Brown University, June 1972

Differential cross sections for the scattering of CCl_4 by Kr, of CCl_4 by isooctane, and of CH_2Cl_2 by isooctane are reported for the ranges of average relative kinetic energy between 1.43 and 12.6, 1.80 and 26.8, and 1.83 and 16.7 kcal mole⁻¹ respectively.

The molecular beam apparatus, constructed for the study of these systems, consists of several parts. The primary beam oven produces an effusive beam at low pressures and a supersonic one at higher pressures. An accelerated beam can be formed by seeding the heavier beam particles into an excess of He. A light-weight velocity selector, which has disks with narrow slots produced by chemical etching, provides two open channels having different resolutions. Use of these two channels permits accurate alignment of the beam with the axis of the selector. The cross beam source is capped with a fused array of glass capillaries which produce a beam with a relatively narrow spread in angular distributions. The detector which is sensitive to molecules containing atoms of high electron affinity, such as halides, produces negative ions at a hot niobium surface. The construction and performance of the apparatus are discussed in detail. Efficiencies for the formation of negative ions at surfaces for a variety of beam-filament combinations are also presented.

The results of the measurements on the scattering at the higher energies for the three systems all show primary rainbow structure. For the run with $\text{CCl}_4 + \text{Kr}$ at $\bar{E} = 3.60 \text{ kcal mole}^{-1}$ super-numerary, or coarse, rainbow oscillations are observed. The primary rainbow structure and the coarse rainbow oscillations are used to determine parameters for an assumed form of the interaction potential. The decrease in the measured differential cross sections at large angles below the ones calculated for elastic scattering from the same potential implies the presence of a substantial amount of inelastic scattering.

A Kihara potential, which provides an impenetrable core of radius r_∞ is chosen for the form of interaction between two polyatomic molecules or a polyatomic molecule and an atom to account for the main feature of the observations. The parameters for this potential form, the well depth ϵ , the distance of separation at the minimum r_m , and $\alpha' = r_\infty/r_{\text{min}}$, are found to be: $\alpha' = 0.2$, $\epsilon = 0.57 \text{ kcal mole}^{-1}$ and $r_m = 5.2 \text{ \AA}$ for $\text{CCl}_4 + \text{Kr}$; $\alpha' = 0.6$, $\epsilon = 0.89 \text{ kcal mole}^{-1}$ for $\text{CCl}_4 + i\text{-C}_8\text{H}_{18}$ and $\alpha' = 0.5$ and $\epsilon = 0.89 \text{ kcal mole}^{-1}$ for $\text{CH}_2\text{Cl}_2 + i\text{-C}_8\text{H}_{18}$. The total inelastic cross sections Q_{inel} and the threshold energies $V(r_{\text{min}})$ for the inelastic excitations are estimated from a simple optical model, for $\text{CCl}_4 + \text{Kr}$, $Q_{\text{inel}} \geq 20$, ≥ 24 , and $\geq 47 \text{ \AA}^2$ corresponding to $V(r_m) \leq 0.59$, ≤ 2.22 , and $\leq 5.54 \text{ kcal mole}^{-1}$ for $\bar{E} = 1.43$, 3.60 and $12.6 \text{ kcal mole}^{-1}$, respectively; and for $\text{CCl}_4 + i\text{-C}_8\text{H}_{18}$, $Q_{\text{inel}} \geq 56$, $\geq 96 \text{ \AA}^2$ corresponding to $V(r_{\text{min}}) \leq 0.7$, $\leq 3.9 \text{ kcal mole}^{-1}$, for $\bar{E} = 1.80$ and $15.1 \text{ kcal mole}^{-1}$, respectively.

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77. THE SCATTERING OF I ATOMS BY KRYPTON. M. J. Cardillo, M. S. Chou, and E. F. Greene, Chemistry Department, Brown University, Providence, R. I. 02912.

The well depth for the interaction potential of I atoms and Kr atoms is estimated from measurements of the differential cross section. A beam of I atoms, produced by thermal dissociation of I_2 , is velocity selected and scattered from a cross beam which emerges from a source at 132°K. The scattered I atoms are detected by the formation of negative ions at a hot surface of thoriated tungsten. In some experiments the I atoms are accelerated by sending them into an excess of He. From the rainbow structure observed in experiments at relative initial kinetic energies of 2.6, 3.2, and 8.6 kcal/mole the well depth is estimated to be 0.5 ± 0.1 kcal/mole for a potential of the Lennard-Jones (12-6) or the exp-6 ($\sim 12-14$) forms. The rainbow structure is not well resolved. This may be the result of scattering which occurs from two potentials (both $^2\Sigma$ and $^4\Pi$ states are formed from I and Kr atoms in their ground states) having nearly equal well depths. The scattering shows no evidence for well depths of the size suggested from the interpretation of the temperature dependence of the rate of recombination of I atoms in the presence of an excess of a rare gas, 1.2 to 2.8 kcal/mole for I atoms and Ar (J. A. Blake and G. Burns, J. Chem. Phys. 54, 1480 (1971)).