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

Progress Report

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October 1972 - October 1973

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PREPARED FOR THE U.S. ATOMIC ENERGY COMMISSION UNDER
CONTRACT AT(11-1)-3129

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ABSTRACT

The unfolding of molecular beam scattering data to yield cross sections, the interpretation of the amplitudes of the glory oscillations in the velocity dependence of the total cross section and the construction of a simple molecular beam apparatus for student experiments on reactive scattering are described in publications. Inelastic scattering of CsCl and CsI by Ar and Xe are being studied over a range of relative kinetic energy of 1 to 2 kcal mole⁻¹ at several laboratory angles. The inelastic cross sections are a substantial fraction of the elastic cross sections at large angles. Beams of halogen containing molecules produce negative ions when they hit surfaces of Nb and LaB₆. On the latter the efficiency of formation of negative ions can be as great as 0.1 for iodides and still larger for bromides. Experiments have shown that a beam of CH₂Cl₂ molecules can be accelerated without significant attenuation by interaction with a beam of electrons. The increase in velocity has been up to 20 percent. Attempts to study the elastic cross sections for the scattering of halogen atoms by the rare gases and the reactive cross sections for the scattering of molecules with internal excitation are continuing.

The work on AEC Contract AT(11-1)-3129 has progressed since October 1972 as follows.

1. Publications

- a. R.P. Creaser, R.P. English, and J. L. Kinsey, J. Chem. Phys., 58, 1321 (1973). Linear least-squares fitting of molecular-beam differential cross section data using spline functions. Reprints are enclosed.
- b. E.F. Greene and E.A. Mason, J. Chem. Phys., 59, 2651 (1973). Interpretation of glory undulations in scattering cross sections: Amplitudes. Copies are enclosed.
- c. Bro. R. J. Conley, E.F. Greene, and S. M. McInnis, J. Chem. Educ., (submitted for publication). A molecular beam apparatus for student experiments on reactive scattering. Preprints are enclosed.

2. Status of current research

- a. The efficiency with which molecules form positive and negative ions when they collide with hot surfaces has been studied for several combinations of molecules and surfaces over a range of surface temperature and kinetic energies of the beam. The molecules include CCl_4 , CsI , CsCl , Br_2 , CH_3I and the surfaces which have been used are Nb, Re and LaB_6 . Figure 1 shows the temperature dependence of the electron current I_{e1} emitted from a Nb surface as well as the currents of positive (I_+) and negative (I_-) ions formed when a CsCl beam hits this surface. Analysis of these results shows that the apparent work function of Nb is $\phi_{\text{Nb}} = 4.6 \pm 0.2$ eV which is about 0.5 eV

higher than values often quoted in the literature. Fig. 2 shows a corresponding plot for dependences for the currents I_+ and I_- from beams of CsI on a LaB_6 surface. At the most favorable temperatures (approximately 1250°K) the efficiencies for the formation of negative ions (presumably I^- and Br^-) from beams of CsI and Br_2 incident on LaB_6 are about 0.10 and 0.5 respectively. These relatively high values may make LaB_6 a useful detector for beams of halogen containing molecules and possibly also a useful source of negative ions of these halogens. In addition studies of this type may help to provide understanding of the interaction of molecules with surfaces at high temperatures.

- b., Studies of inelastic scattering of alkali halide molecules by inert gases have been in progress for several years but now seem at last to be giving reliable results. The program planned is now half completed. It consists of measuring the scattering of velocity selected beams of CsI and CsCl from cross beams of Ar and Xe each for three different kinetic energies in the range 1 to 2 kcal mole^{-1} with velocity analysis of the scattering at 3 different laboratory angles. Similar experiments with the elastic scattering of Cs from Ar and Xe serve as checks to assure satisfactory

understanding of the parameters of the apparatus. An example of two recent experiments is shown in Fig. 3. The numbered lines beside the curve for $\text{CsCl} + \text{Ar}$ show how many vibrational quanta of CsCl would have to be transferred to translational energy of relative motion to produce scattered intensity at that particular analyzer spread. The results should be helpful in providing some understanding of energy transfer in collisions and for comparison with theoretical studies of inelastic scattering.

- c. The acceleration of beams of heavy molecules by seeding them into an excess of a light gas such as He and letting the mixture flow through a nozzle into a vacuum chamber is well established as a useful technique for producing collisions at super thermal energies. Preliminary experiments have been carried out to test the possibility of accelerating neutral molecules by subjecting them to repeated collisions with a stream of much lighter particles, namely electrons. An electron current of several hundred mA over a cross sectional area of about 1 cm^2 is constrained by a magnetic field to flow along the molecular beam for a path of approximately 10 cm. Fig. 4 shows how the presence of the electrons affects the velocity distribution of a coaxial beam of CH_2Cl_2 . There is an appreciable shift to higher molecular speeds

when the electron current is on. Although the increase in speed is only about 20%, the effect may be expected to increase as the various parameters are made more nearly optimum. The experiment suggests the intriguing possibility that electron beams may be used to control the speed and angular distributions of beams of neutral molecules.

- d. Attempts were made to study differential cross sections for the scattering of halogen atoms by rare gas atoms. These cross sections might have yielded the depth of the potential well for such pairs as I-Ar and would have been of interest in connection with theoretical work on the rate of recombination of I atoms to form I_2 in the presence of an excess of Ar. The first step in this project was the production of a well collimated cross beam of Ar having a narrow velocity distribution. This was achieved by constructing a nozzle source followed by a skimmer and a collimating aperture. The cross beam can provide up to approximately 2% attenuation of a primary beam of atoms such as Cs and the angular and speed distributions of the Ar beam are satisfactorily narrow. This is shown by both the rise and the following abrupt fall in the laboratory differential cross section near the maximum scattering angle permitted by kinematic

restraints for the collision of a heavy particle (Cs) with a lighter one (Ar). See Fig. 5.

Unfortunately the experiments possible with Cs + Ar were not directly repeatable with I + Ar because the detectors used, the production of negative ions at surfaces of Nb and LaB₆, were somewhat too insensitive (Nb) or produced too large a background of electrons (LaB₆) to be immediately usable. This has meant that no improvements over the preliminary results reported last year for halogen atoms scattered by rare gases have been achieved as yet.

- e. Improvements in the methods of data collection, particularly in connection with the measurements of inelastic scattering (section 2b), are being attempted. The scattering signal from the detector filament has been recorded up to this time as an analog signal on an electrometer; soon it will be processed digitally and counted. Plans for the new arrangement have been made and some of the new equipment necessary has been assembled and tested. This change should improve both the accuracy and the convenience of doing the experiments.
- f. A proposal was made to study the effect of internal excitation of one of the reactants in a chemical reaction on the cross section σ_R . The reaction

$$\text{K} + \text{HCl} \longrightarrow \text{KCl} + \text{H}$$
 was considered as a standard

since the work of Odiorne, Brooks, and Kasper (J. Chem. Phys., 55, 1970 (1971)) showed a strong dependence of σ_R on the vibrational excitation of HCl. Several methods of exciting internal states of molecules, such as HCl, have been considered in detail. Two useful possibilities seem to be a) passage of a beam through a hot tube and b) electron bombardment of the molecules in the beam by electrons at low energies. Neither has been tried in an actual experiment as yet, but both seem to be interesting and good candidates for experiments.

4. Personnel

During the past year various people have been involved with and contributed to the projects which have been supported by the contract. The symbols in parentheses after the names refer to sections of this report.

Dr. S.M. Bobbio (2a, 2c, 2d) left in August 1973 to accept appointment as an Assistant Professor in the Chemistry Department at the University of Georgia.

Dr. S.E. Johnson (2a, 2f) also left in August 1973. He is now a staff member at the Institute for Defense Analysis.

Dr. R.L. Hall (2b, 2e) received his Ph.D. from Yale and is completing his first year as a research associate.

Dr. Cary C.T. Chiou (2a, 2c) arrived in September 1973 after receiving his Ph.D. from Kent State University.

Mr. W.D. Armstrong (2b) should finish his work for his Ph.D. during the coming year.

Mr. H. Lambropoulos (2a, 2c), a second year graduate student, has just begun experimental work.

Mr. N. Sondergaard (2c) a graduate student who has just returned to Brown after a year's leave of absence, is also just starting experimental work.

Miss V. Vaida (2a) and Mr. S. McInnis (1c) were undergraduates working on molecular beam projects. Miss Vaida received her undergraduate degree last June and is now a graduate student at Yale.

The collaboration with Professor E.A. Mason (1b) continues and may become more extensive.

As has been true in the past the principal investigator, Professor E. F. Greene, spends 50% of his time on the work supported by the contract. This is expected to continue.

CsCl Beam on Nb Surface at Temperature T

a) Electron Emission I_{el}

b) Negative Ion Current I_-

c) Positive Ion Current I_+

Fig. 1

$\log \frac{I_{el}(A)}{T(^{\circ}K)^2}$

$\log I_-(A)$

$I_+(A) \times 10^9$

$T = 1850^{\circ}K$

$T = 1400^{\circ}K$

$10^4/T(^{\circ}K)$

Fig. 2

Temperature dependence of the positive (I_+) and negative (I_-) ion currents from a CsI beam incident on a LaB_6 surface reduced by the corresponding I_+ from a Nb surface. Since the latter produces positive ions with approximately unit efficiency, the ratio is the ionization efficiency on LaB_6 .

Velocity Analysis of CsCl and Cs Beams Scattered by Ar

Fig. 3

CsCl + Ar

8° laboratory angle

v_S 280 Hz

E 1.94 kcal/mole

4

3

2

1

0

LOG I

Arrows show location expected
for forward (f) and backward
(b) elastic scattering

Cs + Ar

8° laboratory angle

v_S 320 Hz

E 1.99 kcal/mole

b

f

100

160

v_A (Hz)

220

280

1

Velocity Distribution I of CH_2Cl_2 Beam without (•) and with (O) Acceleration by a Coaxial Beam of Electrons.

Fig. 5

Differential Scattering Cross Section I for
Cs from Ar at a Relative Initial Kinetic
Energy of $1.42 \text{ kcal mole}^{-1}$

(arrows show kinematic limits for
the scattering of monoenergetic
and unidirectional beams with
the nominal values of the actual
beams)

Resolution of Cs velocity selector
($\Delta v/v$) $\circ$ 15%, $\bullet$ 6%

I
(arbi-
trary
units)

Laboratory scattering angle (deg.)