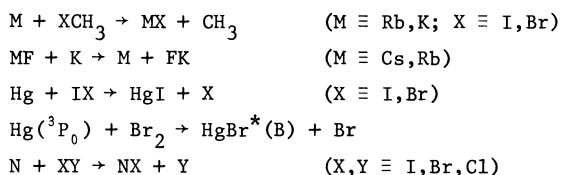MOLECULAR REACTION DYNAMICS BY THE CROSSED MOLECULAR BEAM TECHNIQUE: A FEW RECENT EXAMPLES

Richard B. Bernstein

Department of Chemistry, Columbia University, New York, N.Y. 10027, U.S.A. and The University of Texas, Austin, TX 78712, U.S.A.

Abstract – Several recent examples are presented of experimental studies by the author and his co-workers on the microscopic chemical dynamics of elementary reactions via the crossed molecular beam technique. The reactions investigated include the following:

$$M + XCH_3 \rightarrow MX + CH_3 \qquad (M \equiv Rb,K; \; X \equiv I,Br)$$

$$MF + K \rightarrow M + FK \qquad (M \equiv Cs,Rb)$$

$$Hg + IX \rightarrow HgI + X \qquad (X \equiv I,Br)$$

$$Hg(^3P_0) + Br_2 \rightarrow HgBr^*(B) + Br$$

$$N + XY \rightarrow NX + Y \qquad (X,Y \equiv I,Br,Cl)$$

INTRODUCTION

The subject of molecular dynamics is concerned with the microscopic, molecular mechanism of elementary chemical reactions (Ref. 1). Fundamental details of the intimate process of reaction via collision of atoms and molecules can be provided from experiments which make use of the crossed molecular beam method. Typically, measurements are made of the angular and recoil velocity distributions of the nascent products of a binary molecular reaction, from which a number of important features of the intermolecular potential energy hypersurface can be deduced fairly directly.

At the previous IUPAC Congress the author reviewed the mutual interplay of theory with experiment in the field of molecular reaction dynamics (Ref. 2). The present paper is devoted to the presentation of a few case studies, examples of elementary reactions investigated by the crossed beam technique in the author's laboratory, which have been subjected to detailed theoretical-computational analysis.

RESULTS

The first of these examples consists of a precise quantitative measurement of the translational energy dependence of the total reaction cross section for a direct-mode, rebound reaction, $Rb + ICH_3 \rightarrow RbI + CH_3$ (Ref. 3), serving as a test of various theoretical predictions. A quantitative determination of the ratio of the cross section for this reaction to that of the closely related reaction with potassium over a wide energy range has been carried out (Ref. 4), allowing comparison with several theoretical dynamical calculations in the literature. These experiments, taken together with previously published results, have confirmed the existence of small translational energy thresholds E_0 for these reactions, beyond which the reaction cross section $\sigma_R(E_{tr})$ rises to a maximum with increasing translational energy E_{tr} and then declines to a minimum at energies ≥ 0.9 eV.

Very recent experiments on the reactions of K and Rb with CH_3Br (Ref. 5) have shown clear evidence for appreciable energy thresholds (ca. 0.1-0.2 eV), corresponding to substantial activation barriers. These results account for the very small thermal cross sections for the exoergic CH_3Br-alkali family of reactions.

The second study deals with the complex-mode reactions $CsF,RbF + K \rightleftarrows [CsFK,RbFK] \rightarrow Cs,Rb + FK$. The branching ratios for the decay of the collision complexes have been measured as a function of the relative translational energy (Ref. 6), and the influence of the rotational energy of the diatomic reagent has been directly determined (Ref. 7 & 8). It is of interest

to note that for the CsF reaction, which is endoergic, the reactive branching fraction F_R increases with E_{tr}, and the reactivity is enhanced by reagent rotational energy, E_{rot}, while for the exoergic RbF reaction, F_R decreases with E_{tr} and with E_{rot} as well. The results have been interpreted in terms of the RRKM-Herschbach (RRKMH) model for formation and decay of a long-lived triatomic complex (Ref. 9).

The third investigation involves first the endoergic (1.15 eV) reaction $Hg + I_2 \rightarrow HgI + I$, for which the translational energy threshold, E_0, has been experimentally determined (Ref. 10). It is found that E_0 is essentially equal to the endoergicity, implying that the intrinsic activation barrier for the reaction is, for practical purposes, zero. Evidence is presented from angular distribution measurements over a wide range of translational energies that the reaction proceeds via the insertion of Hg into I_2 to form the normally stable IHgI molecule, which must decay (because of its excess internal energy) either into the products $HgI + I$ or the reactants $Hg + I_2$. The onset of collision-induced dissociation (at 1.54 eV) is observed (Ref. 11). An empirical potential energy surface for this system has been deduced (Ref. 12) from these results. The entire body of experimental data can be understood in terms of an extended version of the RRKMH theory, assuming the presence of a barrier of ca. 0.5 eV in the entrance channel. Confirmatory experiments have been carried out for the analogous reaction of Hg with IBr (Ref. 13); the (different) thresholds for the formation of both HgI and HgBr products have been overcome by translational excitation.

The fourth investigation deals with the reaction of metastable Hg atoms, i.e., $Hg(6^3P_0) + Br_2 \rightarrow HgBr^*(B^2\Sigma^+) + Br$, observed in a crossed beam experiment via the chemiluminescence of the $HgBr^*$ product at 500 nm (Ref. 14). The cross section is smaller by more than an order of magnitude than that reported in the literature for the analogous reaction with $Hg(6^3P_2)$ atoms. This difference in reactivity is apparently a spin-orbit effect, suggesting a potential energy barrier for the $^3P_0$ reaction which is absent for the $^3P_2$ case.

The final example consists of a series of bimolecular beam reactions of atomic nitrogen (Ref. 15). Five reactions of the type $N + XY \rightarrow NX + Y$ (where $X,Y \equiv I,Br,Cl$) have been observed using the crossed molecular beam scattering technique. The NX product is mass spectrometrically detected over a range of scattering angles. From the product intensities it is concluded that the cross sections (for the exoergic reactions) are large (i.e., essentially gas-kinetic). A number of other reactions of atomic nitrogen reported in the literature on the basis of flame, discharge and other types of bulk, gas phase, experiments occurred with only negligible cross sections when the experiment was carried out under single-collision (beam vs. beam) conditions. Few of them appear to be bimolecular elementary reactions.

CONCLUDING REMARKS

This paper has reviewed a few examples of elementary chemical reactions studied recently by the author and his co-workers by means of the crossed molecular beam technique. Due to considerations of brevity, it has, unfortunately, been impractical to refer to the many significant contributions of other molecular beam laboratories around the world. It should be emphasized, however, that molecular beam chemistry is an activity now being actively pursued in many laboratories scattered throughout IUPAC-land, and the combined knowledge derived from such molecular dynamics studies is of great value in providing an understanding of the microscopic mechanism of elementary chemical reactions.

REFERENCES

1. R.D. Levine and R.B. Bernstein, Molecular Reaction Dynamics, Clarendon Press, Oxford (1974); Japanese edition, H. Inouye, Editor, Tokyo Press (1976).
2. R.B. Bernstein, 25th IUPAC Congress, Jerusalem; Israel J. Chem. 14, 79 (1975).
3. S.A. Pace, H.F. Pang and R.B. Bernstein, J. Chem. Phys. 66, 3635 (1977).
4. K.T. Wu, H.F. Pang and R.B. Bernstein, J. Chem. Phys. (submitted).
5. H.F. Pang, K.T. Wu and R.B. Bernstein (to be published).
6. S. Stolte, A.E. Proctor and R.B. Bernstein, J. Chem. Phys. 65, 4990 (1976).
7. S. Stolte, A.E. Proctor, W.M. Pope and R.B. Bernstein, J. Chem. Phys. 66, 3468 (1977).
8. L. Zandee and R.B. Bernstein (to be published).
9. S. Stolte (to be published).

10. B.E. Wilcomb, T.M. Mayer, R.B. Bernstein and R.W. Bickes, Jr., J. Amer. Chem. Soc. 98, 4676 (1976).
11. T.M. Mayer, B.E. Wilcomb and R.B. Bernstein, J. Chem. Phys. 67, (1977), in press.
12. T.M. Mayer, J.T. Muckerman, B.E. Wilcomb and R.B. Bernstein, J. Chem. Phys. 67, (1977), in press.
13. S. Hayashi, T.M. Mayer and R.B. Bernstein (unpublished).
14. S. Hayashi, T.M. Mayer and R.B. Bernstein, Chem. Phys. Lett. (submitted).
15. R.L. Love, J.M. Herrmann, R.W. Bickes, Jr. and R.B. Bernstein, J. Amer. Chem. Soc. (submitted).