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INTRODUCTION

Recent advances in methods of quantum mechanical calculations, electronic computer capabilities and microscopic experimental methods, have put us in a position to understand, evaluate and extend our current knowledge of elementary chemical reactions. It is certain that in the future, information derived from first principles will become more important in understanding chemical processes, although chemistry will remain largely an experimental science.

Microscopic experiments, such as molecular beam methods are not the general means for obtaining precise data on rate constants. They are designed not only to reveal detailed information on reaction dynamics with which to gain a clear understanding of macroscopic phenomena, but also to provide a benchmark for the future development of quantum chemical methods for solving the problems of chemical kinetics. Actually, collection of rate constants alone is not sufficient to understand many chemical phenomena. For example, in the modelling of chemical lasers, it is necessary to have detailed information on reaction dynamics.

We will discuss contributions which crossed molecular beams have made to our understanding of elementary chemical reactions. It is likely that the advancement of crossed beam methods will make it an important tool for obtaining new chemical information in the future.

An understanding of elementary chemical reactions ultimately requires a knowledge of how the fundamental laws of mechanics work to produce the observed reaction rates. The dynamical description of chemical reactions is a problem in mechanics, the solution of which is provided by quantum mechanics, although the mathematical machinery is not yet sufficiently developed that a quantitative rate constant can be obtained routinely from first principles. The rapid development of methods to calculate potential energy surfaces and to obtain microscopic information about chemical reactions from such surfaces is demanding precise experimental results for evaluation of theory. The crossed molecular beam method is particularly well suited to provide just this knid of detailed microscopic information for use as standards of comparison. Initial state specification has become quite sophisticated with techniques for producing very narrow velocity distributions, molecules in selected ro-vibrational states and beams of oriented molecules. Product velocity distributions are used to obtain the partitioning of energy between translation and internal excitation. Angular distributions of product may contain information on the lifetime and preferred orientation of the collision complex, and on angular momentum disposal. In some cases, with measurement of chemiluminescence, or using the laser induced fluorescence method, one can obtain product quantum state distributions. The theoretical models, developed to calculate thermal rate constants have also been advanced to calculate microscopic parameters, such as the product energy and angular distributions.

The interplay between microscopic experiments and theoretical advancements could be best exemplified in the reaction of F + H_2,[1] a system which has received great attention by theoreticians as well as experimentalists. Ab *initio* and semi-empirical calculations of the potential energy hypersurface for the ground electronic state of FH_2, have provided a basis for the computation of rate constants and product energy distributions. Microscopic parameters have been calculated with extensive 3-D classical trajectory calculations. Exact 1-D quantum calculations have been computed on some potential energy surfaces and extensive 3-D quantum mechanical calculations are expected to be carried out in the near future. For the simple reactions such as F + H_2, with the advancement of more efficient methods of scattering calculations, it will be possible to calculate reliable rate constants from first principles. The reliability of the calculations eventually will rest on the accuracy of the potential energy surface. Here, the information on reaction dynamics obtained by the microscopic experiment becomes invaluable. Chemiluminescence and chemical laser techniques have provided detailed product vibrational-rotational state distributions. In crossed molecular beam[2] experiments of F + D_2, favorable kinematics makes it possible to obtain angular distributions of various product vibrational states. The exoergicity of the reaction (31.5 kcal/mole) plus the initial relative kinetic energy permits population of the fourth vibrational state of DF products. At low collision energies, the product in each vibrational state is mainly backscattered as expected, since the linear configuration has the lowest activation energy. As the collision energy is increased, the shift of product to the forward direction occurs at different rates for different vibrational levels. The slightly endoergic and sharply backward peaked V=4 state is shifted more toward forward scattering while the V=3 state is only slightly affected. It is just this type of microscopic behavior which provides the theoretician with important tests of the potential energy surface. Until the surface can reproduce these detailed microscopic measurements, the reliability of rate constants calculated will remain questionable. Of course, the product state distributions obtained from microscopic experiments are essential in the understanding of HF chemical laser and other macroscopic phenomena involving the reaction of $F + H_2$.

The fact that the molecular beam method can be used to investigate molecules under collision free or single collision conditions makes it a very unique tool for the investigation of important intramolecular energy transfer processes in unimolecular reactions. Molecular beams have recently been used extensively to study unimolecular decay processes. Polyatomic radicals or molecules can be produced in a dissociative state either as collision complexes or from the absorption of many infrared laser photons. With the energized complex decomposed in a collisionless environment, the efficiency of intramolecular energy transfer which is manifested in the dynamics of decomposition can be studied without the ambiguity of secondary or wall reactions. The primary products are positively identified by direct detection. The rate of energy randomization is compared with an experimental clock. For complexes formed by chemical activation, the rotational period serves as the standard of time; the degree of symmetry of the product angular distribution about the center of mass reveals the lifetime of the complex relative to the rotational period. In multiphoton excitation, it has been found that the molecules absorb photons to an average energy level at which the dissociation rate approximately equals the up-excitation rate. A good estimate of the molecule's lifetime can be obtained from the laser pulse width for a given laser energy. The products of the unimolecular decomposition are angle and velocity analyzed to give product translational energy distributions, which are used to evaluate the extent of energy randomization before decomposition and thus test the validity of this assumption in RRKM theory. RRKM theory, with modification to account for angular momentum conservation,[3] can predict product translational energy distributions for those cases where the exit energy barrier does not exist. Theoretical methods for the treatment of exit channel coupling effects in reactions with a potential barrier have yet to be developed. While RRKM rate constants are quite sensitive to the vibrational frequencies of the complex which may be poorly known, the product energy distribution is most affected by the better-known energetics and the extent of energy randomization. This makes the molecular beam measurements particularly useful for evaluating the postulates of the theory.

In recent bulk phase multiphoton studies[4] it has been reported that the dissociation may occur non-statistically, the primary dissociation channel being other than that predicted by RRKM theory. In particular, multiphoton dissociation of $CFCl_3$ was reported to produce CFCl as a primary product. This suggests the very attractive possibility of mode-selective bond-breaking. The identification of primary products, on which these conclusions were based, can be exceedingly difficult in the bulk phase where collision events may be important. In a molecular beam experiment, identification of products is unambiguous and measurement of the product translational energy distribution provides a test of the statistical model. Multiphoton dissociation studies of fifteen systems[5] have clarified the original confusion. The primary product of $CFCl_3$ dissociation is $CFCl_2$, as expected if the excitation energy is rapidly redistributed over internal modes. The product translational energy distributions of all systems studied agree well with RRKM calculations, strongly suggesting that the intramolecular relaxation must be much shorter than a nanosecond, the estimate lifetime, for these heavily halogenated hydrocarbons under given excitation conditions. The results of molecular beam experiments have stimulated the development of theoretical models to explain the dissociation rates, product yields, and dependence on laser characteristics.

The formation of collision complexes in crossed molecular beams provides another chance to explore the unimolecular decay process.

The energized radical molecule is formed suddenly, with excess energy above the dissociation limit varying from near zero to tens of kilocalories. The lifetime may range from subpicosecond to nanoseconds. This opens the possibility for identifying a range of applicability of the energy randomization postulate in statistical theory. The product translational energy of a large number of bimolecular reactions[6] which proceed with complex formation have been compared to statistical calculations. In reactions of halogen atoms with unsaturated hvdrocarbons there is evidence that the internal energy of the complex is not always randomized over all the internal modes. An example is the recent study of Cl + C_2H_3Br and C_3H_5Br.[7] Far more energy is found in product translation than would be expected from statistical theory. With the collision complex lifetime calculated to be under one picosecond, it is likely that the high frequency vibrational modes especially those involving C-H stretching are too decoupled from the skeletal vibrations to share fully the available energy before decomposition occurs.

The microscopic behavior of chemical systems is directly observable with the use of molecular beams. This information helps elucidate complicated macroscopic phenomena, increasing our knowledge of the dynamical processes occuring in the chemical system. The crossed molecular beam method is not, however, particularly well-suited for the direct accurate determination of thermal rate constants. The differential reactive cross section obtained in a scattering experiment has units of relative intensity. Uncertainities in product detection efficiency prohibit the assignment of absolute intensity directly. In most cases, in order to extract the absolute total reactive cross section from the measured differential cross section at a given relative velocity, the small angle elastic scattering of one of the reactants must be determined for comparison.[8] If the mass of the reactant is not very different from the product mass, the detection efficiency will be similar after account is taken of the difference in ionization efficiency. Calculations of the absolute elastic scattering cross section, based on an assumption about the long range attractive potential is used to assign absolute intensity to the differential reaction cross section, which is integrated to give the total reactive cross section. The London constant, C_6, for the long range interaction is often estimated using the Slater-Kirkwood equation[9] and known polarizabilities. In order to obtain a thermal rate constant, one would measure the total reactive cross section for a wide range of relative velocities and integrate for a thermal distribution. These reaction would not occur with a thermal distribution of rotational states if a supersonic beam is used since rotation is substantially relaxed in the supersonic expansion. Individual total cross section estimated by the above method may have errors in excess of 50%. Thermal rate constants obtained in this manner would sometimes be subject to large uncertainities.

While the crossed molecular beam technique is not expected to yield highly accurate thermal rate constants, it remains a valuable source of information for the bulk phase experimentalist. In bulk phase experiments, secondary reactions are frequently encountered as obfuscating complications in the determination of reaction mechanisms. The primary collision event may produce a species with sufficiently short lifetime that its existence is completely obscured. This transience does not diminish the importance of the intermediate in the reaction mechanism. The result can be observation of "mysterious" behavior of the system, with no model successfully explaining all observations. When a radical intermediate is postulated to explain the experimental data, the paucity of information concerning nature and energetics of the radical reduce the plausibility of the explanation. Crossed molecular beams provide an unambiguous solution to the question of primary reaction products and offer information about the reaction energetics, thereby explaining peculiar behavior of bulk-phase systems. One example of this type of application is the reaction of I_2 with F_2. The reaction was studied in a low pressure flow system by Johnston et al.,[10] who measured the chemiluminescence from the $A^3\pi_0{}^+$ states of IF. They provided strong evidence that the reaction proceeds with low activation barrier. The energy of the fluorescence also indicates that the IF must be produced in a step which is exoergic by about 65 kilocalories. These observations are inconsistent with either of the generally accepted mechanisms for this type of exchange reaction; a four-center exchange, or an atom-molecule chain reaction. A cross beam study[11] of $F_2 + I_2$

provided answers to the question of mechanism. The single collision environment permitted the exciting observation of I_2F as the primary product of the single collision. The existence of such radical halogen triatomics had often been postulated as intermediates in photochemical reactions but their high reactivity had prevented direct observation. Variation in collision energy was used to establish a threshold energy for I_2F formation of 4 kilocalories. This easily explains the observed low activation energy. At higher collision energies IF production is observed. Analysis of product velocity and angular distributions show that the IF product is not sufficiently energetic to have come from the highly exoergic four-center reaction and is asymmetrically distributed about the center of mass, a kinematic impossibility from the four-center reaction. Thus the IF is produced from decomposition of the initially formed I_2F. It is interesting that IF produced from the reaction F + I_2F would have sufficient energy to produce the chemiluminescence observed by Johnston et al. The molecular beam method allowed direct observation of the radical intermediate I_2F, determination of the energetics of its formation, and elimination of the four-center reaction as a possible mechanism for the chemiluminscent reaction of $I_2 + F_2$ producing IF at thermal energies.

The molecular beams method, not only provides important information on unimolecular and bimolecular reactions, but also plays a very important role in the understanding of termolecular reactions. In the past, theoretical understanding of termolecular recombination was hindered by the lack of reliable information on the interaction potential. A theoretical treatment of halogen atom recombination in a rare gas environment requires a knowledge of the rare gas-halogen potential surfaces. The simple radical molecule complex mechanism involves the formation of halogen-rare gas dimers, unbound or metastable, with subsequent attack by another halogen atom. The attractiveness of the halogen-rare gas potential will strongly affect the rate of reaction in this model. Molecular beams have been used to investigate potential energy functions of $F(^2P_{3/2,\ 1/2})$ interacting with $Xe(^1S_0)$. Scattering occurs off three states, the $X\frac{1}{2}$, $I\frac{3}{2}$ arising from the $^2P_{3/2} + {}^1S_0$ asymptote and the $II\frac{1}{2}$ arising from the $^2P_{1/2} + {}^1S_0$ asymptote. The differential elastic cross sections for scattering at three energies[12] were fit quite well by an $X\frac{1}{2}$ potential with $\varepsilon = 3.359$ kcal/mole and $R_m = 2.293$ Å and $I\frac{3}{2}$, $II\frac{1}{2}$ similar to the Ne-Xe potential. The $X\frac{1}{2}$ ground state, while more weakly bound than ordinary chemical bonding is considerably stronger and R_m substantially shorter than the Van der Waals interaction exhibited by the Ne-Xe system. This detailed information on many open shell systems will become available in the near future and a more realistic understanding of termolecular recombination can be expected.

As molecular beam methods advance, we can expect important microscopic information to become available to chemical kineticists. The difficulties encountered in the characterization of combustion processes as a result of the rapid radical reactions should be alleviated by molecular beam studies with newly developed radical sources. In particular the development of sources of O atom, CH_2 and CH_3, should reveal valuable information on elementary reactions which has previously eluded bulk experimentalists. The increasing sophistication of quantum chemistry and molecular scattering calculations is making possible the study of reaction dynamics from first principles, Molecular beams will surely make a significant contribution by providing strong guidance through the determination of detailed information about the primary results of the reaction event. In particular, new emphasis on state selection of the reactants in beams, will advance our understanding of the importance of vibrational and rotational energy in the dynamics of chemical reactions.

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