TILDEN LECTURE*

Molecular Beam Reactive Scattering

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1 Introduction

Since its inception as a useful technique for the study of chemical reaction dynamics, which featured in the Faraday Discussion on Inelastic Collisions of Atoms and Simple Molecules,[1] the method of molecular beam reactive scattering has flourished. Such a wide range of techniques are now employed and such a wide range of systems have been investigated that a comprehensive review would be both inappropriate and impossible to restrict to a single lecture. Discussion will therefore be restricted to measurements of some atom and free radical reactions of non-metallic species, particularly those of interest to combustion and upper atmosphere chemistry. Since the primary purpose of reactive scattering experiments is to explain the observed dynamics in terms of the form of the reaction potential energy surface, particular attention will be paid to this aspect. In many respects, the aim of reactive scattering studies is not so much the determination of the potential energy surface for a single reaction but rather the determination of as many features as possible of the potential energy surfaces for many reactions with different chemical characteristics. As chemists, our ultimate goal must be to assemble a chemistry of reaction potential energy surfaces just as there already exists a chemistry of the structures of stable molecules. In this way, the structure of potential energy surfaces may be understood in terms of their electronic structure, and the observed reaction dynamics understood as resulting from the form of the surface *via* the laws of classical and quantum mechanics which govern the nuclear motion. Hence the subject matter of this lecture will comprise but a part of the full scope of its title and the reader is referred to recent reviews[2] for a more comprehensive outlook. Here attention will concentrate on some recent developments and through them seek to point out some of the ways ahead.

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*Delivered at a symposium of The Royal Society of Chemistry, Faraday Division, at University College, London, on 23 October, 1980.

[1] D. R. Herschbach, *Discuss. Faraday Soc.*, 1962, **33**, 149; for the first observations of reactive scattering see T. H. Bull and P. B. Moon, *Discuss. Faraday Soc.*, 1954, **17**, 54; E. H. Taylor and S. Datz, *J. Chem. Phys.*, 1955, **23**, 1711.

[2] R. Grice in 'Gas Kinetics and Energy Transfer', A Specialist Periodical Report, ed. P. G. Ashmore and R. J. Donovan, The Royal Society of Chemistry, London, vol. 4, 1981, p. 1; M. R. Levy, *Prog. React. Kinet.*, 1981, **10**, 1,

2 Experimental Techniques

The basic design of molecular beam reactive scattering apparatus employing mass spectrometric detection by Lee, McDonald, Le Breton, and Herschbach,[3] has been elaborated over the past decade as shown in Figure 1, to include seeded supersonic atom beam sources[4] and cross-correlation time-of-flight analysis[5] of reaction products. The use of supersonic atom beam sources has the advantages over earlier effusive sources of narrow beam velocity distributions, higher beam intensities, and ready variation of the beam velocity over a wide velocity range by changing the molecular mass of the buffer gas used in the supersonic expan-

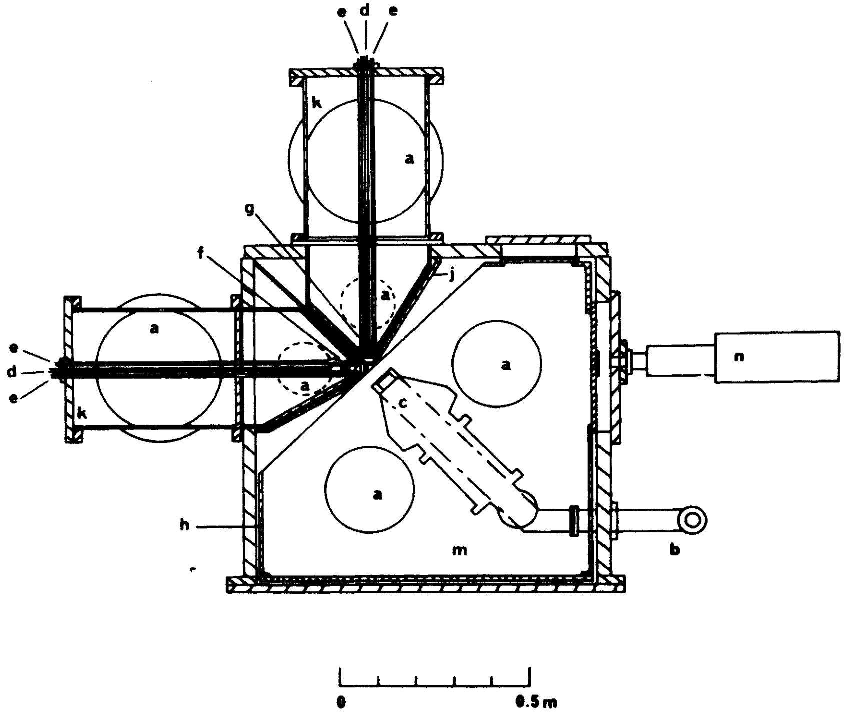

Figure 1 *Diagram of molecular beam reactive scattering apparatus:* a, *oil diffusion pumps;* b, *liquid nitrogen cold trap;* c, *mass spectrometer detector;* d, *gas inlet;* e, *water cooling tubes;* f, *microwave discharge source;* g, *cross beam nozzle source;* h, *liquid nitrogen cooled cold shield;* j, *differential pumping bulkhead;* k, *source chamber;* m, *scattering chamber;* n, *beam monitor mass spectrometer*

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[3] Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, *Rev. Sci. Instrum.*, 1969, **40**, 1402.

[4] N. Abauf, J. B. Anderson, R. P. Andres, J. B. Fenn, and D. G. H. Marsden, *Science*, 1967, **155**, 997.

[5] V. L. Hirschy and J. P. Aldridge, *Rev. Sci. Instrum.*, 1971, **42**, 381; C. V. Nowikow and R. Grice, *J. Phys. E*, 1979, **12**, 515.

sion. Seeded supersonic beam sources of alkali,[6] hydrogen,[7] halogen,[8] and oxygen[9] atoms have all been used in reactive scattering experiments. Until recently these advantages had been confined to atom beam sources with the more difficult task of producing free radical beams being achieved only with effusive sources,[10,11] This situation is now being remedied, however, with the development of supersonic free radical sources[12] which use the pyrolysis method for the production of CH_3 and CF_3 radical beams and the discharge method for OH radical beams. The cross-correlation time-of-flight method[5] offers a ten-fold improvement in signal retrieval efficiency over the conventional time-of-flight method[13] and is normally the method of choice for measuring velocity distributions of reactive scattering in the presence of significant background noise. However, the conventional method proves to be adequate for monitoring[14] the velocity distribution of the reactant atom or free radical beam where the magnitude of the signal intensity poses little problem. These techniques now permit the measurement of differential cross-sections[15] as a function of initial translational energy for a wide range of bimolecular reactions, including the resolution of individual product vibrational states[16] in favourable cases.

There have been similar developments over this period in the use of the infrared chemiluminescence[17] and laser-induced fluorescence[18] methods of determining distributions of product vibrational and rotational states. In the most favourable cases, differential cross-sections may be determined for individual product states from laser fluorescence measurements[19] of Doppler profiles. Additional information on reaction dynamics may also be gained from the dependence of reaction on reactant orientation and from the orientation of product angular momentum; properties which have proved to be accessible *via* laser excitation of reactants[20] and chemiluminescence detection[21] of products.

[6] R. A. Larsen, S. K. Neoh, and D. R. Herschbach, *Rev. Sci. Instrum.*, 1974, **45**, 1511

[7] J. W. Hepburn, D. Klimek, K. Liu, J. C. Polanyi, and S. C. Wallace, *J. Chem. Phys.*, 1978, **69**, 4311.

[8] J. M. Farrar and Y. T. Lee, *J. Chem. Phys.*, 1975, **63**, 3639; J. J. Valentini, M. J. Coggiola and Y. T. Lee, *Rev. Sci. Instrum.*, 1977, **48**, 58.

[9] P. A. Gorry and R. Grice, *J. Phys. E*, 1979, **12**, 857; S. J. Sibener, R. J. Buss, C. Y. Ng, and Y. T. Lee, *Rev. Sci. Instrum.*, 1980, **51**, 167.

[10] I. Veltman, A. Durkin, D. J. Smith, and R. Grice, *Mol. Phys.*, 1980, **40**, 213.

[11] L. C. Brown, J. C. Whitehead, and R. Grice, *Mol. Phys.*, 1976, **31**, 1069; J. A. Logan, C. A. Mims, G. W. Stewart, and J. Ross, *J. Chem. Phys.*, 1967, **64**, 1804.

[12] J. H. Williams, G. L. Duncan, D. J. Smith, and R. Grice, to be published.

[13] J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.*, 1972, **56**, 769.

[14] F. E. Davidson, A. R. Clemo, G. L. Duncan, R. J. Browett, J. H. Hobson, and R. Grice, *Mol. Phys.*, 1982, in the press.

[15] P. A. Gorry, C. V. Nowikow, and R. Grice, *Mol. Phys.*, 1979, **37**, 329.

[16] R. K. Sparks, C. C. Hayden, K. Shobatake, D. M. Neumark, and Y. T. Lee, in 'Horizons of Quantum Chemistry', ed. K. Fukui and B. Pullman, D. Reidel Publishing Company, Dordrecht, 1980, p. 91; Y. T. Lee, *Ber. Bunsenges. Phys. Chem.*, 1982, in the press.

[17] J. W. Hudgens and J. D. McDondald, *J. Chem. Phys.*, 1977, **67**, 3401.

[18] R. N. Zare, *Faraday Discuss. Chem. Soc.*, 1979, **67**, 7.

[19] E. J. Murphy, J. H. Brophy, and J. L. Kinsey, *J. Chem. Phys.*, 1981, **74**, 331.

[20] R. N. Zare, *Ber. Bunsenges. Phys. Chem.*, 1982, in the press; C. T. Rettner and R. N. Zare, *J. Chem. Phys.*, 1981, **75**, 3636.

[21] R. J. Hennessy, Y. Ono, and J. P. Simons, *Mol. Phys.*, 1981, **43**, 181.

Thus it is apparent that quite a comprehensive range of techniques has now been developed for the measurement of reactive scattering from a wide range of chemical reactions. Even information on termolecular reactions may be gained[22] from studying the reactions of van der Waals molecules produced in supersonic expansions.

3 Recent Results

In recent years there has been considerable activity in the study of oxygen atom reactive scattering which has revealed a fairly coherent picture of O atom reaction dynamics. These studies employed microwave or radio-frequency discharge sources with O atoms seeded in He buffer gas to give high collision energies $E \sim 35\,\mathrm{kJ\,mol^{-1}}$ and in Ne or Ar buffer gas to give lower collision energies $E \sim 14\,\mathrm{kJ\,mol^{-1}}$ closer to the thermal energy range. An interesting variation in dyanamics is exhibited by the reactions of ground state $O(^3P)$ atoms with halogen molecules. The $O + Cl_2$ reaction[23] shows essentially stripping dynamics over this energy range, with higher product translational energy for scattering in the forward direction than for the wide angle scattering. However the $O + Br_2$ reaction[24] proceeds *via* a short-lived collision complex at low collision energy with a product translational energy distribution in accord with the RRKM–AM model[25] for scattering *via* a long-lived complex. At higher collision energy the forward scattering retains a product translational energy distribution in accord with the RRKM–AM model but there is greater scattering into the backward direction with a significantly higher product translational energy. This remarkable dependence of reaction dynamics on collision energy is shown even more dramatically by the $O + I_2$ reaction which follows a long-lived collision complex mechanism[26] at very low collision energy $E \sim 3\,\mathrm{kJ\,mol^{-1}}$, but becomes dominated by rebound scattering at high collision energy $E \sim 40\,\mathrm{kJ\,mol^{-1}}$, as shown in Figure 2. The reactions of O atoms with the heteronuclear halogen molecules ICl and IBr forming OI products,[27] proceed *via* long-lived collision complexes over the full range of collision energy. Thus the O atom reactions with halogen molecules evidently involve stable intermediates but the observed dynamics depend on the total energy available to the reaction products arising from the collision energy and reaction exoergicity, relative to the binding energy of the intermediate.

The reaction of O atoms with CF_3I molecules[28] favours backward scattering of OI product at low collision energy, as shown in Figure 3, but the scattering becomes isotropic at higher collision energy, as shown in Figure 4. Essentially

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[22] D. R. Worsnop, S. J. Buelow, and D. R. Herschbach, *J. Phys. Chem.*, 1981, **85**, 3024.

[23] P. A. Gorry, C. V. Nowikow, and R. Grice, *Mol. Phys.*, 1979, **37**, 347; R. J. Browett, J. H. Hobson, F. E. Davidson, and R. Grice, *ibid.*, 1981, **43**, 113.

[24] D. P. Fernie, D. J. Smith, A. Durkin, and R. Grice, *Mol. Phys.*, in the press.

[25] S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.*, 1972, **12**, 564.

[26] D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, *Mol. Phys.*, 1975, **29**, 1813; A. Durkin, D. J. Smith, and R. Grice, *Mol. Phys.*, to be published.

[27] A. Durkin, D. J. Smith, and R. Grice, *Mol. Phys.*, in the press.

[28] P. A. Gorry, C. V. Nowikow, and R. Grice, *Mol. Phys.*, 1979, **38**, 1485.

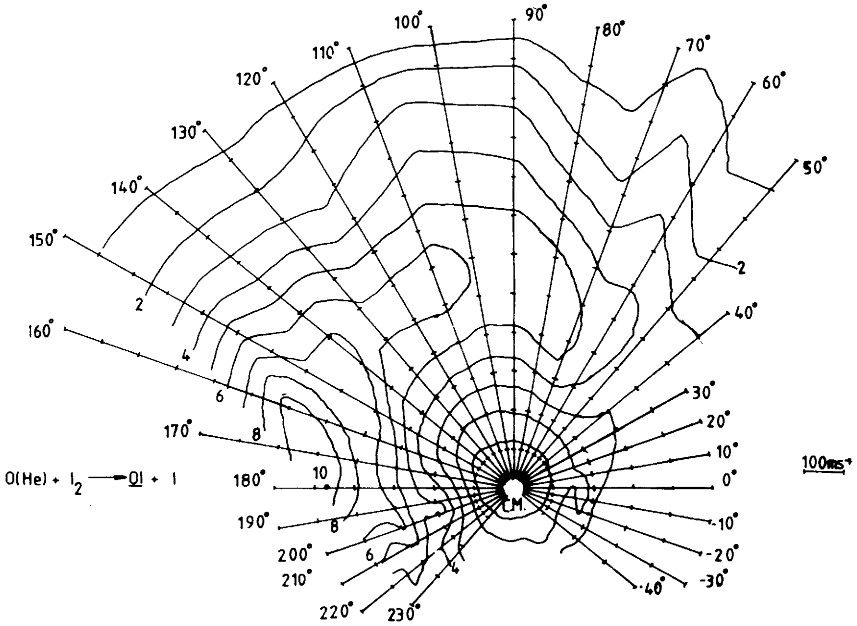

Figure 2 *Polar contour map of* OI *flux for the* O + I_2 *reaction with* O *atoms seeded in* He *as a function of centre-of-mass scattering angle* θ *and velocity* u, *at an initial translational energy* E = 43 kJ mol^{-1}. *Incident* O *atom direction is denoted by* $\theta = 0°$, *incident* I_2 *direction by* $\theta = 180°$

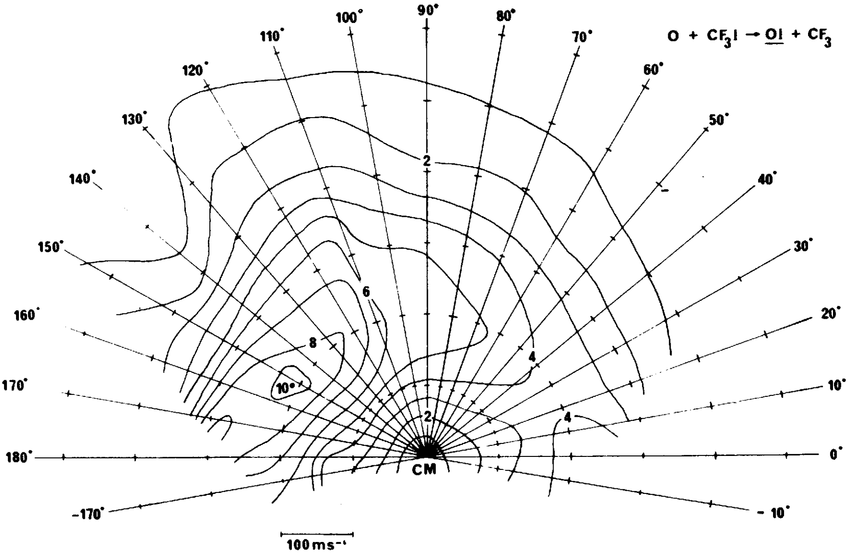

Figure 3 *Polar contour map of* OI *flux for the* O + CF_3I *reaction with* O *atoms seeded in* Ne *at an initial translational energy* E = 14 kJ mol^{-1}

(Reproduced by permission from ref. 28)

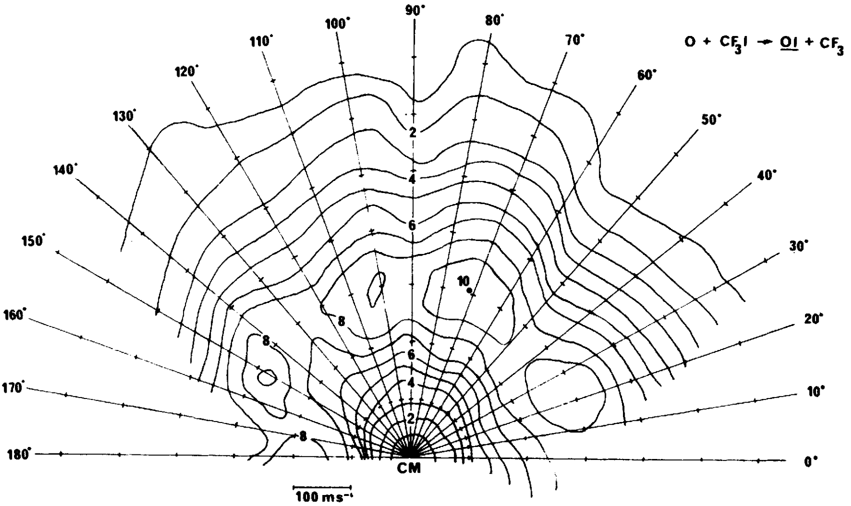

Figure 4 *Polar contour map of* OI *flux for the* O + CF$_3$I *reaction with* O *atoms seeded in* He *at an initial translational energy* E = 32 kJ mol^{-1}
(Reproduced by permission from ref. 28)

isotropic scattering is also observed[29] for the reactions of C_2F_5I and C_3F_7I molecules. The product translational energy distributions show significant energy transfer from initial translational energy to internal modes of the reaction products but this does not reach the limit corresponding to full randomization of energy over all internal modes of the reaction intermediate. The dynamics of these O atom reactions contrast with the reactions of D atoms with CF_3I, C_2F_5I, and C_3F_7I molecules,[30] which show strongly backward scattering of DI product with a very large fraction $f' \sim 0.8$ of the total energy available to reaction products being disposed into product translation. These reaction dynamics are very similar to those of the D + Br_2 reaction, but with a greater disposal of energy into product translation and little if any disposal of energy into internal modes of the product fluoroalkyl radicals. Thus the direct dynamics of the D atom reactions involve strong repulsion between the reaction products without significantly exciting internal motion of the fluoroalkyl radicals. Consequently, the substantial energy transfer to internal modes of reaction products observed in the O atom reactions, must be attributed to rather indirect dynamics, which still fall short of the complete energy randomization expected for a long-lived collision complex.

The reactions of O atoms with sulphur-containing molecules have also been studied. The reaction of CS_2 molecules[15] gives stripping dynamics with OS product scattering in the forward direction and a fraction $f' \sim 0.3$ of the total available energy being disposed into product translation. The reaction of O

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[29] R. J. Browett, J. H. Hobson, P. A. Gorry, C. V. Nowikow, and R. Grice, *Mol. Phys.*, 1980, **40**, 1315; R. J. Browett, J. H. Hobson, and R. Grice, *ibid.*, 1981, **42**, 425.

[30] F. E. Davidson, G. L. Duncan, and R. Grice, *Mol. Phys.*, 1981, **44**, 1119.

atoms with H_2S molecules[14] results in the displacement of an H atom and almost isotropic scattering, perhaps slightly favouring the backward hemisphere.

$$O + H_2S \rightarrow HSO + H \tag{1}$$

Although the exoergicity of the reaction shown in equation (1) is uncertain, it appears that a major proportion of the total available energy is disposed into product translation. The total cross-section for this reaction [equation (1)] measured as a function of collision energy[14] shows a threshold energy $E_0 = 14 \pm 2\,\text{kJ mol}^{-1}$, in agreement with the activation energy for the overall reaction of O atoms with H_2S molecules in the gas phase, thus confirming the importance of reaction pathway (1). Hydrogen atom displacement pathways have also been identified in the reactions of O atoms with the unsaturated hydrocarbon molecules C_6H_6,[31] C_2H_4, and C_2H_2.[32] The benzene reaction [equation (2)][31] proceeds *via* a long-lived triplet intermediate, which may either dissociate to the phenoxy-radical and an H atom or may undergo intersystem crossing to form a vibrationally excited singlet phenol molecule with a lifetime ~ 1 ms, which is sufficiently long for the molecules to reach the detector.

$$\begin{aligned} O + C_6H_6 &\rightarrow C_6H_5O + H \\ &\rightarrow C_6H_5OH \end{aligned} \tag{2}$$

The angular distributions for the ethene [equation (3)] and ethyne [equation (4)] reactions[32,33] are also close to isotropic but slightly favour sideways and forward scattering, indicating that the triplet intermediates of these reactions have lifetimes comparable to their rotational periods.

$$O + C_2H_4 \rightarrow CH_2\text{—}CHO + H \tag{3}$$

$$O + C_2H_2 \rightarrow CH\text{—}CO + H \tag{4}$$

The structure of the CH_2—CHO radical has been identified from the laser induced fluorescence spectrum,[34] and the dependence of the total cross-sections on collision energy,[35,33] as shown in Figure 5 for $O + C_2H_2$, yield threshold energies $E_0 = 5 \pm 3$ and $8 \pm 3\,\text{kJ mol}^{-1}$, which confirm the importance of reaction pathways (3) and (4). Both reactions dispose substantial energy into product translation, which indicates repulsion between the reaction products just as in the H atom displacement reaction [equation (1)] of H_2S molecules.

A much greater change in chemical bonding is observed[36] in the reaction of O atoms with C_2F_4 molecules, which leads to scission of the C=C double bond [equation (5)].

$$O + C_2F_4 \rightarrow F_2CO + CF_2 \tag{5}$$

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[31] S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, and Y. T. Lee, *J. Chem. Phys.*, 1980, **72**, 4341.

[32] R. J. Buss, R. J. Baseman, P. Casavecchia, T. Hirooka, and Y. T. Lee, *8th Int. Symp. Mol. Beams*, 1981, 44; R. J. Buss, R. J. Baseman, G. He, and Y. T. Lee, *10th Int. Conf. Photochem*, 1981.

[33] A. R. Clemo, G. L. Duncan, and R. Grice, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, in the press.

[34] K. Kleinermanns and A. C. Luntz, *J. Phys. Chem.*, 1981, **85**, 1966.

[35] A. R. Clemo, F. E. Davidson, G. L. Duncan, and R. Grice, *Chem. Phys. Lett.*, 1981, **84**, 509.

[36] P. A. Gorry, R. J. Browett, J. H. Hobson, and R. Grice, *Mol. Phys.*, 1980, **40**, 1325.

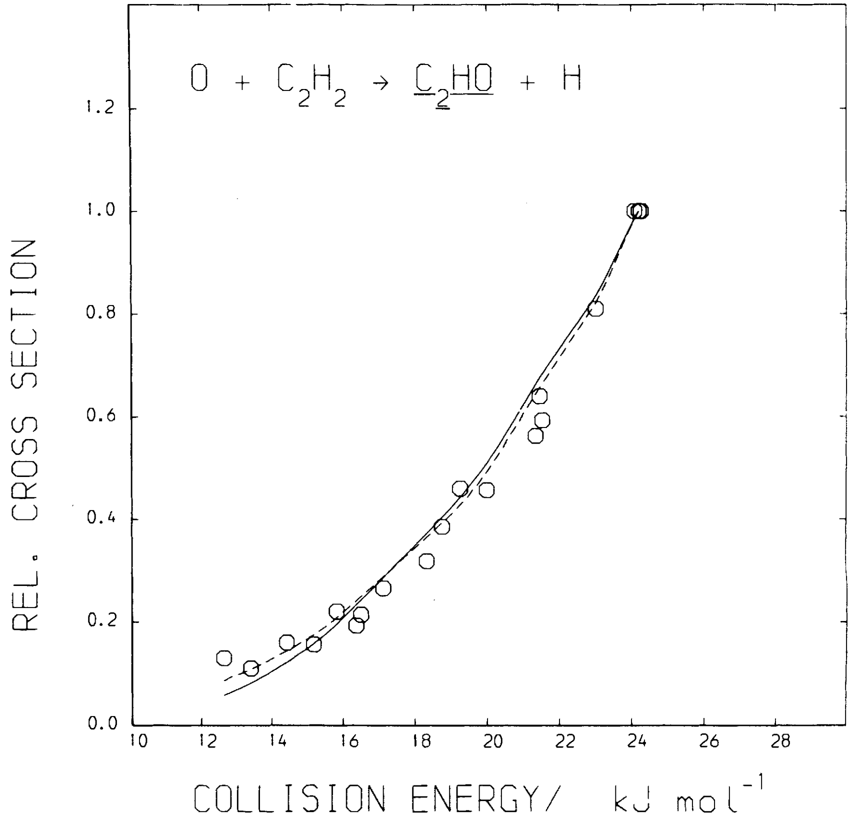

Figure 5 *Total cross-section for the* $O + C_2H_2$ *reaction as a function of initial translational energy*

The angular distribution of reactive scattering is again close to isotropic but slightly favours the forward direction, indicating that the lifetime of the triplet intermediate is comparable to its rotational period. The product translational energy distribution is close to but lies slightly above that predicted by the RRKM–AM model[25] for long-lived collision dynamics. The reactions of electronically excited $O(^1D_2)$ atoms may be studied using the radio-frequency discharge source when the corresponding reactions of ground state $O(^3P)$ atoms are inhibited by an activation energy. The reaction of CH_4 molecules[37] studied in this way, shows an H atom displacement pathway [equation (6)], whereas the reaction of H_2 molecules[38] follows a long-lived collision complex mechanism.

$$O(^1D_2) + CH_4 \rightarrow CH_3O + H \qquad (6)$$

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[37] P. Casavecchia, R. J. Buss, S. J. Sibener, and Y. T. Lee, *J. Chem. Phys.*, 1980, **73**, 6351.

[38] R. J. Buss, P. Casavecchia, T. Hirooka, S. J. Sibener, and Y. T. Lee, *Chem. Phys. Lett.*, 1981, **82**, 386.

The abstraction of H atoms from hydrocarbon molecules by ground state O(^3P) atoms has been studied[39] by laser induced fluorescence detection of the product OH radicals. This shows increased vibrational excitation along the series of primary, secondary, tertiary H atom abstraction, but low rotational excitation in all cases.

In contrast to the wealth of information which has been accumulated on O atom reactions, there has been little work on free radical reactions owing to the greater experimental difficulties involved. An effusive source of OH radicals has been used in a preliminary study of the OH + Br_2 reaction,[10] which is found to proceed *via* a long-lived collision complex with mild forward–backward peaking and a product translational energy distribution in accord with the RRKM–AM model.[25] Thus the scattering is very similar to that observed for the O + Br_2 reaction[40] at low collision energy. Early work with an effusive CH_3 radical source[11] has shown that the reactions with halogen molecules give rebound scattering and significant disposal of energy into product translation. More recent measurements[41] using He buffer gas to accelerate the CH_3 radicals show that scattering from the CH_3 + Br_2 reaction is shifted to smaller angles at increased collision energy. Thus the reactive scattering of CH_3 radicals with halogen molecules follows very similar dynamics to the corresponding D atom reactions.[13]

4 Reaction Dynamics and Electronic Structure

The reactions of ground state O(^3P) atoms with singlet molecules necessarily begin on a triplet potential energy surface. The method of frontier orbitals[42] predicts that one unpaired electron in an O atom $2p$ orbital will overlap initially with the electrons in the highest occupied orbital of the reactant molecule. The structure of the triplet intermediate and the geometry of its dissociation to reaction products is then determined by minimization of the exchange repulsion between the two unpaired electrons. When these electrons are both located on the same atom or adjacent atoms, this minimization, may be achieved by the electrons occupying mutually orthogonal orbitals, as in the O(^3P) atom. When the electrons are each located on rather distant atoms the exchange repulsion will be minimized mainly by their spacial separation and depends less on the orthogonality of the occupied orbitals. All such intermediates may be regarded as triplet diradicals.[43] However, the lowest triplet potential energy surface is usually underlain by a singlet potential energy surface with bonding which corresponds to perfect pairing of the electrons and which may have a significant ionic contribution to the wavefunction.[43] Hence the observed reaction dynamics

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[39] P. Andresen and A. C. Luntz, *J. Chem. Phys.*, 1980, **72**, 5842.

[40] D. D. Parrish and D. R. Herschbach, *J. Am. Chem. Soc.*, 1973, **95**, 6133.

[41] P. Somssich, K. Strein, and H. Schmiedel, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 401.

[42] R. G. Pearson, 'Symmetry Rules for Chemical Reactions', Wiley-Interscience, New York, 1976; I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions', Wiley-Interscience, New York, 1976.

[43] L. Salem and C. Rowland, *Angew. Chem. Int. Ed. Engl.*, 1972, **11**, 92.

are determined by the properties of the triplet potential energy surface and the probability of transition to the underlying singlet surface.

In the reactions of halogen molecules XY the triplet intermediate has a bent O—X—Y configuration. The $^3A''$ symmetry of the electronic state minimizes exchange repulsion by placing one unpaired electron in an a'' orbital and the other in an a' orbital. The electronegativity ordering rule of Herschbach[40] predicts the greatest stability when the least electronegative halogen atom occupies the central location. The stability of the intermediate with respect to reaction products is also influenced by the reaction exoergicity. Thus the O + ICl, IBr reactions have the most stable intermediates with the I atom in the central location and exhibit only a long-lived collision complex mechanism. The O + Cl_2 reaction with a Cl atom in the central location has the least stable intermediate and exhibits only a stripping mechanism. The stabilities of the intermediates in the O + Br_2 and I_2 reactions are reduced with respect to products by the reaction exoergicities. These reactions approach long-lived complex dynamics only at the lowest collision energies. At higher collision energies some reactive trajectories may pass directly through the attractive well in the exit valley of the potential energy surface[44] and especially in the I_2 case, reaction at larger impact parameters becomes inhibited by the inertia of the halogen molecule. This results in diminished forward scattering and a predominance of rebound scattering with higher product translational energy. Thus, it appears that the observed dynamics of the halogen molecule reactions may be explained by nuclear motion which is confined to the $^3A''$ potential energy surface. However the situation is less clear for the reactions of O atoms with the fluoroalkyl iodides. Donovan[45] has suggested that these reactions undergo a triplet–singlet transition in the entrance valley of the potential energy surface to form a singlet iodoso-intermediate O—I—CF_3, which is more stable than the triplet intermediate with a similar structure. Indeed the broad distribution of product translational energy observed for these iodine atom abstraction reactions would be compatible[29] with product formation from both a long-lived singlet intermediate and a shorter-lived triplet intermediate. If the triplet intermediate has ^3E symmetry in the collinear configuration, Renner–Teller splitting[46] will give rise to $^3A''$ and $^3A'$ states on bending. The lifetime of the most stable triplet intermediate with $^3A''$ symmetry with respect to the plane of bent O—I—CF_3, may be shortened by transitions to the less stable $^3A'$ state induced by rotation or vibration of the fluoroalkyl group in near collinear configurations. This is less likely for the $^3A''$ intermediates in the halogen molecule reactions since such transitions can only be induced in this case by spin–orbit interaction in the near collinear O—X—Y configuration with $^3\pi$ symmetry.

The reactions of O(^3P) atoms with halogen molecules are initiated by the

[44] D. E. Fitz and P. Brumer, *J. Chem. Phys.*, 1979, **70**, 5527.

[45] M. C. Addison, R. J. Donovan, and J. Garraway, *Faraday Discuss. Chem. Soc.*, 1979, **67**, 286.

[46] G. Herzberg, 'Electronic Spectra of Polyatomic Molecules', Reinhold Van-Nostrand, New York, 1966.

overlap of one unpaired electron in an O atom $2p$ orbital with the electrons in the antibonding π_g orbital of the halogen molecule. In the reaction of O(^3P) atoms with H_2S molecules the initial overlap is with the lone pair electrons in the $3p$ orbital located on the S atom. Thus the O atom approaches in a direction perpendicular to the plane of the H_2S molecule but, according to Walsh molecular orbital theory,[47] forms a triplet intermediate which is less acutely pyramidal and which has $^3B_1$ symmetry in the planar configuration. It has been proposed[14] that the triplet intermediate dissociates with a lifetime of less than one rotational period with the H atom departing in the plane of the product HSO($^2A''$) radical, as shown in Figure 6. A barrier to dissociation in the exit valley of the potential

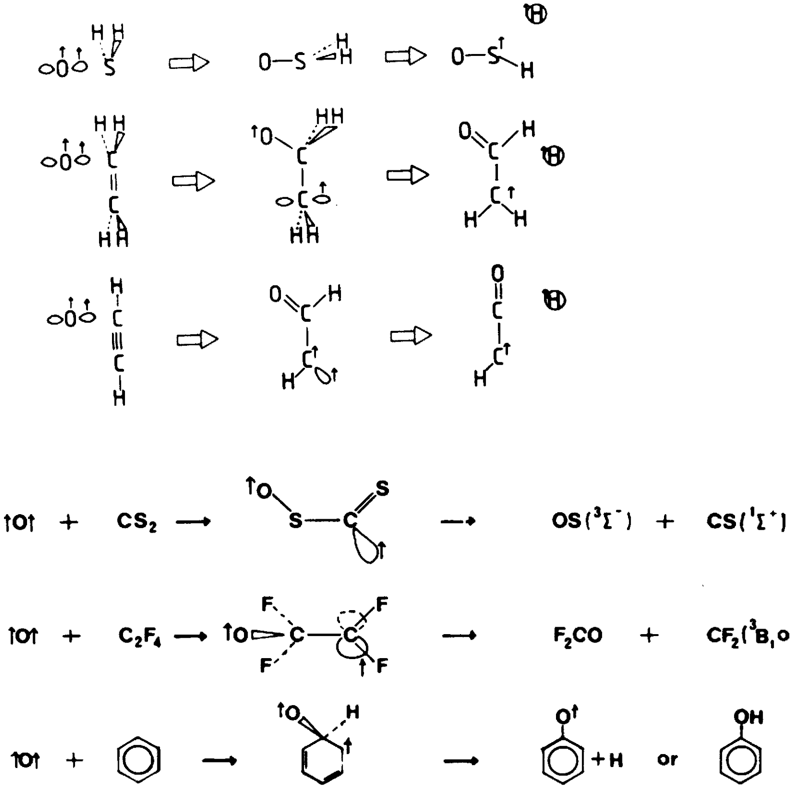

Figure 6 *Schematic diagram of the mechanisms of* O(^3P) *atom reactions*

energy surface determines the reaction activation energy and provokes repulsion between the departing reaction products. The reaction of O(^3P) atoms with CS_2 molecules is also initiated by overlap with lone pair electrons located on a sulphur

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[47] A. D. Walsh, *J. Chem. Soc.*, 1953, 2306.

atom since the highest occupied molecular orbital of CS_2 is a π_g nonbonding orbital located entirely on the S atoms.[48] A slightly extended version[15] of Walsh molecular orbital theory suggests that the triplet intermediate has a planar bent and probably *cis* configuration but gives no strong prediction as to whether the electronic symmetry is $^3A''$ or $^3A'$. Indeed the triplet diradical structure shown in Figure 6 would have the unpaired electron spins well separated by being located on the O atom and the C atom, thereby minimizing the exchange repulsion for either symmetry. The formation of such a bent triplet intermediate from the collinear CS_2 molecule followed directly by scission of the central S—C bond would seem likely to provoke rotational excitation of the OS and CS products rotating in opposite senses,[15] but no direct measurement of the product rotational state distributions has so far been made to check this.

The addition of $O(^3P)$ atoms to unsaturated carbon–carbon bonds involves initial overlap of an O atom $2p$ orbital with the π bonding orbital of the carbon–carbon bond, which requires that the direction of approach of the O atom be approximately perpendicular to the plane or axis of the molecule. *Ab initio* calculations[49] show that the triplet intermediate formed in the reaction of ethyne molecules has an almost collinear $\mathrm{O{=}CH{-}\ddot{C}H}$ carbene structure with $^3A''$ electronic symmetry as illustrated in Figure 6. The hydrogen atom product departs from the central carbon atom in the plane of the intermediate and of the product $HC_2O(^2A'')$ radical. Thus, the exchange repulsion is minimized by the orthogonality of the unpaired electrons in a manner very similar to that proposed[14] for the O + H_2S reaction. According to the Cvetanovic mechanism,[50] the reaction of ethene molecules forms a triplet $\cdot O{-}CH_2{-}CH_2\cdot$ diradical, as shown in Figure 6, in which the exchange repulsion between the unpaired electrons is minimized by their location on the O atom and the more distant C atom. Indeed, electronic structure calculations[51] show that the diradical state with $^3A''$ symmetry with respect to the O—C—C plane lies only a little lower in energy than the state with $^3A'$ symmetry and that there is only a small barrier to rotation of the terminal CH_2 group. Moreover, departure of a hydrogen atom from the central C atom leaving a planar $CH_2CHO(^2A'')$ radical requires a rotation of the terminal CH_2 group. Hence, departure of the H atom is not expected to be strongly related to the plane of the radical in this case. The product angular distributions for the O + H_2S, C_2H_2, and C_2H_4 reactions are all close to isotropic, but slight differences between them reflect the differences in the preferred directions of H atom departure. The product translational energies for O + C_2H_2 and C_2H_4 indicate repulsion between reaction products just as for the H_2S reaction, but the reaction threshold energies probably reflect barriers to addition in the entrance valley of the potential energy surface[33] rather than in the exit valley as has been suggested[14] for H_2S. The reaction of

[48] C. R. Brundle and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.*, 1969, **2**, 195.
[49] L. B. Harding, *J. Phys. Chem.*, 1981, **85**, 10.
[50] R. J. Cvetanovic, *J. Phys. Chem.*, 1970, **74**, 2730.
[51] K. Yamaguchi, S. Yabushita, T. Fueno, S. Kato, and K. Morokuma, *Chem. Phys. Lett.*, 1980, **70**, 27.

$O(^3P)$ atoms with benzene molecules also forms a triplet diradical intermediate, as illustrated in Figure 6 where the exchange repulsion is very effectively minimized by delocalization of one unpaired electron over the benzene ring. The triplet C_6H_6O diradical also has a large number of vibrational degrees of freedom so that the lifetime for H atom elimination is so long, ~ 1 ms, that intersystem crossing to form vibrationally excited singlet phenol molecules can also occur.[31] In contrast the reaction of $O(^3P)$ atoms with C_2F_4 molecules forms a triplet diradical intermediate with a structure similar to that formed in the ethene reaction but which dissociates by scission of the carbon–carbon bond with a lifetime comparable to its rotational period. The asymmetry of the product angular distribution indicates[36] that at least a major fraction of the reaction dynamics proceeds only *via* the triplet diradical intermediate, as illustrated in Figure 6.

The very limited data that have so far been gained on free radical reaction dynamics show that their dynamics are similar to the reaction dynamics of atoms which have an electronegativity close to that of the free radical. Thus the dynamics of CH_3 radical reactions with halogen molecules[11] are similar to the repulsive dynamics of the corresponding D atom reactions where both species have similar[52] electronegativities (~ 2.3). Similarly, the OH radical reaction with Br_2 molecules[10] shows attractive dynamics similar to those of the Cl and O atom reactions, and again these species have similar electronegativities (~ 3.5—3.0). However, the intermediate in the OH radical reaction appears to have rather greater stability than that of the Cl atom reaction. Walsh molecular orbital theory[10] suggests that the HO—Br—Br intermediate may gain increased stability by adopting a bent staggered configuration.

5 Conclusions

The range of work described in this lecture gives no more than one example of the present power and future potential of the molecular beam method of investigating chemical reaction dynamics. Most of the experiments quoted involved only the measurement of product angular and velocity distributions which have not as yet been complemented by measurements of the product internal state distributions. Discussion of the results has concentrated on trying to assemble an overall qualitative picture of the dynamics of a rather small range of nonalkali reactions, primarily those of oxygen atoms. As more comprehensive experimental information is assembled we may expect many of the ambiguities and uncertainties to be resolved. A thorough quantitative understanding of non-alkali reaction dynamics will certainly require very comprehensive information since the electronic structure of the potential energy surfaces usually involves the interaction of many more electronic configurations than do the potential energy surfaces of the alkali reactions which provided the subject matter of the first phase[53] of molecular beam reactive scattering work. Much experimental in-

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[52] R. McWeeny, 'Coulson's Valence', Oxford University Press, Oxford, 3rd Edn., 1979: J. Hinze, M. A. Whitehead, and H. H. Jaffe, *J. Am. Chem. Soc.*, 1963, **85**, 148.

[53] D. R. Herschbach, *Adv. Chem. Phys.*, 1966, **10**, 319.

genuity will be required for measurements to be extended over a much wider range of reactions and to investigate as yet little explored properties such as the orientation dependence of reaction,[20,54] the polarization of product angular momentum,[21,55] and the spectroscopy of reaction transition states.[56] There will be increasingly close comparison between experimental data and theoretical calculations of reaction potential energy surfaces and nuclear motion over them.[16,57] The examples quoted in this lecture attempt to show one line of progress towards what must be our ultimate goal: to assemble a chemistry of reaction dynamics to rival that which already exists for stable molecules. At this stage it might be said with apologies to Winston Churchill that 'this is not the end nor even the beginning of the end, we have yet to reach the end of the beginning'.

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[54] Z. Karny, R. C. Estler, and R. N. Zare, *J. Chem. Phys.*, 1978, **69**, 5199; D. H. Parker, K. K. Chakrovorty, and R. B. Bernstein, *J. Phys. Chem.*, 1981, **85**, 466; J. W. Hepburn, D. Klimek, K. Liu, R. G. McDonald, F. J. Northrup, and J. C. Polanyi, *J. Chem. Phys.*, 1981, **74**, 6226; D. van Ende and S. Stolte, *Chem. Phys. Lett.*, 1980, **76**, 13.

[55] G. M. McClelland and D. R. Herschbach, *J. Phys. Chem.*, 1979, **83**, 1445; D. A. Case and D. R. Herschbach, *J. Chem. Phys.*, 1976, **64**, 4212; M. G. Drisant, C. T. Rettner, and R. N. Zare, *J. Chem. Phys.*, 1981, **75**, 2222.

[56] P. Arrowsmith, F. E. Bartozek, S. H. P. Bly, T. Carrington, P. E. Charters, and J. C. Polanyi, *J. Chem. Phys.*, 1980, **73**, 5895; J. C. Polanyi and R. J. Wolf, *J. Chem. Phys.*, 1981, **75**, 5951.

[57] C. H. Becker, P. Casavecchia, P. W. Tiedemann, J. J. Valentini, and Y. T. Lee, *J. Chem. Phys.*, 1980, **73**, 2833.