

several homogeneous WGSR catalysts toward sulfide poisoning^{11b,33} may represent the appropriate type of advantage. However, even greater benefit may derive from "spin-off" technology, examples being the demonstrations of the activity of WGSR catalysts for other homogeneous catalysis applications such as the hydroformylation^{5,6j} and hydrogenation³⁴ of olefins, as well

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as providing models for improved understanding and design of heterogeneous catalysts themselves.

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Reactive Scattering of Ground-State Oxygen Atoms

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The reactions of oxygen atoms in their ground electronic state, O(³P), are of great importance in combustion¹ and upper atmosphere² chemistry. The kinetics of O atom reactions have been widely studied,³ especially by the discharge of flow method. However, if we are to understand the interactions which govern these reactions we must seek more detailed information than is available from conventional measurements where the initial properties of product molecules are obscured by subsequent collisions.

Molecular beam reactive scattering experiments offer a powerful method of measuring the properties of product molecules resulting from single reactive collisions. Beams of molecules are formed in an evacuated scattering chamber at pressures which are so low that the mean free path between collisions becomes much greater than the dimensions of the chamber. Two molecular beams intersect in the scattering chamber, and collisions occur only in the intersection zone. The volume of the scattering zone and the densities of molecules in the beams are limited so as to ensure that only single collisions occur. Some of these collisions, usually a very small proportion $\leq 10^{-4}$, give rise to reaction. The flux of product molecules recoiling from reactive collisions is measured by a mass spectrometer detector which may be rotated about the scattering center. Hence reactive scattering may be measured as a function of scattering angle. If the scattering is interrupted by a suitable chopper placed in front of the detector, the flight time of product molecules from the chopper to the detector may be determined and from this the molecular recoil velocity may be calculated. Suitable detectors may be devised to identify also the vibrational and rotational states of product molecules.

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Indeed, any property of the scattered molecules may in principle be determined by the molecular beam method, though practical experiments are usually limited to the simultaneous measurement of two or perhaps three variables.

The earliest molecular beam studies of O atom reactive scattering used a low-pressure discharge source of O atoms to study the reactions of halogen molecules⁴ and also thermal dissociation of O₂ in a high-temperature iridium oven was used to study the reactions of CS₂ and I₂ molecules.⁵ However, these early experiments using effusive O atom beam sources did not always permit a full resolution of the differential reaction cross sections at a specific initial translational energy. This was due to the Maxwell-Boltzmann velocity distribution of the O atom beams and the lack of a ready means of varying the initial translational energy of the reactive collisions. Velocity distributions of product scattering were measured for the reactions of O atoms with halogen molecules,⁴ but the conventional single-slot time-of-flight method employed was inefficient and was not applicable to reactions with less intense reactive scattering. Thus these pioneering experiments, while demonstrating many fascinating features of O atom reaction dynamics, underlined the need for improved experimental techniques which would allow more detailed investigation of a wider range of reactions.

The dynamics of O(³P) atom reactions are of particular interest since the reactants approach on a triplet potential-energy surface which correlates with reaction products but which is above a singlet potential-energy surface as illustrated in Figure 1. The singlet poten-

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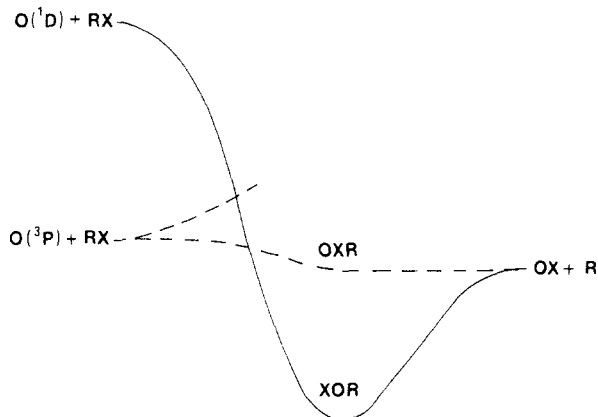


Figure 1. Schematic form of potential energy surfaces for the reactions of $O(^1D)$ atoms with singlet molecules RX . Singlet surfaces are shown by solid curves and triplet surfaces by broken curves.

tial-energy surface often exhibits a minimum corresponding to a bound singlet state of the reaction intermediate while the triplet intermediate is less stable. Thus the reaction dynamics which involve motion only over the triplet surface, with at most a weakly bound intermediate, will differ greatly from the dynamics which follow a transition to the underlying singlet surface. Much more is known about the structure of the ground-singlet intermediate, especially when it constitutes a chemically stable molecule, than of the triplet intermediate which would be formed initially in the reactive collision. Analysis of $O(^3P)$ atom reactive scattering requires an understanding of the form of the triplet potential-energy surface and the probability of triplet-singlet transitions to the underlying singlet potential-energy surface.

The dynamics of chemical reactions are determined by the form of the reaction potential-energy surface, and observed dynamical features may be used to identify characteristics of the surface. Strongly exoergic surfaces without a substantial potential-energy minimum yield direct reaction dynamics with a collision lifetime comparable to a molecular vibrational period. When the potential energy decreases mainly in the entrance valley of the surface, the reaction exoergicity is disposed predominantly into vibrational excitation of the products. However, if the potential energy decreases mainly in the exit valley of the surface, there is greater disposal of energy into product translation except when the reaction involves the transfer of a light atom. In this case repulsion between the products promotes primarily product vibrational excitation. In direct reactions, collisions at large impact parameters yield product scattering in the forward direction while collisions at small impact parameters yield product scattering in the backward direction. When a substantial potential-energy minimum on the surface is accessible to reactive trajectories, these become indirect. If the depth of the minimum is much greater than the reaction exoergicity, the lifetime of the collision complex may become greater than its rotational period in collisions at low initial translational energy. The lifetime of the collision complex decreases when its internal energy is increased by a higher initial translational energy or by reactant vibrational excitation. We shall appeal to these principles in interpreting the observed

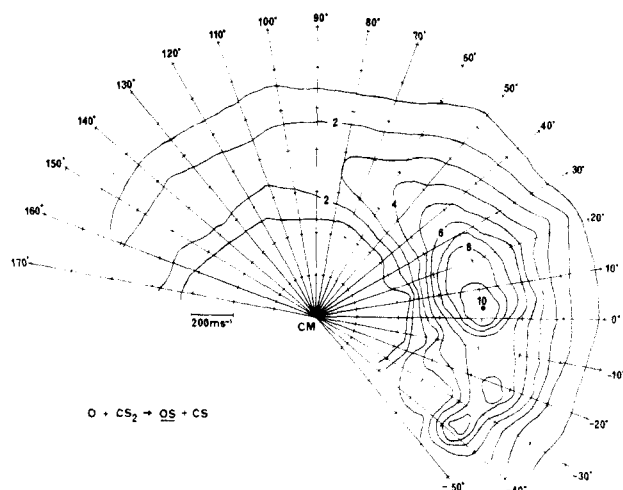


Figure 2. Polar contour map of OS flux for the $O + CS_2$ reaction with O atoms seeded in He as a function of center-of-mass scattering angle θ and velocity u , at an initial translational energy $E = 38 \text{ kJ mol}^{-1}$. Incident O atom direction is denoted by $\theta = 0^\circ$, incident CS_2 direction by $\theta = 180^\circ$. Reproduced with permission from ref 8. Copyright 1979, Taylor & Francis, Ltd.

dynamics of oxygen atom reactions, although the possible involvement of a second potential-energy surface often complicates this interpretation.

Recent Experiments

The deficiencies of the effusive O atom sources which were used in early experiments^{4,5} have now been overcome by the development of high-pressure discharge sources which produce a supersonic beam of O atoms seeded in inert buffer gas.⁶ The use of He buffer gas accelerates the O atoms to high energies, $E \sim 35 \text{ kJ mol}^{-1}$, whereas Ne buffer gas gives an O atom beam of just above thermal energy, $E \sim 13 \text{ kJ mol}^{-1}$. Thus O atom reactive scattering experiments can now be performed over a range of initial translational energy by varying the composition of a He/Ne buffer gas mixture. At the same time the well-defined kinematics and high product flux can be maintained by using an intense supersonic nozzle beam with a narrow O atom velocity distribution. The inefficiency of the conventional time-of-flight method of product velocity analysis has been overcome by use of the pseudo-random cross-correlation time-of-flight method⁷ in which the single slot of the conventional method is replaced by a pseudo-random sequence of teeth and slots. Arrival times of molecules at the detector ion source are measured by a minicomputer interface⁷ just as in the conventional method. The cross-correlation of the arrival time distribution with the pseudo-random sequence of the time-of-flight chopper disk then yields the required time-of-flight distribution. However, the cross-correlation method has a duty factor of $\sim 50\%$ which is optimal for the measurement of signals against a noisy background, rather than the $\sim 5\%$ duty factor of the conventional method. These improvements in technique have increased the sensitivity of reactive scattering apparatus using mass spectrometric detection by a factor ~ 100 . With these improvements it is now possible to measure detailed contour maps of the dif-

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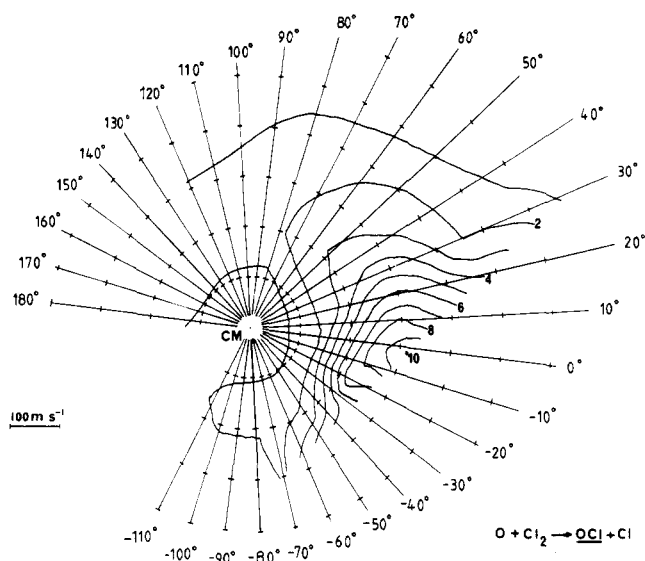
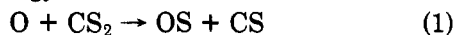


Figure 3. Polar contour map of OCl flux for the $\text{O} + \text{Cl}_2$ reaction with O atoms seeded in Ne at an initial translational energy $E = 13 \text{ kJ mol}^{-1}$.

ferential reaction cross section for a wide range of O atom reactions with well-specified initial translational energy.

The level of detail which can now be achieved is illustrated by the contour map of the differential reaction cross section for the reaction of O atoms seeded in He with CS_2 . This is shown in Figure 2, where the initial translational energy is 38 kJ mol^{-1} and the reaction is



In constructing this contour map, velocity distributions of the product OS were measured⁸ at 27 laboratory scattering angles over the full accessible laboratory angular range and transformed directly to center-of-mass coordinates by the numerical iterative inversion procedure of Siska.⁹ This contour map clearly shows that the $\text{O} + \text{CS}_2$ reaction follows a stripping mechanism with OS product scattering in the forward direction $\theta = 0^\circ$ with respect to the incident O atoms. Similar measurements with O atoms seeded in Ne buffer gas show that this mechanism also applies at lower initial translational energy 13 kJ mol^{-1} .

The differential reaction cross section for O atoms seeded in Ne with Cl_2 molecules shown in Figure 3 has been measured in recent experiments¹⁰ with more extensive and accurate velocity measurements than in the previous experiments¹¹ (eq 2). The contour map of

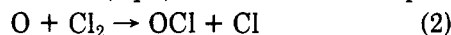


Figure 3 shows essentially a stripping mechanism with little indication of a very significant peak in the backward direction; an upper limit¹⁰ to the relative height of a backward peak was estimated to be $\lesssim 0.4$. The differential reaction cross section for O atoms seeded in He with Cl_2 molecules¹¹ also peaks strongly in the forward direction, with a significantly higher product velocity in the forward direction than for the wide-angle scattering. Thus the reactive scattering of $\text{O} + \text{Cl}_2$ at

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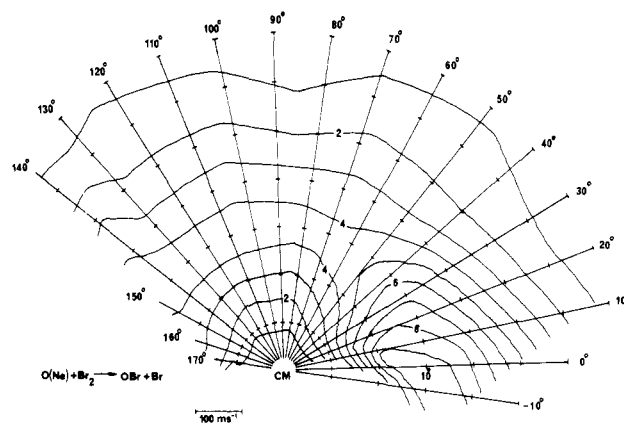
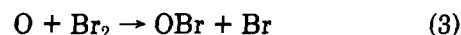


Figure 4. Polar contour map of OBr flux for the $\text{O} + \text{Br}_2$ reaction with O atoms seeded in Ne at an initial translational energy $E = 14 \text{ kJ mol}^{-1}$.

high energy appears to consist of a stripping component peaking in the forward direction and a wide-angle scattering component arising from collisions at small impact parameters. The potential-energy surface for the $\text{O} + \text{CS}_2$ reaction does not appear to have a significant potential-energy well compared with its reaction exoergicity. In the case of the $\text{O} + \text{Cl}_2$ reaction, the singlet potential-energy surface has a deep potential-energy well corresponding to the OCl_2 molecule, but this does not appear to be involved in the dynamics of the $\text{O} + \text{Cl}_2$ reaction, which do not follow a long-lived collision complex mechanism. Thus we may conclude that both of these reactions are confined to their triplet potential-energy surfaces.

Rather different reaction dynamics are exhibited by the $\text{O} + \text{Br}_2$ reaction (eq 3). Figure 4 shows the dif-



ferential reaction cross section for O atoms seeded in Ne with Br_2 molecules¹² which has a similar form to the differential cross section for O atoms seeded in Ne with Cl_2 molecules, though with greater intensity in the backward direction indicating a short-lived collision complex with a lifetime less than its rotational period. However the differential reaction cross section for O atoms seeded in He with Br_2 molecules of Figure 5 shows slightly increased scattering in the backward direction, with significantly higher recoil velocities than in the forward direction. Thus it appears that the reaction dynamics for the $\text{O} + \text{Br}_2$ reaction at low initial translational energy are confined to the triplet potential-energy surface which has only a modest potential-energy hollow corresponding to the $\text{O}-\text{Br}-\text{Br}$ configuration as proposed by Herschbach.⁴

Previous angular distribution measurements by Clough, O'Neill, and Geddes on the $\text{O} + \text{I}_2$ reaction⁵ have also indicated an increased backward intensity at higher initial translational energy compared with a long-lived collision complex at lower energy. These authors attributed this rebound behavior at high energy to a shortened lifetime for triplet $\text{O}-\text{I}-\text{I}$ complexes formed in collisions at small impact parameters. Such an interpretation would also be compatible with the increased backward recoil velocities observed for $\text{O} + \text{Br}_2$ at high energies. The lack of such a rebound com-

(12) D. P. Fernie, D. J. Smith, A. Durkin, and R. Grice, to be published.

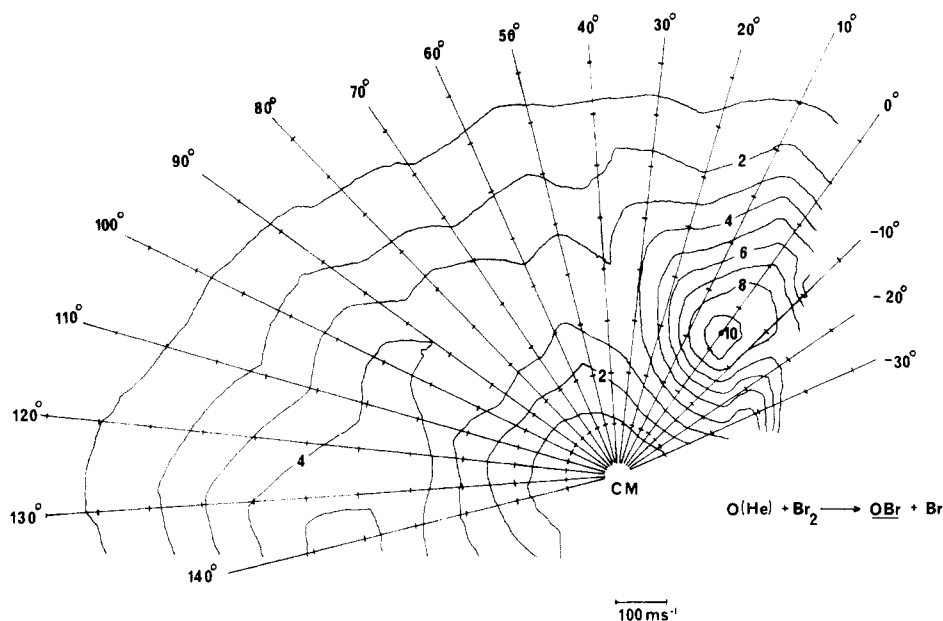
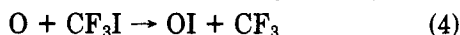


Figure 5. Polar contour map of OBr flux for the O + Br₂ reaction with O atoms seeded in He at an initial translational energy $E = 30 \text{ kJ mol}^{-1}$.

ponent for the O + Cl₂ reaction must then be attributed to the lighter mass of the Cl atoms, permitting rotation of an O–Cl–Cl collision complex even in collisions at small impact parameters.

The reaction of O atoms with CF₃I molecules presents¹³ quite different dynamics from the reactions with halogen molecules (eq 4). Scattering of OI product



from O atoms seeded in Ne favors the backward hemisphere but becomes essentially isotropic for O atoms seeded in He buffer gas. This indicates that reaction occurs at smaller impact parameters than for the reactions of halogen molecules, with repulsive interactions at small internuclear distances. The product translational-energy distributions are strongly skewed with respect to the initial translational energy, with a peak at lower energy and a tail extending up to the full energy available to reaction products. This indicates that substantial energy transfer occurs to internal modes of the CF₃ and OI radicals. The extent of this energy transfer is confirmed by measurements on the O + C₂F₅I,¹⁴ C₃F₇I¹⁵ reactions which show decreasing product translational energy as the complexity of the departing fluoroalkyl radical increases along the homologous series despite the increasing reaction exoergicities along this series. Thus the dynamics of I atom abstraction from perfluoroalkyl iodides by O atoms appears to be mainly confined to the triplet potential-energy surface which is essentially level. However this triplet potential-energy surface is probably above the singlet potential-energy surface corresponding to the iodoso molecule OICF₃¹⁶ which is stable with respect to reaction products by $\sim 100 \text{ kJ mol}^{-1}$. Consequently any reactive collisions which undergo a triplet–singlet transition would form a long-lived OICF₃ collision

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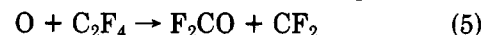
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(16) D. Naumann, L. Deneken, and E. Renk, *J. Fluorine Chem.*, **5**, 509 (1975).

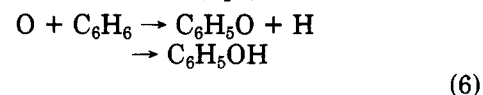
complex. While it is clear that the majority of reactive collisions do not proceed via a long-lived collision complex mechanism, the broad forms of the product angular and translational energy distributions would be compatible with a contribution $\lesssim 20\%$ from long-lived OICF₃ complexes formed by triplet–singlet transitions in the entrance valley of the potential-energy surface.

The reaction of O atoms with tetrafluoroethylene molecules represents a much greater rearrangement of O atoms which we have discussed so far (eq 5). The



differential cross section shown in Figure 6 for the reaction of O atoms seeded in He with C₂F₄ molecules¹⁷ favors the forward hemisphere and disposes only about 10% of the energy available to products into translation. Because of the asymmetry observed in the differential reaction cross section, we may conclude that the reaction proceeds via a triplet diradical intermediate¹⁸ with a lifetime comparable to its rotational period. In this intermediate the O atom is bonded to only one C atom of C₂F₄ rather than equally to both as would be the case for a singlet epoxide intermediate as illustrated in Figure 7. This is consistent with the formation of electronically excited CF₂(³B₁) product, but the observed product translational energy distribution does not preclude the formation of singlet CF₂(¹A₁) following a triplet–singlet transition as the diradical dissociates, or in some part by the formation of a singlet epoxide intermediate.

Two product channels have been identified by Lee and co-workers¹⁹ in the reactive scattering of O(³P) atoms with benzene molecules (eq 6). The first reaction



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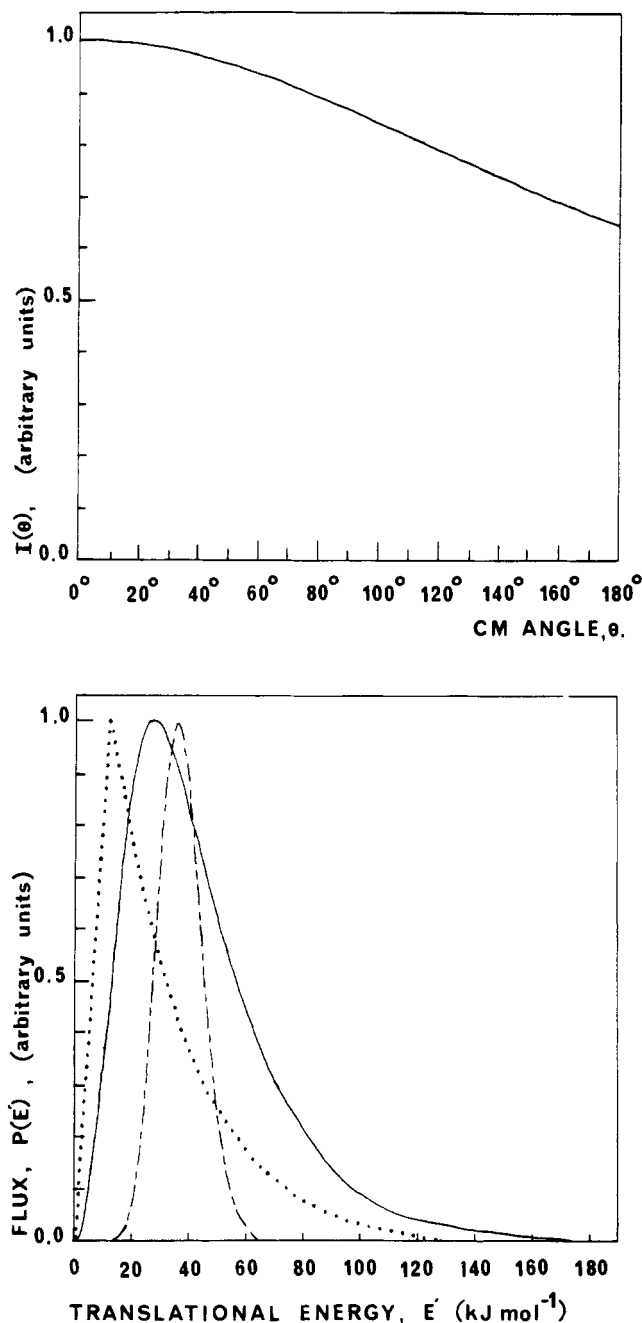
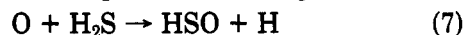


Figure 6. Product angular and translational energy distributions for the $O + C_2F_4$ reaction with O atoms seeded in He at an initial translational energy $E = 36 \text{ kJ mol}^{-1}$. Dotted curve shows the prediction of a long-lived collision complex model. Broken curve shows the initial translational energy distribution. Reproduced with permission from ref 17. Copyright 1980, Taylor & Francis, Ltd.

channel forming the phenoxy radical is attributed to dissociation of the triplet diradical intermediate C_6H_6O while the second channel is attributed to the formation of long-lived vibrationally excited phenol molecules in the ground singlet electronic state following a triplet-singlet transition. The second channel is increased relative to the first by increasing the initial translational energy, indicating that the triplet-singlet transition probability increases with energy. The second channel is also increased relative to the first by the substitution of perdeuteriobenzene (C_6D_6).

A displacement reaction pathway has also been identified¹⁰ in the reactive scattering of $O(^3P)$ atoms

with H_2S molecules (eq 7). The HSO product is observed for O atoms seeded in He at an initial translational energy $E = 35 \text{ kJ mol}^{-1}$ but not for O atoms seeded in Ne at $E = 13 \text{ kJ mol}^{-1}$. This indicates an activation energy $E_a > 13 \text{ kJ mol}^{-1}$ which may be identified with the endoergicity of this reaction pathway.



Electronic Structure

The method of frontier orbitals²⁰ stresses the overlap of the lowest unoccupied orbital and the highest occupied orbital of the reactants during the initial stages of a reactive collision. In the reactions of $O(^3P)$ this implies the overlap of a singly occupied O atom p orbital with the highest occupied orbital of the reactant molecule. In CS_2 and H_2S , this is a nonbonding Π orbital on the S atoms, in C_2F_4 and C_6H_6 a bonding Π orbital, in the halogen molecules an antibonding Π_g orbital, and in CF_3I a nonbonding p orbital on the I atom. In all cases this leads to a triplet intermediate, and the reaction dynamics depend upon the properties of this intermediate and the probability of transition to a more stable singlet electronic state.

The Cvetanovic mechanism¹⁸ for addition of $O(^3P)$ to a carbon-carbon double bond forming a triplet diradical intermediate²¹ has been supported³ by analysis of the products from the reactions of olefins. The formation of a triplet diradical in the reaction of C_2F_4 molecules, as illustrated in Figure 7, is supported by the asymmetry observed in the angular distribution of CF_2O reactive scattering. However, the lifetime of the OC_2F_4 diradical is much shorter than the diradical formed in the olefin reactions, being roughly comparable to its rotational period, due to the exoergicity of the $O + C_2F_4$ reaction which is large even for the formation of electronically excited $CF_2(^3B_1)$ product. A similar mechanism may be proposed for the addition of $O(^3P)$ to the carbon-sulfur double bond of CS_2 forming a bent planar triplet diradical, as illustrated in Figure 7. In this case the triplet diradical constitutes the transition state rather than a bound intermediate for the reaction which proceeds by a direct stripping mechanism. A planar bent structure for this triplet transition state is confirmed⁸ by Walsh molecular orbital theory for molecules of the form BAAB. However the triplet diradical C_6H_6O formed by $O(^3P)$ with C_6H_6 , as illustrated in Figure 7, is likely to be longer lived due to the larger numbers of degrees of freedom and thus accumulates a significantly probability of transition to the ground singlet state of phenol. Due to the stability of the C_6H_5OH ground state, the lifetime of the vibrationally excited phenol product $\tau \sim 1 \text{ ms}$ is comparable to its flight time to the detector.

In contrast, the initial overlap of the $O(^3P)$ atom unpaired p electron with the halogen lone pair electrons of a halogen or fluoroalkyl iodide molecule does not yield a triplet diradical. Rather the triplet reaction intermediates in these reactions seem likely to involve overlap of one unpaired p electron of the O atom with

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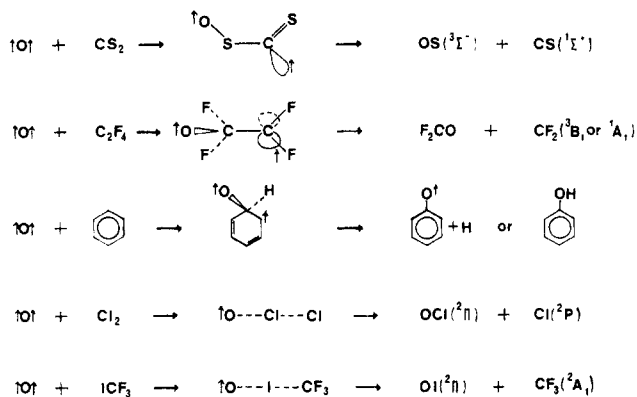


Figure 7. Schematic diagram of the mechanisms of $O(^3P)$ atom reactions.

the antibonding halogen-halogen or iodine-carbon σ orbital in a manner similar to the reaction of an F or Cl atom which has only a single unpaired p electron. In the reaction of $O(^3P)$ atoms with H_2 molecules this results²² in a collinear O-H-H transition state of $^3\Pi$ symmetry, and this situation also applies²³ to the abstraction of H atoms from hydrocarbon molecules by $O(^3P)$ atoms. Although interaction of the other unpaired p electron on the O atom with the Π electrons of the halogen or fluoroalkyl iodide molecule may result in a bent transition state of either $^3A'$ or $^3A''$ symmetry, this general picture would suffice to explain the dynamics of these reactions via the triplet potential-energy surface.

The triplet surfaces for the halogen reactions are more attractive than for the fluoroalkyl iodides and indeed result in a long-lived collision complex for the $O + ICl, I_2$ reactions.^{4,24} Herschbach has suggested⁴

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that the lowest triplet state in the collinear configuration has $^3\Sigma^-$ symmetry. Although this would initially require an O atom lone pair projected toward the halogen molecule and imply strong reactant repulsion, it might be accessible from a strongly bent initial configuration. Our results on the $O + Cl_2, Br_2$ reactions indicate that the potential-energy wells on these triplet surfaces are shallower than those for $O + ICl, I_2$. This accords with the electronegativity ordering rule proposed by Herschbach⁴ whereby the least electronegative atom occupies the central location for the most stable O-X-Y complex. Additional experiments are presently under way to study the dynamics of the $O + ICl$ reaction at high initial translational energy in order to resolve this question further.

Conclusions

Recent improvements in the techniques of crossed molecular beam reactive scattering now permit the measurement of differential reaction cross sections as a function of initial translational energy for a wide range of oxygen atom reactions. The dynamics of $O(^3P)$ atom reactions present more complexities than many other atom reactions which have been studied in molecular beams, due to the interaction of triplet and singlet electronic states. The results which have been gained so far give some indication of the electronic structure of the potential-energy surfaces involved. However more experimental measurements and electronic structure calculations will be required before a complete picture of oxygen atom reaction dynamics is obtained.

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Translational and Internal Energy Accommodation of Molecular Gases with Solid Surfaces

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The nature and degree of energy equilibration when molecular gases interact with solid surfaces, both reactively and passively, are important in gas-surface chemical kinetics and affect many areas of science and technology. Gas-surface energy occurs in processes

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ranging from coal gasification to heterogeneous catalysis, from supersonic and high-altitude flight to the fabrication of sophisticated solid-state electronic and optical devices, from energy conversion to materials fabrication. Gas-surface energy transfer is an initial step in vapor condensation to grow solid materials. It plays a role in the evaporation of solids to form complex molecular entities. It plays a similar role in corrosion and volatilization in high-temperature environments. Indeed, most reactions and interactions between gases and solid surfaces involve, as a first step, and perhaps as a last step, some degree of equilibration between the gaseous molecules and the surface. It is not surprising