REACTIVE SCATTERING OF O(^{1}D) + H$_2$

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The angular and velocity distribution of OH product from the O(^{1}D) + H$_2$ reaction at 2.7 kcal/mole collision energy has been obtained in a crossed molecular beam study. The product is found to be forward—backward symmetric, most of the reaction occurs through insertion of the oxygen to form ground electronic state H$_2$O

1. Introduction

Atomic oxygen in the first excited electronic state (^{1}D) reacts readily with hydrogen to yield OH and H under single-collision conditions. The room-temperature rate constant for O(^{1}D) + H$_2$ [1] is 10^7 times greater than that of O(^{3}P) + H$_2$ [2]. The drastically different chemical behavior is a manifestation of major differences in the potential energy surfaces for the two reactions. Whereas the most favorable approach of O(^{3}P) to the H$_2$ molecule is collinear with an 8 kcal/mole barrier, there appears to exist no barrier to insertion of O(^{1}D) into the H$_2$ bond along a perpendicular approach to yield ground electronic state H$_2$O. The H$_2$O molecule formed from O(^{1}D) insertion into H$_2$ has 161 kcal/mole internal excitation and readily loses an H atom. The overall reaction O(^{1}D) + H$_2$ → OH + H is exothermic by 43 kcal/mole, so that the OH may be excited vibrationally to v = 4. Two recent studies have reported measurements of the internal energy distributions of the OH product using the LIF method. Luntz et al. [3] and Smith et al. [4] have each obtained the distribution of rotation energy for the v = 0 and v = 1 states of OH product, while predissociation of electron-

ically excited OH prevented detection of higher vibrational states.

These studies agree that the rotational population is strongly inverted, the rotational energy distribution being considerably hotter than statistical. They find that the vibrational populations for v = 0 and v = 1 agree with statistical expectation and the implication, then, is that higher rotational states are excessively populated at the expense of translational energy. The translational energy distribution should exhibit dynamical effects which make it also deviate from the statistical distribution.

Classical trajectory calculations have been carried out on several potential energy surfaces by different research groups. Sorbie and Murrell [5] (SM) have used an empirical surface to obtain differential cross sections $\sigma(\theta)$ and product energy partitioning for the reaction at low collision energy. The calculations of Whitlock, Muckerman and Fisher [6] (WMF) were performed with a semi-empirical surface at several collision energies up to 6 kcal/mole. Schinke and Lester [7] (SL) have recently reported trajectory calculations on an ab initio surface at 0.5 and 5.0 kcal/mole. The various calculations of $\sigma(\theta)$ have generally agreed that there is forward—backward symmetry at low collision energy with strong peaking at 0° and 180° [note that the $P(\theta)$ reported by SM and SL must be divided by sinθ to yield $\sigma(\theta)$]. At higher collision energies, however, SL find an increase in back scattering, while the $\sigma(\theta)$ of WMF retains symmetry but exhibits very intense peaking on the relative velocity

vector. Calculations of the product rotational distribution by SL have agreed quite well with the non-statistical, LIF results of Luntz et al. [3]. WMF have divided the trajectories into insertion and abstraction channels and have noted differences in the energy partitioning according to reaction mechanism. The abstraction process yielded high vibrational and low rotational energy while insertion reactions produced distributions more like the LIF results, that is, statistical vibrations with hot rotations. WMF find that 20–25% of the reactions occur by the abstraction mechanism.

We report here the first measurement of the product angular and velocity distributions for the reaction $O(^1D) + H_2 \rightarrow OH + H$. The principal features of the flux contour map yield information about the mechanistic details of the reaction. The product translational energy distribution, $P(E')$, has been derived and is compared with the statistical and trajectory calculations.

2. Experimental

Molecular beams of oxygen atoms and hydrogen molecules were crossed under single-collision conditions in a scattering apparatus which has been previously described [8]. A recent description of the oxygen atom beam source [9] includes a discussion of the conditions necessary to produce $O(^1D)$. In order to produce a beam of oxygen atoms containing $O(^1D)$, an rf discharge is maintained in a quartz nozzle in 200 Torr of a 5% O_2 in helium gas mixture. During expansion through a 0.18 mm orifice, the $O(^1D)$ atoms are not effectively quenched by collisions with helium so that the resulting beam contains a small percentage of the species. The measured velocity distribution of the oxygen atoms was found to peak at 2.37×10^5 cm/s with fwhm of 20%. Expansion of 24 atm of pure H_2 from a 0.03 mm nozzle produced a beam with narrow velocity distribution peaking at 2.67×10^5 cm/s with fwhm of 9%. The two beams intersected at an angle of 90°. The mean collision energy was 2.71 kcal/mole with a fwhm of 13%. The OH product detected at mass 17 was measured with a rotable quadrupole mass spectrometer with electron bombardment ionizer. To obtain the angular distribution, the hydrogen beam was chopped with a 150 Hz tuning fork and the signal was taken as the difference between the chopper-open and chopper-closed counts. No data were taken within

7.5° of the oxygen beam where spurious effects appear as a result of the large flux of background gas into the detector. At the peak of the angular distribution, the signal intensity at mass 17 was 3000 counts/s with a background 5300 counts/s.

Velocity distributions of the product were obtained using the cross-correlation time-of-flight method [10]. The reaction product was chopped by a rotating disk with a pseudo-random sequence of 255 elements and the modulated intensity was collected by a 255 channel scaler with a 12 μs channel width. The data accumulated in the 255 channel scaler were transferred periodically to a minicomputer for cross-correlation computation and display of the time-of-flight spectrum. The flight path from the slotted disk to the ionizer was 17.0 cm. Data accumulation times varied from 15 min to 1 h depending on signal intensity.

The oxygen beam is known to contain large amounts of the ground-state $O(^3P)$, but this species does not interfere because the range of collision energies is below its threshold for reaction with H_2.

3. Results and analysis

The angular distribution of OH product is shown in fig. 1 with typical error bars representing the 95% confidence limit, and a solid line showing the calculated
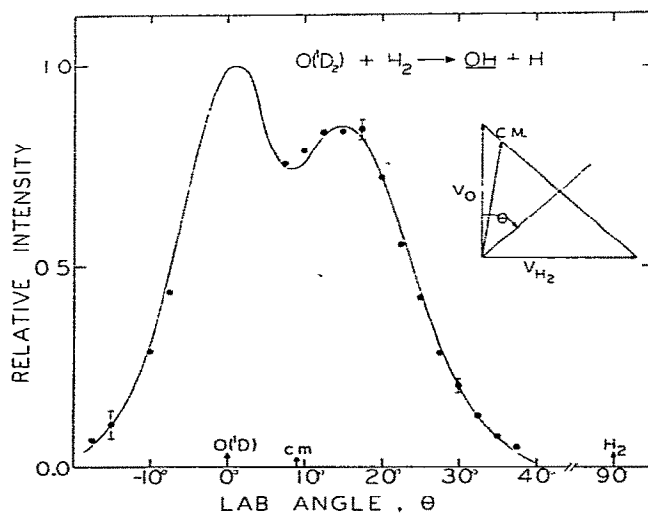

Fig. 1. Laboratory angular distribution of OH product. Dots are measured intensity. Solid line is the calculated distribution.
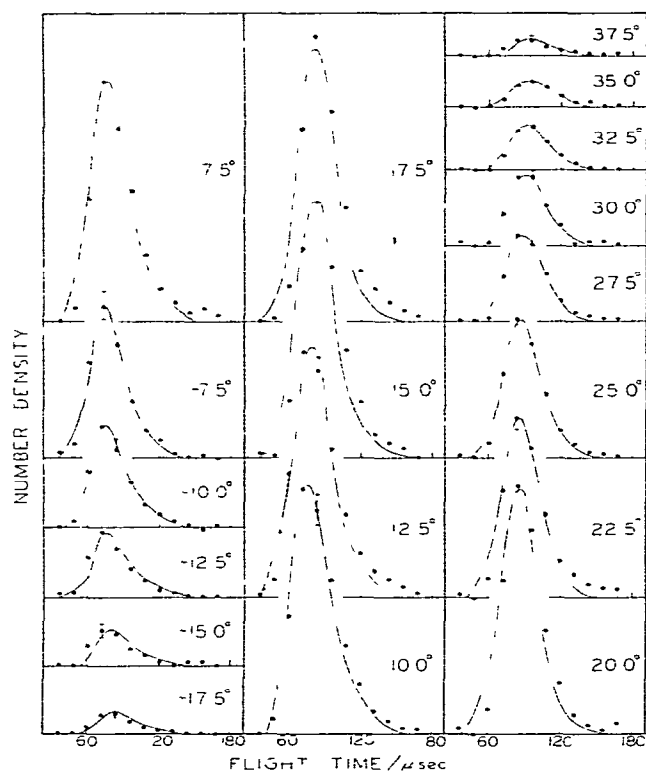
Fig. 2. Time-of-flight spectra of product OH at 18 laboratory angles. Solid lines are the best-fit calculated curves.

Fig. 3. Contour map showing center-of-mass flux of OH product.

best fit. Product velocity distributions were measured at 18 angles and are shown in fig. 2 together with the best fit calculated curves. The velocity distributions have been normalized to the relative intensities at each angle. In fig. 3 is shown a countour map of the OH product flux distribution obtained from the raw data with the deconvolution method of Siska [11]. The product is distributed quite symmetrically about 90° in the center-of-mass reference frame and is seen to peak strongly on the relative velocity vector. Initial deconvolution of the data with the method of Siska gave an estimate of the product distribution in the center-of-mass reference frame. From this preliminary deconvolution it was evident that there was essentially no coupling between $\sigma(\theta)$ and $P(E')$, the product translational energy distribution. The data was then fit by the direct convolution method with the assumption of a separable $\sigma(\theta)$ and $P(E')$. Shown in fig. 4 are the $\sigma(\theta)$ and $P(E')$ (solid lines) which produce the best
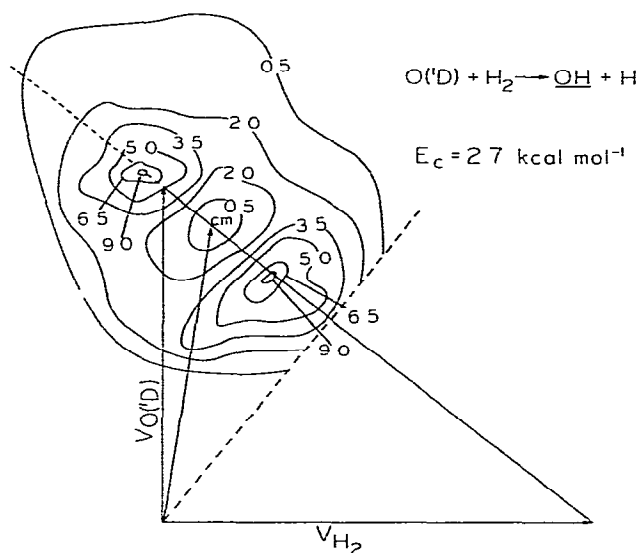
fit to both the angle and velocity data. An excellent fit was obtained with a $\sigma(\theta)$, fig. 4a, which is symmetrical about 90° with the ratio of intensity at 90° to that on the relative velocity vector $\sigma(90°)/\sigma(0°) = 0.33$. The measured $P(E')$ peaks at 10 kcal/mole which is ≈20% of the total available energy. Also shown in fig. 4b is a phase space calculation [12] of the $P(E')$ (dashed line). The total cross section was taken to be 25 $Å^2$ which is the calculated capture cross section if the long-range attraction is dominated by the dispersion forces.

This capture cross section corresponds to an effective cross section of 5 $Å^2$ because only one of the 5 scattering surfaces is reactive at these collision energies [13]. This effective capture cross section agrees well with the measured value [1] 3.6—8.1 $Å^2$. The exit channel C_6 long-range force constant was calculated to be 202 kcal $Å^6$ using the Slater—Kirkwood method [14], and it was assumed that no potential barriers exist in either the entrance or exit channels. The calculated $P(E')$ is in fair agreement with the measured $P(E')$ although it predicts somewhat greater average translational energy.
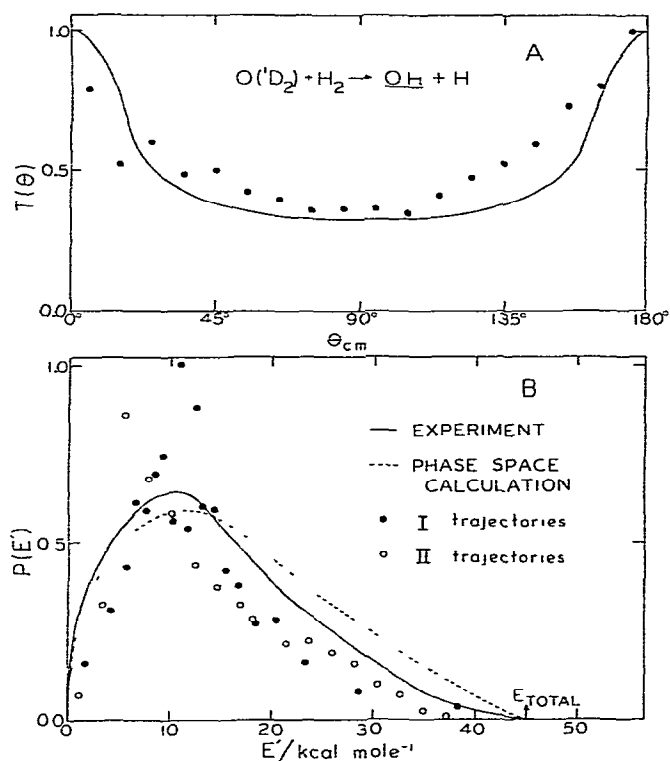
Fig. 4. Product angular and energy distributions. (A) Solid line is the experimentally determined c.m. angular distribution. Dots are the classical trajectory results of SL for 5.0 kcal/mole collision energy. (B) Solid line is the experimental product translational energy distribution, dashed line is a phase space calculation. Open circles are classical trajectory results of Muckerman [15], closed dots are the classical trajectory results of Luntz [16].

4. Discussion

The two principal mechanisms which have been suggested for this reaction are direct abstraction of a hydrogen atom and insertion to form ground electronic state H_2O which subsequently dissociates. The insertion reaction is associated with an approach of the oxygen perpendicular to the H_2 bond. The various caculations of potential energy surfaces have agreed that no barrier exists for a C_{2v} approach, and this is also in accord with the absence of an activation energy for the reaction. The abstraction channel is expected to result from a collinear approach. The presence of a barrier to collinear approach will influence the dynamics of the

reaction by affecting the relative rates of the two channels. With a low barrier, the direct abstraction may compete effectively with the insertion channel. For example, WMF found on their surface II, for which there exists no barrier to insertion and less than 1 kcal/mole barrier to collinear approach, that reaction at low collision energy (0.9 kcal/mole) results in 80% insertion, while at higher collision energy (5 kcal/mole) the insertion channel decreases to 75%.

The relative importance of the abstraction and the insertion mechanism is probed by the crossed molecular beam experiment in the measurement of the angular distribution, because the symmetry of the product angular distribution reflects the nature of the reaction intermediate. If the collinear abstraction process has a potential energy barrier of ≈ 1 kcal/mole, at collision energy of 2 to 3 kcal/mole this process leads to backscattered product, as in the reaction of $F + H_2$, while insertion should produce a symmetric angular distribution even if the lifetime of the H_2O complex is not as long as a rotational period. Our observation of a symmetrical center-of-mass angular distribution suggests that the principal mechanism at this collision energy is likely to be insertion and either the potential energy barrier of collinear abstraction is higher than our collision energy of 2.7 kcal/mole or the potential energy surface is such that even a very near collinear approach will interact with both hydrogen atoms strongly and go through an insertion intermediate. Forward—backward symmetry in the angular distribution is usually interpreted as evidence that the lifetime of the complex exceeds a few rotational periods. But for the insertion reaction involving homonuclear diatomic molecules, such as $O(^1D) + H_2$, as long as the interaction between the O atom and each of the H atoms becomes equivalent in the reaction complex and the probability of the bond rupture is the same for both OH bonds, then even if the lifetime of the complex is just a fraction of a rotational period, symmetry in the probability of bond rupture should give forward—backward symmetry in the angular distribution. More specifically, the oxygen insertion into the H_2 bond produces H_2O with 161 kcal/mole internal excitation, a large fraction of which appears as large-amplitude bending motion with the H_2O intermediate undergoing inversion with a period less than 0.1 ps. Thus for this reaction, the intermediate H_2O should lose memory of the reactant direction of approach

after several bending vibrations and the forward and backward direction become equally probable for product OH.

We have also obtained the laboratory angular distribution of product from the reaction at a mean collision energy of 4.0 kcal/mole. At this higher collision energy, the product remains symmetrically distributed about $90°$ in the center-of-mass reference frame, and the angular distribution is fit quite well with the same $\sigma(\theta)$ and $P(E')$ shown in fig. 3, which were derived from the low-energy data. This is as expected if no change in mechanism occurs because the addition of several kilocalories of collision energy does not change the total excitation energy of the complex appreciably and should have a very small effect on the product energy distribution which is dominated by the large exoergicity. There is, thus, no evidence to suggest that the collinear mechanism overcoming the entrance barrier contributes significantly to the reaction in contradiction to the classical trajectory studies of SL which show some angular asymmetry at a collision energy of 5 kcal/mole.

The product is observed to peak on the relative velocity vector with a minimum intensity at $90°$, about 0.33 of the peak intensity at the collision energy E_c = 2.71 kcal/mole. Several of the classical trajectory calculations are in reasonable agreement with this angular distribution although direct comparison is impossible because the calculations are not for reaction at the same collision energy. In particular SL have found $\sigma(90°)/\sigma(0°)$ = 0.36 on their ab initio surface III for E_c = 5.0 kcal/mole. The result of this calculation, shown in fig. 4a with our experimental curve, however, exhibits some asymmetry with the product slightly favoring the backward hemisphere, and at lower collision energy (0.5 kcal/mole) a larger ratio $\sigma(90°)/\sigma(0°)$ = 0.45 is observed. At E_c = 5 kcal/mole, on their semi-empirical surface, WMF found a symmetrical distribution but the angular peaking was very strong, $\sigma(90°)/\sigma(0°)$ = 0.08. These minor differences in the results of classical trajectory calculations and our experimental findings might suggest the necessity of further improvement of the potential energy surface of this system. In view of the formation of a strongly bound H_2O complex, quantum effect should not be the main cause of these minor differences.

The $P(E')$ which has been derived from the experimental data is in fair qualitative agreement with the phase space calculation shown in fig. 4b. The LIF measurements of Luntz et al. [3] and of Smith et al. [4] suggest that a less than statistical amount of energy should appear in translation because product rotations are highly excited. The deviation of our measured $P(E')$ toward lower average energy than the statistical calculation is in qualitative agreement with the LIF results however, given the uncertainties in the experiment and the model parameters, our experimental results alone are not conclusive evidence to infer a non-statistical translational energy distribution of reaction product. In fig. 4b the experimental $P(E')$ is compared to a trajectory study of Muckerman [15] at 2 kcal/mole collision energy and to a trajectory calculation of Luntz [16]. The calculated distributions are both narrower but agree well with the experimental $P(E')$ in the average product translational energy.

If the product OH molecules were formed in low rotational states, the individual states of the OH would be separated in the TOF spectra, therefore the absence of such vibrational structure is evidence that product rotations are indeed highly excited. We have observed that, under single-collision conditions, essentially all the $O(^1D)$ reacts by insertion into the H_2 bond and, subsequently, the OH product departs rotating rapidly with low translational energy.

Acknowledgement

References

[1] J.A. Davidson, C M. Sadowski, H.I. Schiff, G.E. Streit, C.J. Howard, D.A. Jennings and A.L. Schmeltekopf, J. Chem. Phys. 64 (1976) 57.

[2] R.N. Dubinsky and D J. McKenney, Can. J. Chem. 53 (1975) 3531.

[3] A.C. Luntz, R. Schinke, W.A. Lester Jr. and Hs.H. Günthard, J. Chem. Phys. 70 (1979) 5908.

[4] G.K. Smith, J E. Butler and M.C. Lin, Chem. Phys. Letters 65 (1979) 115;
G.K. Smith and J.E. Butler, J. Chem. Phys. 73 (1980) 2243.

[5] K.S. Sorbie and J N. Murrell, Mol. Phys. 31 (1976) 905.

[6] P.A. Whitlock, J.T. Muckerman and E.R Fisher, Theoretical Investigation of the Energetics and Dynamics of the Reactions $O(^3P, {}^1D) + H_2$ and $C({}^1D) + H_2$, Research Institute for Engineering Sciences, Wayne State University, Detroit (1976).

[7] R. Schinke and W A. Lester Jr., J. Chem. Phys 72 (1980) 4893.

[8] Y.T. Lee, J.D. McDonald, P.R. Lebreton and D.R. Herschbach, Rev. Sci. Instr. 40 (1969) 1402.

[9] S J Sibener, R J. Buss, C Y. Ng and Y.T Lee, Rev Sci. Instr. 51 (1980) 167.

[10] K Sköld, Nucl. Instr. Methods 63 (1968) 114.

[11] P.E. Siska, J. Chem. Phys. 59 (1973) 6052.

[12] J.C. Light, Discussions Faraday Soc. 44 (1967) 14; P. Pechukas, J.C. Light and C. Rankin, J. Chem. Phys. 44 (1966) 794.

[13] R.E. Howard, A.D. McLean and W.A. Lester Jr., J. Chem. Phys. 71 (1979) 2412.

[14] J.C. Slater and J.G. Kirkwood, Phys. Rev. 37 (1931) 682

[15] J.T. Muckerman, private communication.

[16] A.C Luntz, private communication