Reactive Scattering of O(^{3}P) + CF$_3$I

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The reaction of O(^{3}P) + CF$_3$I has been studied with an rf discharge, supersonic oxygen atom beam source in a crossed beam arrangement. At a collision energy of 2.2 kcal/mol, the reaction yields exclusively IO + CF$_3$ radical products. The angular and velocity distributions of the product show that the reaction involves complex formation with the intermediate living greater than or equal to one rotational period. Only a small fraction of the available energy is partitioned into product translation, in good agreement with a statistical model. The reaction is believed to remain confined to the triplet surface forming a CF$_3$–I–O complex.

Introduction

Among the earliest applications of the molecular beam method to the study of oxygen atom chemistry were reactions with halogen molecules.[1] These are chemically interesting in that the ground-state reactants approach each other on a triplet potential energy surface which is an excited state of the triatomic intermediate with one electron promoted from the $3\pi^*$ to the $3\sigma^*$ orbital. The atomic arrangement in the ground singlet state of a triatomic molecule containing two halogen atoms and an oxygen atom (X$_2$O) cannot be predicted easily from the electronegativity rule[2] which states that the most electronegative atom will be located in the position of highest electron density. For these 20 electron systems, the 3π and the $3\pi^*$ molecular orbitals are completely filled in the ground state, resulting in no region of particularly high electron density. F$_2$O, Cl$_2$O, and Br$_2$O are all found to have an XOX arrangement although the relative electronegativity of oxygen has changed from most positive in F$_2$O to most negative in Cl$_2$O and Br$_2$O. In the triplet state, however, with one electron promoted to a $3\sigma^*$ molecular orbital, the highest electron density should be on the end atoms, directing the most electropositive atom to the center. In the reaction of O + ICl, the intermediate would be expected to have the arrangement OICl if there is no intersystem crossing to the ground electronic surface. The arrangement ClOI should be more likely on the singlet surface in analogy with BrOBr. In a molecular beam study of O + ICl by Grice and co-workers,[3] it was reported that IO is the only product, and that the angular distribution of product was consistent with a long-lived complex model. Insertion of the oxygen into the ICl bond would be expected to lead to formation of an OCl product which is energetically more favorable. Thus this study suggests that the reaction is confined to the triplet surface.

The reaction of oxygen with CF$_3$I is expected to be similar to the O + ICl system. The oxygen atom approaching on the triplet surface should form a complex with a central iodine atom, while intersystem crossing to the ground singlet surface might lead to the oxygen atom inserting in the C–I bond. However, the O + CF$_3$I reaction differs from O + ICl in that the CF$_3$IO complex has a greater number of vibrational degrees of freedom than ClIO. These additional modes would be expected to cause the CF$_3$IO complex to have a longer lifetime than ClIO if these complexes are of comparable stability, and if there

is a statistical redistribution of the energy released during complex formation.

Grice and co-workers[4] have reported a study of O + CF$_3$I at two collision energies in a crossed molecular beam arrangement. The results which we present here for O + CF$_3$I differ qualitatively in several important ways from those of Grice and co-workers. In particular, the translational energy distribution of the products is found to agree well with statistical calculations, in contrast to the previous study which reported highly nonstatistical results.

Experimental Section

The crossed beam apparatus and data acquisition techniques were similar to those described previously.[5] The reaction is studied under single collision conditions by crossing two molecular beams at right angles in a region with background pressure about 10^{-7} torr. Products are detected by an electron bombardment ionization quadrupole mass spectrometer which rotates about the collision region in the plane of the two beams.

The oxygen atom source, described in detail elsewhere,[6] employs a high-pressure rf plasma, localized near the nozzle, to achieve a high oxygen flux reasonably with reasonable narrow velocity spread and 80% dissociation. With a 5% O$_2$ in argon mixture at 100 torr pressure, the peak velocity was found to be 1050 m s^{-1} with a fwhm velocity spread of 40%. The CF$_3$I beam was an expansion of 250-torr pure gas from a 0.1-mm quartz nozzle at room temperature. The CF$_3$I was obtained from PCR Research Chemicals, Inc., and was used without further purification. The beam velocity distribution was determined by the time-of-flight method to have a peak velocity of 366 ms^{-1} with fwhm velocity spread of 30%. This terminal velocity implies that the supersonic expansion effectively converted translational, rotational, and two low-frequency vibrational degrees of freedom to beam kinetic energy. Under these conditions the reacting CF$_3$I should have an average internal energy around 1 kcal mol^{-1}. The mean collision energy for the CF$_3$I reaction is 2.18 kcal mol^{-1} with fwhm = 0.8 kcal mol^{-1}. Laboratory angular distributions of IO product number density were taken by repeated scans of

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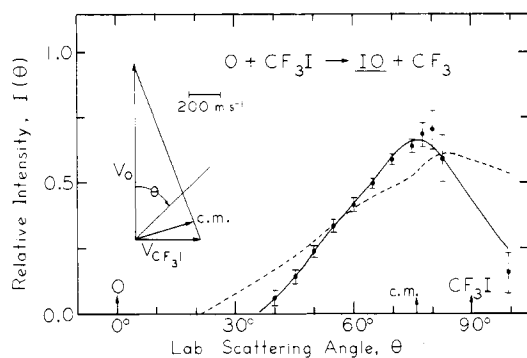
Figure 1. Laboratory angular distribution of mass 143, IO product. Error bars are two standard deviations of the mean. Solid line is the calculated best fit. Dashed line is calculated by using the reported $P(E)$ and $T(\theta)$ from ref 4.

100-s counts at each angle. The oxygen beam was modulated at 150 Hz with a tuning fork and the signal obtained by subtracting the chopper-closed count from the chopper-open count. The IO product signal intensity at the peak of the angular distribution was approximately 15 counts per second with background 30 counts per second. Velocity distributions at each angle were obtained with the cross-correlation time-of-flight technique with 12 μs per channel time resolution. For this purpose a disk with a pseudorandom sequence of 255 slots was placed in front of the detector to modulate the product. Counting time varied from 1 to 3 h at an angle.

Results

The only observed product of the O + CF$_3$I reaction was the IO radical. Taking into account uncertainties in the relative detection efficiencies of CF$_3$O and IO, we estimate that, if if the more exoergic channel producing I + CF$_3$O ($\Delta H \sim -40$ kcal/mol) is occurring at all, it accounts for less than 10% of the reaction.

The laboratory angular distribution of IO product is shown in Figure 1 with error bars showing two standard deviations of the mean of ten measurements. The product is found to peak strongly near the center-of-mass (CM) angle with no evidence of bimodality, suggesting that little of the available energy has gone to translation. The product time-of-flight (TOF) distributions at seven laboratory angles are shown in Figure 2. A single peak close to the center-of-mass velocity is observed at each angle reinforcing the impression that the translational energy of the product is low.

The angular and velocity data were analyzed by two techniques. A direct inversion of the data using the iterative deconvolution technique of Siska[7] produces a two-dimensional map of product flux in the CM reference frame. From this map, one can observe the overall features of the reaction, such as symmetry of the product about the relative velocity vector and whether there is coupling of the CM angular distribution ($T(\theta)$) and the product translational energy ($P(E)$). The Siska method is very sensitive to noise in the raw data and typically results in high-energy tails on the derived $P(E)$, particularly for systems in which the spread in the center-of-mass velocities is large and the product detected is much more massive than the leaving group. Thus we also generally fit the data by direct convolution of a trial $P(E)$ and $T(\theta)$ over the beam velocity spread with automatic variation of the functions to achieve the best fit. This technique also greatly facilitates the derivation of error bars for the $P(E)$,
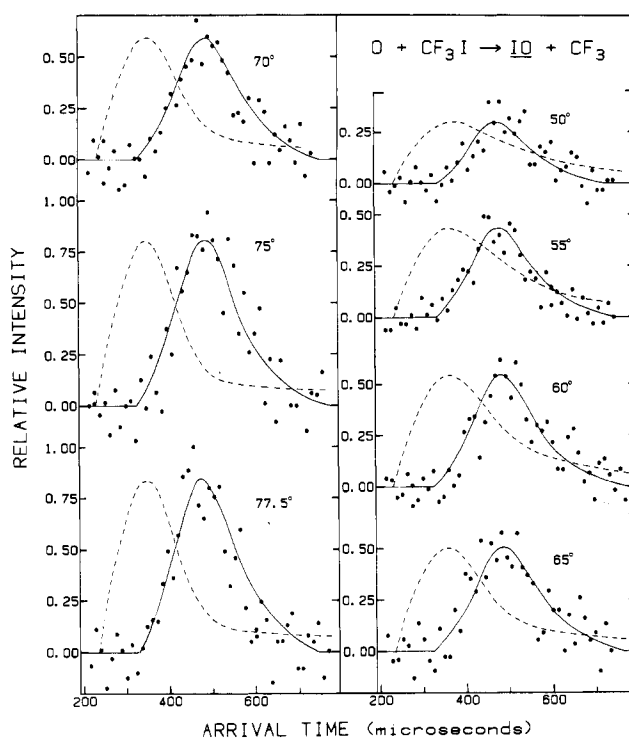
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Figure 2. Time-of-flight distributions for mass 143, at seven lab angles. Solid lines are the calculated best fit. Dashed lines are calculated by using the $P(E)$ and $T(\theta)$ from ref 4.
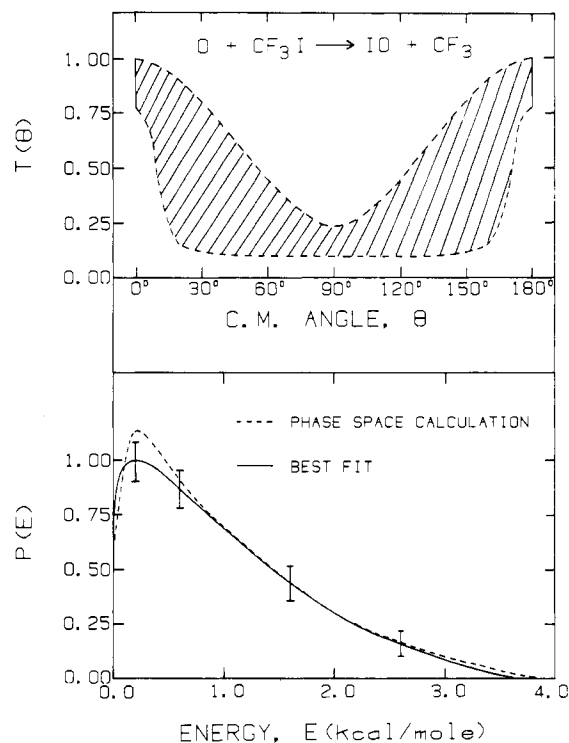

Figure 3. Product translational energy distribution, $P(E)$, and CM angular distribution, $T(\theta)$, obtained in this experiment. Shaded region shows experimental uncertainty in $T(\theta)$.

without which the distributions are less meaningful.

In Figure 3 is the contour map of CM flux for IO product which was derived from the data. The contours represent the deconvoluted flux which, when averaged over the reactant beam velocities and other machine broadening effects in the transformation of CM to the laboratory coordinate system, will produce the best-fit solid lines shown in Figures 1 and 2.
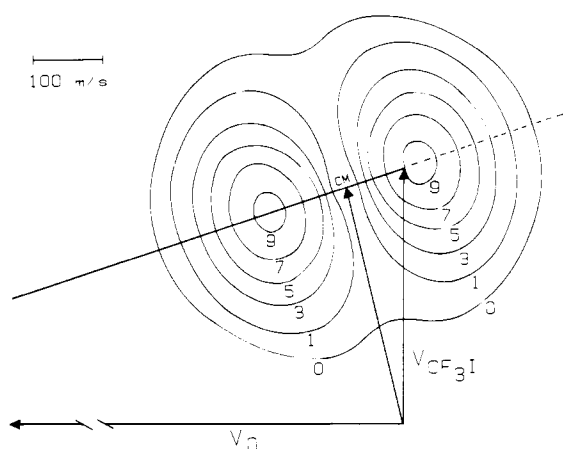
Figure 4. Contour map of CM flux of IO product in velocity space. The canonical Newton diagram is superimposed.

The distribution function $P(E)$ and $T(\theta)$ are shown in Figure 4. The peak of the translational energy is quite low, and represents only 10% of the available energy. Also shown is a statistical calculation of the $P(E)$ using the phase space theory of Light.[8] The agreement between calculated and observed distributions is seen to be excellent.

The function $T(\theta)$ shows strong peaking on the relative velocity vector as is characteristic of reaction in which orbital angular momentum plays a larger role than molecular angular momentum. The observed $T(\theta)$ exhibits fairly good symmetry with possibly very slight preference for forward scattering of the IO product with respect to the oxygen atom direction.

Discussion

The $O(^3P)$ atom approaches CF_3I on a triplet surface, the features of which have not been well characterized. Because many reactions of $O(^3P)$ have been found to resemble those of ground-state fluorine atoms we look to the analogous reaction $F + CH_3I$ for similarities. The existence of a CH_3-I-F molecule was deduced from reactive scattering experiments[9] and the complex was later synthesized in a crossed beam experiment.[10] The CH_3-IF and CH_3I-F bond energies were found to be 13 and 26 kcal/mol, respectively. Thus, in analogy we might expect a moderate well on the CF_3I-O triplet surface. The addition complex would be predicted to have the more electropositive iodine atom in the central position.

The CM angular distribution which is measured here suggests that a complex is formed which lives greater than or approximately equal to a rotational period. The strong peaking on the relative velocity vector, at 0 and 180°, is characteristic of reactions in which orbital angular momentum (L) predominates in the entrance channel and the product orbital angular momentum is strongly correlated to it. Because the CF_3I beam is a supersonic expansion in which rotational cooling is extensive, the molecular angular momentum (J) of the reactants is low, and L is likely to dominate the entrance channel with a moderate size of reaction cross section.

Donovan has suggested[11] that the dynamics of this reaction may be dominated by the well in the singlet surface,

with the reaction always proceeding with intersystem crossing. This mechanism cannot be ruled out by our data. However, we believe that the singlet complex is more likely to have the oxygen atom inserted between the CF_3 and the I. The CF_3 often behaves like a halogen atom and the structure of the complex might be expected to resemble the other halogen–oxygen singlet species, BrOBr or ClOCl. General rules of atomic ordering in triatomics[2] do not lead to a clear picture for those species because there is no region of dramatically higher electron density. If it is true that the singlet species has the configuration CF_3-O-I, then the decomposition would surely favor production of CF_3O + I which is far more exoergic. Absence of CF_3O product leads to the conclusion that the preferred geometry of the complex is CF_3-I-O.

The amount of energy appearing as translation is quite low, with the peak in the distribution occurring at about 0.4 kcal/mol. In comparing this with statistical predictions, it is necessary to assume several features of the reaction which are not well established. The distribution of angular momenta in the complex depends on the reactivity as a function of impact parameter, the opacity function, which can only be roughly estimated. If the long-range force is estimated from polarizabilities, and used to calculate a capture cross section, the result is 59 $Å^2$. This seems inconsistent with the relatively small observed room temperature rate constant, $k = 1 \times 10^{-11}$ cm^3 moleule^{-1} s^{-1} (corresponding to about 2 $Å^2$ cross section if the activation energy is near zero). A strong orientation dependence of the reactants could cause the opacity function to deviate markedly from that predicted by a simple long-range force treatment. Indeed the phase space calculation for the $P(E)$, in which the angular momentum distribution is determined by the C_6 constant, predicts slightly more translational energy than is observed. When the angular momentum effects are decreased by assuming a cross section of 34 $Å^2$, the calculated $P(E)$ gives a reasonably good fit to the experimental angular and velocity distributions. It is assumed in these calculations that the reaction is exothermic by 2 kcal/mol, estimated from published heats of formation.[12]

A previous study of $O + CF_3I$ using the crossed molecular beams technique has been reported by Grice et al.[4] The results which we report here directly contradict the findings of the Manchester group in several important ways. Of particular significance is the difference in $P(E)$ for reaction at similar collision energy. In contrast to the slow product in good agreement with statistical theory which we observe, Grice reports product with average energy more than twice the statistical average. In fact, they report some product with translational energy exceeding twice the available energy, a physical impossibility. There is also no agreement between the $T(\theta)$ distributions in the two studies. The strong peaking on the relative velocity vector which we attribute to correlation of reactant and product orbital angular momentum was not seen in the previous study. Instead, a broad angular distribution favoring backscattering at low energies and becoming isotropic at higher collision energies was reported. The dashed lines in Figures 1 and 2, calculated by using the $P(E)$ and $T(\theta)$ from ref 4, demonstrate the poor agreement between the two studies.

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The reason for the major discrepancy between the results of the two studies is not readily apparent. There are significant differences in the raw data which cannot be reconciled by comparing the reported operating conditions. Deconvolution of the data requires precise and accurate knowledge of the beam conditions, because high-energy tails on the molecular beam, unaccounted for in the analysis, would manifest themselves as impossibly high energy products. Dimers in the beam may also result in skewing of the product angular distribution because the center of mass of the dimer reaction is located closer to the reactant beam.

While the difference between the two studies remains a mystery, our results make a strong case for the existence of a relatively stable intermediate. We believe the excellent agreement between our $P(E)$ and the statistical calculation is not simply fortuitous but indicates energy redistribution in a long-lived intermediate. The near symmetry of $T(\theta)$ about 90% argues for the existence of a complex with a lifetime comparable to or longer than a rotational period. The strong peaking of $T(\theta)$ on the relative velocity vector reflects the expected dominance of L over J in the reaction.

Conclusion

The reaction of O + CF$_3$I is found to give IO product exclusively, apparently because the reaction remains confined to the triplet surface. A reaction complex having the structure CF$_3$IO is formed which has a lifetime greater than or equal to one rotational period. The translational energy of the products agrees well with the results calculated by using statistical theory.

Registry No. CF$_3$I, 2314-97-8; atomic oxygen, 17778-80-2.

Optical Spectra of Oxygen Adsorbed on Evaporated Silver Films

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A stress birefringence polarization modulation ellipsometer was used to study the interaction of oxygen with vapor-deposited silver films. Difference optical spectra for the interaction at 525 K and an ambient oxygen pressure in the 10^{-2}-torr range are consistent with the formation of a thin surface oxide. In addition, data are presented for optical changes arising from room-temperature annealing and dichloroethane roughening of silver films.

Introduction

Although there exists an extensive literature concerning the interaction of oxygen with silver,[1,2] the system continues to be the source of vigorous investigation. Part of this interest stems from the ability of silver to catalyze the partial oxidation of ethylene.

Hall and King[3] measured the sticking probability for oxygen on evaporated silver films and found an initial value of 10^{-2}–10^{-3} followed by a rapid decrease to 10^{-5} at low oxygen coverages. At least three different adsorbed states have been distinguished for oxygen on silver by thermal desorption (TDS). These occur at 173, 580, and 773 K. Barteau and Madix[4] in a combined isotope exhange–TDS study determined that the species desorbing at 173 K is molecular oxygen whereas the desorption peak at 580 K corresponds to atomic oxygen. The desorption peak at approximately 770 K which is commonly observed subsequent to exposure at temperatures greater than 473 K[5] is attributed to lattice-incorporated oxygen. A dominant theme in research on the epoxidation reaction is that the relative population of oxygen species is a decisive factor in the selectivity toward partial oxidation over combustion.[1,2]

It is well-known that great care must be taken in the study of oxygen adsorption onto Ag. Albers et al.[6] report that for reproducible results for oxygen adsorption on Ag(111) a CO pressure of less than 2% of the oxygen pressure is required. In addition to the CO clean off reaction further complications arise from the fact that oxygen adsorption transforms the erstwhile inactive silver into a strong adsorber of a variety of gases.[7] For polycrystalline and defective samples, further confusion arises because of the sensitivity of the interaction to substrate structure.[5,6]

In this report results are included for the interaction of dichloroethane with silver and for the optical changes brought about by the room-temperature annealing of freshly deposited films. These results are included because dichloroethane is used as a moderator in the commercial process to enhance selectivity toward epoxidation[1,2] and because surface microstructure changes on oxygen adsorption.[5,8]

An analysis of spectroscopic ellipsometry data yields information on surface electronic and geometric structure,

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