Scattering of K Atoms from Oriented CF$_3$I
Reaction at Both "Ends"

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The reaction of K atoms with CF$_3$I molecules has been studied using oriented molecules. If the I end is closest to the incoming K atoms, KI is formed and recoils backwards in the centre of mass system. If the CF$_3$ end is closest to the incoming K atoms, KI is again formed but scatters forwards in the CM. This is in contrast to the oriented CH$_3$I + Rb reaction in which no forward scattering is observed from configurations with CH$_3$ closest to the incoming Rb.

These observations find possible explanation in two (probably related) mechanisms. Even for CF$_3$I oriented in what appears to be an unfavorable configuration, it is possible for the K atom to fly past the CF$_3$ group and strike the I. This is expected to be less likely in CH$_3$I because the CH$_3$ shields the I more than does CF$_3$.

For CF$_3$I (but not CH$_3$I) charge transfer to a repulsive ionic state is postulated. The products are expected to recoil along the direction of the molecular axis and this roughly accounts for the experimental angular distribution.

The concept that chemical reactions occur only for specific orientations of the reactants is appealing and intuitive. Experimental evidence for such steric effects became known early in the study of chemical kinetics when it was observed that all gas kinetic collisions did not yield reaction, even if they were energetic enough. Thus the steric factor had both an intuitive and experimental basis, but unfortunately it could not be reliably predicted and has given way to an alternate description involving the entropy of activation. For some reactions, predictions based on parameters assumed for the transition state are in rough agreement with experiment, but uncertainties in the experimental data preclude our extracting much information about how the steric requirements are related to molecular structure.

Recent molecular beam experiments have allowed direct verification (a) that steric requirements are real and significant, and (b) differ radically with molecular structure. The early experiments were performed on K + CH$_3$I and Rb + CH$_3$I and results were in general accord with chemical intuition: reaction occurred preferentially at the I end of the molecule. Preliminary investigation of the K + CF$_3$I reaction, however, indicated quite the opposite: KI was preferentially formed when K was directed towards the CF$_3$ end of the molecule. We have extended these measurements and now find in addition to the early results, that K will also react if directed towards the I end. The angular distribution of scattered KI from these configurations is quite different, but indicates that in each case reaction takes place directly and without complex formation.

EXPERIMENTAL

A schematic diagram of the apparatus is shown in fig. 1. CF$_3$I effused from a room temperature glass multi-channel array A and was Stark-state selected by an inhomogeneous

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electric hexapole field (F) identical to that previously described and charged to ±12 kV. This field selects molecules in states for which cos θ is negative, where classically θ is the angle between the dipole moment and the electric field. For symmetric tops, \( \cos \theta = \frac{MK}{J(J+1)} \). These state selected molecules pass adiabatically into a region of uniform electric field (~40 V cm\(^{-1}\)) created by the charged homogeneous field plates, (H, H'). In this uniform electric field, the selected states correspond to specific laboratory orientations; the direction of orientation in the laboratory may be changed by simply changing the polarity of the uniform field. Region X is a grounded copper box which contains parallel plate electrodes which must be charged in order for the state selected molecules to make adiabatic transitions to the uniform field. If the field in X is zero, the states are randomized and the beam is no longer oriented.

The potassium beam effused from a single chamber 540 K stainless steel oven (O) with an orifice 0.1 mm diam. heated to 640 K. This beam passed through holes in H, H' and was collected in the liquid nitrogen trap (T). (Plate H contained a slot 1 cm high to pass scattered particles.) A surface ionization detector (D') was used to monitor the K beam intensity.

![Diagram of apparatus](image)

**Fig. 1.**—Scale drawing of apparatus, except for dimensions given in cm. Cross hatched areas are 77 K. A—glass capillary array, D,D'—surface ionization detectors, F—electric hexapole field, H,H'—homogeneous field plates, M—magnetic electron multiplier, O—oven, P—pump, Sh—shutter, T—beam trap, X—disorienting field region.

Scattered particles were detected with a standard two wire (single crystal W, Pt–W alloy) surface ionization detector (D) which could be rotated in plane about an axis passing through the scattering centre. The detector was limited to sweeping the range 30-94°. Ions formed on the wires were focused through a simple ion lens onto a Bendix Model 306 electron multiplier. The multiplier was operated at a gain of ~10\(^5\) and the output was measured as current by a Keithley BR610 electrometer and displayed on a recorder.

Even though the state selecting field is optically opaque (a molecule needs to be deflected to pass through) a number of molecules are transmitted at zero applied voltage. The
intensity of this "shadow beam" is comparable to that of the state selected beam, and was used to study the scattering of unoriented molecules. The scattered signal was recorded in two ways. The scattering due to the shadow beam was recorded as the beam on-off signal difference. The scattering due to the oriented beam was recorded as the high voltage state selecting field on-off signal difference.

Angular distributions were determined with each filament for scattering of the shadow beam and for scattering of the oriented beam in the "heads" and "tails" configurations. The Pt-W alloy filament was operated in the non-detecting mode and monitored by periodic checks of the electron emission. The relative efficiencies for ionization of K on each filament were determined on each run by measuring the (non-reactive) scattering from a shadow beam of methanol for scattering angles from 30° to 60°. The Pt-W readings were then normalized to those from the W filament. The Pt-W data for CF3I were adjusted by the same factor; similar results obtained if the W and Pt-W readings for CF3I were normalized for wide angle scattering of CF3I in the "tails" orientation.

The possible reaction products, KF or KI, are both surface ionized and consequently the beam experiments do not distinguish between them, but a large amount of indirect evidence suggests that the product is solely KI. The C—I bond is much weaker than the C—F bond (56 as compared with 117 kcal mol) so the reaction to form KF is approximately thermoneutral whereas that to form KI is exoergic by 24 kcal mol. Velocity analysis experiments show that about 10 kcal mol energy is converted to translational energy of the products. This strongly suggests that the product cannot be KF, but uncertainty in the bond energy does not allow us to rule it out unambiguously. In addition, we have run diffusion flame experiments on K+CF3I and find mainly (> 90%) KI. Gaseous products include C2F6 and C3F8 and indicate that for the gas phase reaction KF is probably formed in secondary reactions of K with CF3 radials. Similar results were obtained in flame studies of Na with CF3I. The possibility of formation of KCF3 is excluded by electric deflection experiments and as before we conclude that the product is KI.

RESULTS

The angular distribution of KI from the unoriented shadow beam is shown in fig. 2. This angular distribution is in very close agreement with that obtained in the velocity analysis experiments, which show that the scattered product is rather broadly distributed, and the most probable amount of internal energy converted to translation is ~10 kcal mol.

When the molecules are oriented, a completely different angular distribution results and is shown in fig. 3. If the K atoms impinge on the negative end of the molecule, ("tails") the KI formed is scattered into smaller angles and is more sharply peaked than in the unoriented case. Bombardment of the positive end ("heads") causes the KI to be scattered into larger angles and again seems more sharply peaked. Because of the large electronegativity of fluorine, we assume that the iodine is the positive ("heads") end of the molecule.

A velocity vector diagram is shown in fig. 4. Because the oriented molecules have been selected by a deflection method favouring low velocities the CF3I velocity is represented by the most probable beam velocity at 150 K as calculated in ref. (5). The KI scattered from "heads" clearly peaks backwards in the CM and that scattered from "tails" peaks forwards. The angular distribution of KI from "heads" is almost identical to that obtained for CH3I (unoriented) and suggests that reaction for "heads" results from a direct K—I impact followed by rebound of the KI.

Elaborate schemes are not necessary to explain how the potassium atom can strike the "tail" but react with the "head". The molecules are not perfectly oriented; instead there is an almost continuous distribution of molecules with cos θ ranging from 0 to —1. (In an unoriented beam cos θ varies from +1 to —1.) For CF3I under these conditions —cos θ averaged over the distribution of orientations is 0.34
(θ = 71°), so reaction is not restricted to collinear encounters. In addition, the incoming K atom is not restricted to hit the CF₃ end of the molecule in the "tails" configuration; the CF₃ end is merely the closest end of the oriented molecule. This means that it is possible for the K atom to fly past the CF₃ and still strike the I end. Nothing would hinder the forward progress of the newly formed KI and forward type of scattering would result. This is schematically illustrated in fig. 5. Note that in the "heads" configurations, the newly formed KI runs into the CF₃ and consequently scatters in the backward direction.

Fig. 2.—Angular distribution of KX (assumed to be KI) scattered from unoriented molecules.

Because of the surprising initial result⁴ that reaction occurred only at "tails", we were concerned with the possibility that these results were due to some spurious electrical effects. No such spurious effects are present however. (As long as there are no extra sources of ions, such as ionization guages.) All elements of the experiment must be present in order to observe the signals shown in fig. 3: both beams must be on, the state selecting high voltage must be on, and a uniform electric field (> ~12 V cm⁻¹) must be applied in region HH'. Confirmation that the signals were
Fig. 3.—Open points—angular distribution of KI scattered from the "tails" configuration. Filled points—angular distribution of KI scattered from the "heads" configuration. Half filled points show angular distribution of molecules which have been oriented but then randomized prior to scattering.

Fig. 4.—Newton diagram for scattering of oriented molecules. Most probable CF$_\text{3}$I velocity is that for a beam from an oven at 150 K as calculated in ref. (5). The arrow denotes the direction of the applied field (for one polarity); the average molecular axes are oriented 71° with respect to this direction. The experimental peaks are at 90° and 45°.
indeed reactive scattering from oriented molecules was provided by the scattering of disoriented molecules as shown also in fig. 3. If the electric field is zero in the well shielded copper box X, it was previously observed 5 that molecules would not make adiabatic transitions as they traversed the field. As a consequence, the oriented beam can be re-randomized if this field is zero. The scattering from this disoriented beam is intermediate in magnitude between the "heads" or "tails" scattering. It is further unaffected by the polarity of the uniform field H, H'. It should be noted that the angular distribution from disoriented molecules is similar in shape to the sum of the angular distribution for scattering from "heads" and "tails". These are not, and should not be, identical to the scattering from unoriented molecules because the state selection process preferentially removes molecules which have $\cos \theta = 0$.

**DISCUSSION**

Even though the degree of orientation is rather small $^{15}$ ($\theta \sim 70^\circ$) the difference in the reactivity for the "heads" and "tails" configuration is very large. Among other things, this shows the importance of near "broadside" collisions in contrast to the collinear collisions favoured in calculations. (The fraction of the beam which is perfectly oriented is in fact vanishingly small.) Absence of symmetry in the CM provides evidence that the reaction (even in the "tails" configuration) does not proceed via a long lived complex.

Accurate theoretical interpretation of these results from ab initio calculations will be incredibly difficult due to the complexity of the CF$_3$I molecule; no such calculations presently exist. Monte Carlo trajectory calculations concerned with orientational effects are rare $^{16, 17}$ and will probably require $^{17}$ experimental results to determine the potential surface. Nevertheless, an early calculation of Karplus and Godfrey $^{16}$ showed that for a fairly symmetric surface for K + CH$_3$I ($V_o$), reactive collisions of the "heads" type produced backward scattering whereas collisions of the "tails" type produce more forward scattering, presumably due to the larger impact parameters for the latter case. This, of course, is almost precisely what is observed for K + CF$_3$I. The oriented CH$_3$I + K reaction has not been extensively studied, but for the analogous Rb reaction of CH$_3$I the forward peaked scattering from the "tails" configuration is

![Diagram of forward and backward scattering from the "heads" and "tails" configuration.](image-url)
absent,\(^3\) even though CH\(_3\) is smaller than CF\(_3\) and it would appear that tail end attack of CH\(_3\)I would also give RbI.

Two effects may contribute to the difference in reactivity of oriented CH\(_3\)I and CF\(_3\)I. An oriented molecule precesses rapidly about the total angular momentum vector \(^{18}\) (with the dipole sweeping out a cone of half angle \(\alpha\) where \(\cos \alpha = K/J\)) with an angular velocity \(\Omega = 4\pi BJ\). The frequency of precession is comparable to the reaction time in CH\(_3\)I, but slower for CF\(_3\)I. Since CH\(_3\)I is a very prolate top, extremely low values of \(K\) predominate, the precessional cone is very wide and the I is well shielded by the precessing CH\(_3\). For CF\(_3\)I higher \(K\) states are present, the precession is slower, and the I is less shielded. In addition, the centre of rotation is displaced from the iodine which allows the I to peek out and be plucked off by the K atom.

The charge transfer mechanism \(^{19}\) is also of some use in interpreting the data. This mechanism supposes a long range (-5-10 Å) transfer (curve crossing) of a valence electron from the easily ionized alkali atom to an electrophilic target molecule. Because Coulomb forces between the ions essentially ensure reaction, the reaction radius is essentially the distance at which the electron jump takes place; this fairly satisfactorily explains the scattering of a number of alkali-halogen systems.

Quantitative application of the charge transfer model requires a knowledge of the vertical electron affinity of CH\(_3\)I and CF\(_3\)I which in turn requires the potential curves for the molecule and the negative ion. Unfortunately, for these molecules the potential curves are highly speculative. Some qualitative interpretation is still possible, however. For CH\(_3\) the vertical electron affinity seems to be negative or zero and the electron cannot jump until the alkali atom approaches very closely,\(^{19}\) \(~3.5\) Å. We expect the vertical electron affinity to be larger for CF\(_3\)I. The CF\(_3\) radical is more electronegative than CH\(_3\), the reaction of Na atoms \(^{20}\) is faster for CF\(_3\)I, and the electron capture coefficient for CF\(_3\)I is larger than CH\(_3\)I.\(^{21}\) The electron will jump at a larger distance than in CH\(_3\)I, and since the electron must be placed in an anti bonding orbital centred mainly on I we can expect the molecular ion to decompose\(^{22}\) into CF\(_3\) and I\(^-\). These products will be expelled along the direction of the CF\(_3\)I symmetry axis. Since a considerable amount of translational energy will be imparted to the I\(^-\), the KI product will be found in a CM direction close to that in which the CF\(_3\)I axis was originally aligned.\(^{23}\) If the electron jump takes place at a sufficiently large distance, the reaction probability at the two ends will be comparable. This crude model is in broad general agreement with the results as shown in fig. 4. The average alignment with respect to the applied field \(^{15}\) is 71°, and combined with an observed \(Q\sim 10\) predicts a "tails" peak ~65 and "heads" peak about 95°. The experimental peaks are ~45° and ~90°, but are somewhat uncertain because of some possible nonuniformities in the alignment field and the considerations of ref. (15).

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12 (a) S. Riley and D. R. Herschbach, private communication; (b) A. Rulis and R. B. Bernstein, private communication.
15 As pointed out in ref. (3a), the homogeneous field should be aligned along the relative velocity vector, but in this work the field is parallel (or anti parallel) to the K velocity. This results in a misalignment of ~12° which is of no qualitative significance but will probably shift the peaks in the angular distribution.
20 E. Warhurst, Quart. Rev., 1951, 5, 44.
22 A somewhat similar situation exists in ICl and IBr in reaction with K. (G. H. Kwei and D. R. Herschbach, J. Chem. Phys., 1969, 51, 1742). Here, however, dissociation to X⁻ + I is expected because of the higher electron affinity of X, and the product is KX not KI. For CF₃I however, the electron affinities of CF₃ and I are comparable, and KCF₃ is observed not to be the product.
23 A similar mechanism has been proposed to account for the trends in angular distributions of H atoms reacting with unoriented halogens and diatomic alkali molecules. (Y. T. Lee, R. J. Gordon and D. R. Herschbach, J. Chem. Phys., 1971, 54, 2410; J. D. McDonald, P. R. LeBreton, Y. T. Lee and D. R. Herschbach, J. Chem. Phys., 1972, 56, 769.)