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Reactions of Oriented Molecules

Molecules can be oriented in molecular beams and their reactions show some unexpected steric effects.

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The Greek philosopher Democritus was perhaps the first (about 400 B.C.) to introduce the concept that different "atoms" have different shapes, and modern structural analysis has now placed his geometrical concepts on a firm basis. Molecules can be characterized by the distances between atoms and the angles between bonds, and large-scale models of molecules can easily be constructed from such information. Scrutiny of such scale molecular models leads to new insight sufficiently frequently to make a set of molecular models standard equipment for the practicing chemist or biochemist.

Despite the utility of these geometrical concepts for understanding and predicting the configuration of stable molecules, these same models are not rigorously applicable to the dynamical processes that occur in a chemical reaction. But in many reactions a single atom or group of atoms is replaced, and geometrical models lead us to believe that reaction will occur only if the new group is in close proximity to the bonding site. Our models thus lead us to expect that chemical reactivity will depend on the orientation of the reagents. This idea has been reinforced by the use of orientation arguments to explain why fast gas-phase reactions do not occur on every gas-kinetic collision.

The kinetic theory bimolecular reaction rate constant, k_{12}, is usually written as (*1*)

$$k_{12} = \rho Z_{12} e^{-E_a/RT}$$

where Z_{12} is the specific gas kinetic collision frequency, E_a is the energy of activation, R is the gas constant, T is the absolute temperature, and ρ is the steric factor, the fraction of collisions in which the reagents are properly oriented. For some simple reactions such as $H_2 + I_2 \rightarrow 2HI$, ρ is between 0.1 and 1, and a simple geometrical interpretation seems reasonable. On the other hand, other simple reactions such as $Br + CHCl_3 \rightarrow CCl_3 + HBr$ require $\rho \ll 1$, and these values have been deemed unreasonably small. As a consequence, ρ has come to be regarded as a "fudge factor" which merely brings experiment and theory together, although the orientation requirements it describes are well accepted. The collision theory of reactions has accordingly fallen into some disrepute in favor of the activated complex theory. This theory (which also has its critics) has merely disguised the role orientation plays, and orientation effects still survive in the guise of the entropy of activation (*1*).

Experimental investigation of orientational requirements has been difficult. Accurate measurement of steric factors (or equivalently, the entropy of activation) would yield some insight into the detailed structure of the activated complex, but sufficiently precise experimental rate data are nearly impossible to obtain, especially in the gas phase. As a result, much of our information is derived from indirect studies in solution despite the complication which may be introduced by the participation of the solvent. Certainly some of the most well known and fascinating examples of steric effects are those which occur in bimolecular nucleophilic substitution (S_N2) reactions such as $Cl^- + CR_3I \rightarrow CR_3Cl + I^-$ (R = alkyl group). Experiments show that the reaction occurs preferentially with inversion of configuration about the central carbon atom, the well-known Walden inversion (*2*). This suggests that the Cl^- attacks from the rear, followed by the inversion of the alkyl groups and the expulsion of the I^-. Alkyl groups sufficiently bulky to prevent the inversion decrease the reaction rate, which strengthens this suggestion.

We are thus presented with the picture that steric requirements are intuitively reasonable and that a variety of indirect evidence supports their existence. Direct experimental studies have been lacking, of course, because of our inability to select orientations in solution or even in the gas phase. But isolating molecules in a molecular beam makes possible the selection of molecules with certain orientations (*3*) and the maintenance of those orientations. The oriented molecules may react with atoms in a second beam which crosses the first, and the reactivity can be studied as the orientation is changed. The earliest such experiments (*4*) were performed by reacting oriented CH_3I with either K or Rb atoms to form CH_3 and either KI or RbI. These experiments showed a clear difference in reactivity at the two "ends" of the molecule and conclusively demonstrated the existence of steric effects. Several other molecules have now been studied, with some surprising results, and in this article I will discuss these experiments as well as the techniques used in orienting molecules. But no results from indirect experiments will be included.

Molecular Beams

A molecular beam is a collection of molecules moving in the same direction under collision-free conditions in an otherwise evacuated space in the geometrical confines of a beam. The collision-free proviso is important for our purposes because a molecule, once oriented, must

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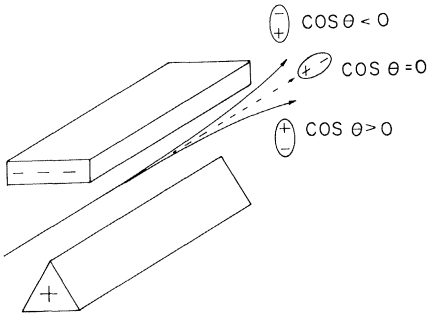


Fig. 1. Deflection of symmetric top molecules with different orientations. The electric field strength is greatest near the knife-edge electrode and the molecules are deflected in directions which minimize their energy in the field. Deflections are greatly exaggerated here.

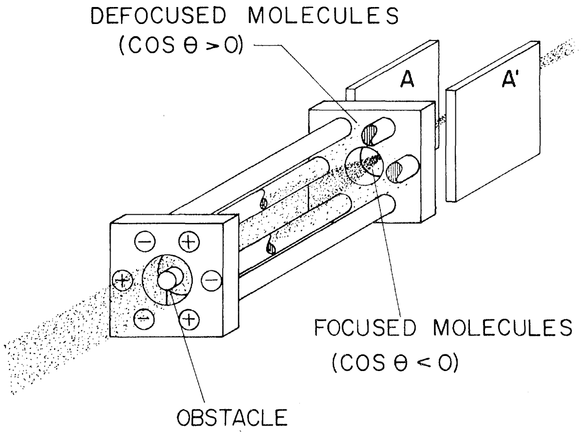


Fig. 2. Deflection of molecules in hexapole field. The entrance obstacle blocks molecules with $\cos\theta = 0$, and molecules with $\cos\theta > 0$ are defocused. Only molecules that can be focused ($\cos\theta < 0$) are passed. A weak uniform field is applied between plates *A* and *A'* to provide a unique quantization axis, and the direction of orientation can be reversed by reversing the polarity of these plates.

not undergo any reorienting collisions before it is struck by the reacting atom. Various reviews discuss in detail the all-important aspects of beam formation and detection and their applications to problems such as determining how energy is partitioned among the reaction products or how long complexes live (*5*). We will note here only that molecular beams are usually formed by effusion of molecules from a small orifice in an oven at low pressures (~ 0.1 torr) into a vacuum chamber. The molecules in the beam are not charged and their energies are typically near thermal. Apertures are used to produce a geometrically defined beam. Two such beams may be crossed, resulting in a small number (≤ 10 percent chance) of collisions between them. The molecules are detected by first ionizing them, and then measuring the ion current. Fast vacuum pumps remove the unreacted beam molecules.

Brute Force—How Not to Orient Molecules

People usually assume that we orient molecules by applying incredibly intense electric fields to physically twist them into alignment. This is possible, but difficult, for molecules that are not rotating. Unfortunately, the rotation which is normally present makes this prohibitively difficult, as illustrated in the following example. Consider a simple molecule such as HCl rotating in an electric field. In zero field the molecule rotates about its center of mass in a plane perpendicular to the angular momentum vector. Because the dipole moment is rotating with the molecule, the effect of an applied field depends on the orientation of the plane of rotation and the field direction. There are two limiting cases: in one case the field is perpendicular to the plane of rotation. If the field is perpendicular to the plane of rotation, it acts to align the dipole throughout the period of rotation. If the rotation is slowed—or equivalently, if the field strength is increased—the degree of alignment is improved. This can be visualized by spinning a rock on the end of a string in the earth's gravitational field. (The classical equations for a rotating dipole in an electric field and a rotating mass in a gravitational field are the same, with the string direction taken to be the analog of the dipole direction.) If the rock is rotated in a horizontal plane it will droop ("align"), and the droop will increase if the speed of rotation is reduced. In the other limiting case, where the electric field (gravitational field) is parallel to the plane of rotation, the field affects the rotation: as the dipole (rock) aligns in the field, the field speeds up the rotation and the dipole very rapidly traverses the perfectly aligned orientation. As the dipole rotates toward an unfavorable orientation (up), the field slows the rotation. The net effect of the field is that the system spends most of its time in the unfavorable (up) position. In other words, it is antialigned. In a rough sense a beam or a gas will contain equal numbers of molecules in the two limiting cases, and application of an electric field will produce roughly equal numbers of aligned and antialigned molecules.

If the field strength is so high as to suppress the rotation, then both orientations will lead to alignment and "brute force" orientation can be accomplished. The cost is prohibitive, however: to stop the rotation the electrical energy of interaction μE (μ is the permanent dipole moment of the molecule and E is the electric field intensity) must be greater than the rotational energy. For a molecule such as HCl, $\mu = 1.05$ debyes and μE becomes equal to the average thermal rotational energy kT at room temperature at a field strength of 12 million volt/cm. (This greatly exceeds our experimental capabilities.)

By averaging over all these rotational states, we have calculated the average orientation one could expect if such an enormous field were applied (*6*). For HCl molecules with a rotational temperature of 300°K in a field of 10^7 volt/cm $\langle \cos\theta \rangle = 0.21$, where θ is the angle between dipole and field and $\langle \cos\theta \rangle$ is the average over all states. (Perfect orientation corresponds to $\langle \cos\theta \rangle = 1$, and the calculated value corresponds to $\theta \sim 78°$.) This is not very much orientation for 10^7 volt/cm. Molecules in the rotationless state, with total angular momentum $J = 0$, are easier to orient; a similar calculation for HCl molecules with $J = 0$ shows that a field strength of only 280 kv/cm is required to produce $\langle \cos\theta \rangle = 0.21$. Techniques are available to obtain beams of molecules in the $J = 0$ state (*7*), but the need to maintain these electric fields in the reaction zone further complicates the experimental problems of maintaining high field strengths, and the presence of the field during the reaction may complicate interpretation of the results (*8*).

Selecting Orientations—Symmetric Top Molecules

The problems associated with brute force orientation of diatomic molecules arise largely because the molecules are rotating and, secondarily, because the dipole moment averages to zero in the course of a complete revolution of the molecule. (Diatomic molecules are pathological examples from this latter standpoint.) But there is a class of molecules whose dipole moments are not averaged to zero by rotation. These are the symmetric tops—molecules in which two of the three principal moments of inertia are equal—and they include molecules with threefold (or higher) axes of symmetry. Examples of such molecules are methyl iodide, chloroform, and phosphine (CH_3I, $CHCl_3$, and PH_3). These molecules are not constrained to rotate about an axis perpendicular to the dipole and, as a consequence, the dipole moment is not averaged to zero by rotation. Their behavior in an electric field is seen most easily by analogy with a child's top (hence the name) spinning in a gravitational field. When properly started, a child's top will spin rapidly about its axis and the axis will precess slowly around the vertical, with the top axis making a (nearly) constant angle θ with the vertical (*9*). Even though the top is rotating, one end is "down" and the other "up" throughout the course of rotation. If a very large number of tops were spun, we would expect tops in all stages—some up, some down, and some sideways. Similarly, a gas of symmetric top molecules such as CH_3I (in a weak field, to supply a spatial direction) would consist of some molecules oriented up, some down, and some sideways. The number up equals the number down in the zero field limit, so on the average the gas would not be oriented. But each individual molecule is oriented, and will remain so until it experiences a collision.

In a molecular beam we eliminate collisions so that we can produce a beam of oriented molecules, either by brute force twisting or by removing molecules in unwanted orientations. Filtering can be accomplished by techniques that are the electrical analogs of the Stern-Gerlach experiment. This is possible because molecules in different orientations have different energies in an electric field (the Stark effect). Classically, the energy of interaction W is given by

$$W = -\bar{\mu} \cdot \mathbf{E} = -\mu E \cos\theta$$

A quantum mechanical treatment shows that $\cos\theta$ is quantized, but for all practical purposes we may regard it as continuous (*10*). The sign of the interaction energy thus depends on whether $\cos\theta$ is positive, negative, or zero.

If a symmetric top molecule is placed in an inhomogeneous electric field, the molecule can minimize its energy by moving in the field. Molecules with positive values of $\cos\theta$ will be deflected toward regions of high electric field and those with negative values will be deflected toward low-field regions. Molecules with $\cos\theta = 0$ will not be deflected.

The simplest sort of inhomogeneous electric field can be generated between a flat electrode and an electrode with a knife edge. (This is the electric analog of the Stern-Gerlach setup.) The field is most intense near the knife edge, and a beam passed through such a set of electrodes will split into three components as shown in Fig. 1. Unfortunately, the deflection is small and the divergence of the two perfectly oriented components is roughly 1°. Extremely well collimated beams would be required to separate the emerging beams cleanly, and the intensity would be too low to perform scattering experiments.

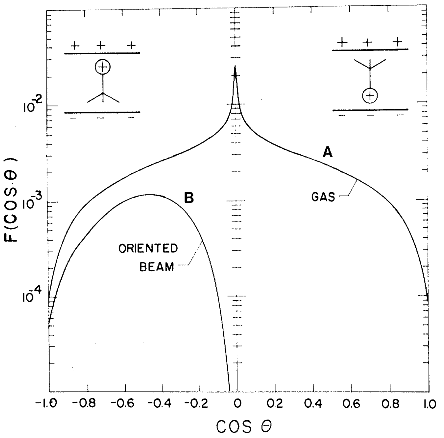


Fig. 3. Calculated distribution of molecular orientations for $CHCl_3$. Curves are smoothed quantum mechanical results. Curve A denotes the orientations found in a gas at 300°K and is symmetric about zero (no net orientation). Curve B denotes the orientations (a configuration) transmitted by the selecting field at 10 kv. Insets show the relation between the dipole and the applied field for a particular sign of $\cos\theta$.

In order to overcome the intensity limitations of the "Stern-Gerlach" field of Fig. 1, the inhomogeneous field is created by six equally spaced rods alternately charged to ~15 kv, as shown in Fig. 2. The beam travels down the axis of the array and, since the field on the axis is zero because of symmetry, molecules with $\cos\theta < 0$ are deflected toward the axis. This has the virtue of focusing molecules with $\cos\theta < 0$, and long path lengths (r) can be used for state separation without concomitant $1/r^2$ losses. Molecules in states with $\cos\theta > 0$ are defocused from the beam, and those with $\cos\theta = 0$ are removed by appropriate obstacles. The array thus serves as a filter to transmit only molecules with $\cos\theta < 0$. The use of such a field to focus symmetric top molecules was suggested by Bennewitz *et al.* (*11*), and its use in orienting molecules was suggested by Kramer and Bernstein (*12*).

This electric field serves to select molecules in certain states, but the molecules are not yet oriented in the laboratory. The molecules that have been selected are oriented in the local electric field, which is not uniform in direction inside the hexapole array. Consequently, a weak (~10 volt/cm) uniform electric field is applied at the exit of the state-selecting array. The local field experienced by a molecule will appear to slowly rotate from the direction inside the inhomogeneous field to the direction of the applied uniform field. The molecule will remain oriented with respect to its local field, and is said to have made an adiabatic transition. [Independent experiments, described in more detail below, have shown that the molecules do make adiabatic transitions (*4*)]. The laboratory orientation of the molecules in the uniform field can be reversed simply by reversing the polarity of the uniform field.

We are thus able to orient molecules in a molecular beam by first selecting only molecules with the proper orientation, and then allowing them to fly into a weak uniform electric field, where their quantum states correspond to laboratory orientation. We must confess, however, that this does not result in the sort of perfect orientation one imagines when holding a model of a molecule. Instead,

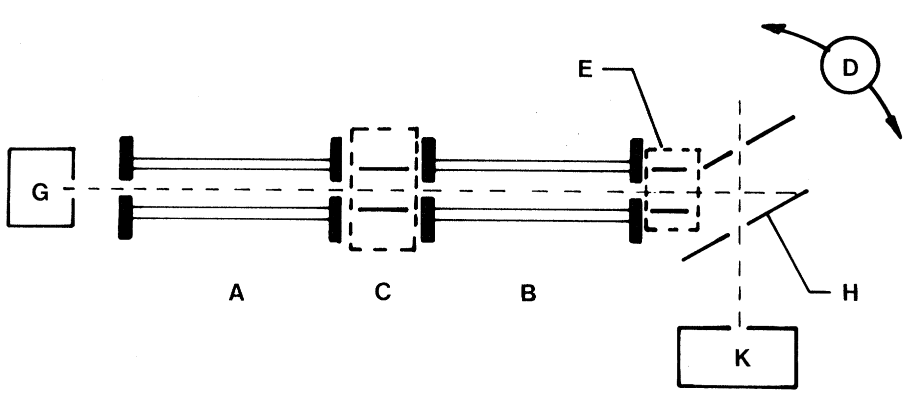


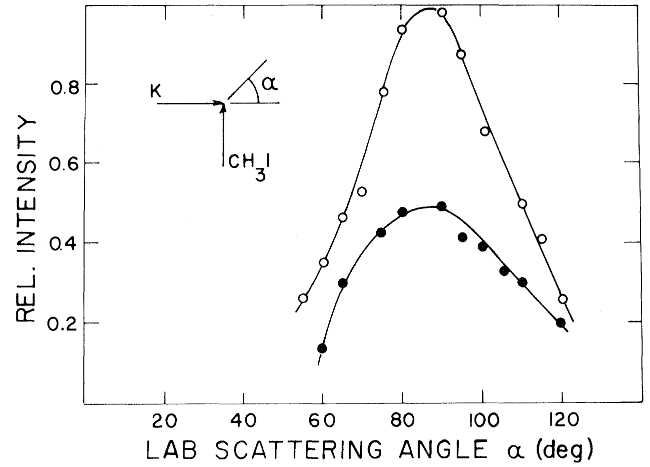
Fig. 4. Schematic of apparatus used in oriented molecule experiments. A beam of symmetric top molecules emerges from G and molecules with the proper orientation are selected by the inhomogeneous hexapole fields A and B. These molecules are oriented in homogeneous field H. Potassium atoms emerge from K and pass through holes in field plates H to react with oriented molecules. Product molecules are detected as a function of scattering angle by rotating detector D. An electric field must be applied in C and E to ensure that the molecules remain oriented.

we have a distribution of orientations. Each molecule in the beam is characterized by a specific orientation with $\cos\theta < 0$ ($90 \leq \theta \leq 180$), but many different values of $\cos\theta$ are possible. The calculated distribution of $\cos\theta$ in a gas and the distribution of $\cos\theta$ after state selection are shown in Fig. 3. The state selection process removes all molecules in the wrong orientations ($\cos\theta \geq 0$) and discriminates somewhat against low values of $-\cos\theta$. But note that the most likely orientation even after state selection occurs for fairly low values of $-\cos\theta$, corresponding to nearly broadside orientation. If the polarity of the uniform field is reversed, the laboratory orientation of each molecule (relative to a space-fixed axis) changes from θ to $\pi - \theta$.

For a molecule such as CH_3I, we are thus able to compare the reactivity of two configurations: the distribution of orientations (configuration) in which the I end is closest to the incoming atom, or that in which the CH_3 end is closest (*13*). We have adopted the convention that the configuration we presume is most reactive is called the "heads" configuration, the other the "tails" configuration. For CH_3I the heads configuration is the one with I closest to the incoming atom.

Reactive Scattering

The experimental apparatus is shown schematically in Fig. 4. A beam of the molecules to be oriented emerges from the oven and travels through the hexapole field. The molecules selected by the hexapole field fly into the uniform electric field applied to the region where the beams cross. Because the molecules make adiabatic transitions into the uniform field, they are oriented along the direction of that field, which is tilted to be parallel (or antiparallel) to the direction of relative approach of the incoming atomic beam. The configuration of the molecules can be changed from heads to tails by reversing the polarity of the uniform field. Reactively scattered molecules are detected as a function of scattering angle and orientation by a detector which can be rotated about an axis passing through the scattering center. Further details on the apparatus and experimental procedures can be found in the original papers.



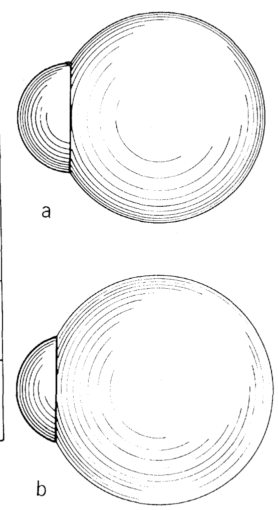
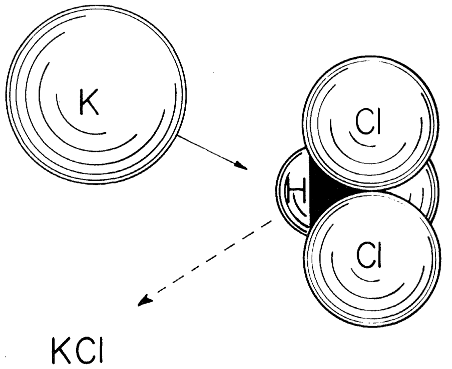


Fig. 5 (left). Representative laboratory angular distribution of KI produced in reaction of K atoms with oriented CH_3I molecules. Open circles are for the heads configuration (I end closest to incoming K) and filled circles are for the tails configuration. Fig. 6 (right). Hard-sphere model used to interpret reactive scattering of alkyl iodides. The alkyl group is assumed to shield the I (small sphere) from attack from the rear, and the size of the alkyl group is chosen to give agreement with experiment. Models are for (a) CH_3I and (b) t-C_4H_9I.



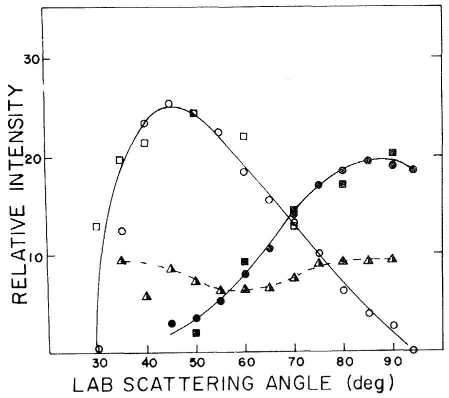


Fig. 7 (left). Model of $CHCl_3$ reaction. The lone H atom apparently offers no hindrance to the formation of KCl and apparently does not influence the direction in which the KCl is ejected. Fig. 8 (right). Angular distribution of KI produced in reaction of K atoms with CF_3I. Filled points denote scattering from the heads configuration and open points denote scattering from the tails configuration. Half-filled points show the angular distribution of scattering from molecules that have been oriented but then randomized before scattering.

Reactions of Iodoalkanes—Chemical Intuition Vindicated (?)

The reaction of oriented CH_3I was studied first (*4*) because it had been extensively studied in other beam experiments (*14*). Representative results for K reacting with CH_3I are shown in Fig. 5. As expected, the heads configuration of the molecule (the negative, or I end) was found to be more reactive. Similar results were found for the reaction of t-butyl iodide (t-C_4H_9I) (*15*). These studies thus conclusively demonstrated the existence of a steric effect.

Most of our ideas regarding steric effects are based on hindrance: the nonreactive end of the molecule presumably gets in the way of the incoming atom. We might thus anticipate that the tails configuration would lead to no reaction at all. However, not all of the molecules are perfectly oriented, and the nonzero reactivity found for the tails configuration is presumably due to the ability of alkali atoms to fly past the CH_3 end and strike the I even though the CH_3 group is closest. (Note that we cannot control the site of impact, but only the end of the molecule closest to the incoming atom.) To see if this can be reconciled quantitatively with experiment an average over the orientations present in the beam must be performed, and two models have been introduced for this purpose. The first, introduced by Beuhler and Bernstein (*16*), approximates CH_3I as a sphere with reactive and nonreactive zones. The second, a similar model of Marcelin and Brooks (*15*), regards an alkyl iodide molecule as similar to the space-filling Fisher-Hirschfelder-Taylor models, with an I sphere connected smoothly to an alkyl group sphere, as shown in Fig. 6. The I is assumed to have its covalent radius, the centers of the spheres are separated by the average C–I bond length, and the size of the alkyl group sphere is varied to reproduce the ratio of reactive cross sections in the heads and tails configurations. The results obtained for CH_3I and t-C_4H_9I are shown in Table 1. The hindering radii required to fit the data are in comfortable agreement with the van der Waals radii, and the gas-phase steric factors predicted from them are in agreement with chemical intuition. A similarly reasonable steric factor of 0.7 was found for Rb + CH_3I by Beuhler and Bernstein (*16*).

Table 1. Steric information for CH_3I and t-C_4H_9I (*15*).

Molecule	Van der Waals radius (Å)	Hindering radius (Å)	Steric factor
CH_3I	2.0	2.5	0.5
t-C_4H_9I	2.7	2.8	0.4

These hard-sphere models thus account nicely for the relative heads and tails reactivities, and we are tempted to pat ourselves on the backs for being right all along. Unfortunately, we know too much. The angular distribution of scattered product molecules gives information about the detailed mechanism of the reaction which is difficult to explain intuitively. The product appears at large (~ 90°) laboratory scattering angles, which correspond in the center-of-mass coordinates to the newly formed KI rebounding in the direction from which the alkali metal came. A long-lived complex is not found. The oriented molecule results still show no complex formation for either heads or tails, and the KI rebounds in each orientation.

A simple hard-sphere model is completely consistent with rebound scattering for the heads configuration: the incident alkali atom hits the I end of the molecule, the KI species hits the CH_3 group, and the KI is bounced back in the direction from which the K came. However, a similar interpretation is not possible for the tails configuration. We would expect that if the K atom flies past the hindering CH_3 group, the KI will be prevented from rebounding by the CH_3 group and will be scattered forward. This, of course, is not what is observed, and the hard-sphere model is inconsistent with the data. Other models could be constructed, and some model trajectory calculations (*17*) suggest that it may be possible to find a potential energy surface that would lead to complicated trajectories which would be different for various orientations. Thus, the reaction might be direct in the heads configuration, but might involve the formation of a complex that lasts for only half a rotation in the tails configuration. Speculation is easy, however, and any potential chosen must now satisfy the large body of experimental information available (for CH_3I), such as the angular distribution, the energy dependence of the cross section, and the partition of energy among the products. Despite considerable theoretical effort, a model that will fit all the data has not yet been found (*18*).

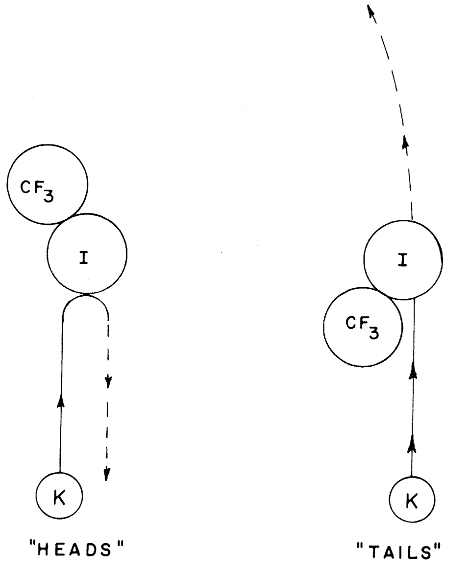


Fig. 9. Schematic of backward scattering from the heads configuration of CF_3I and forward scattering from the tails configuration. (The tails configuration of CH_3I gives backward scattering, unlike the prediction of this simple model.)

Reaction of Chloroform

The geometry of a molecule influences the degree to which it can be oriented. Oblate tops such as $CHCl_3$ or bicycle wheels are easier to spin about their axes than prolate tops such as CH_3I or pencils. We are thus able to prepare a $CHCl_3$ beam with better orientation than a CH_3I beam, but for the reaction $K + CHCl_3 \rightarrow KCl + CHCl_2$ we find no difference in reactivity between the heads and tails configurations (*15*).

This is perhaps easier to understand than the behavior of CH_3I. Figure 7 shows schematically the relative sizes of the large Cl atoms and the very small H atom. There are now three reactive sites on the molecule and the H atom seems to be sufficiently small to offer no hindrance to either the incoming K atom or the outgoing KI molecule. The product KI is scattered backward from both configurations, as suggested by Fig. 7.

Reaction of Trifluoromethyl Iodide—A Nonintuitive Result

Our earliest studies (*19*) of the reaction

$$K + CF_3I \rightarrow KI + CF_3$$

appeared to show that reactivity was greatest in the tails configuration. Subsequent studies (*20*) showed that this result depended on the scattering angle, and representative results are shown in Fig. 8. Backward scattering occurs for the heads configuration, just as it did for CH_3I. The reactivity is approximately the same for the tails configuration, indicating lack of hindrance, but the product is scattered at different angles which correspond to the forward direction. Once again, a long-lived complex is not formed.

The surprising reactivity in the tails configuration cannot be explained by assuming that we are observing KF formation in these collisions, because a large body of evidence strongly suggests (*20*) that KF is not a product. Gas-phase experiments in which macroscopic amounts of salt are collected suggest that KI is the sole product of the reaction (*21*). We are thus left to conclude that the reaction mechanism for the tails configu-

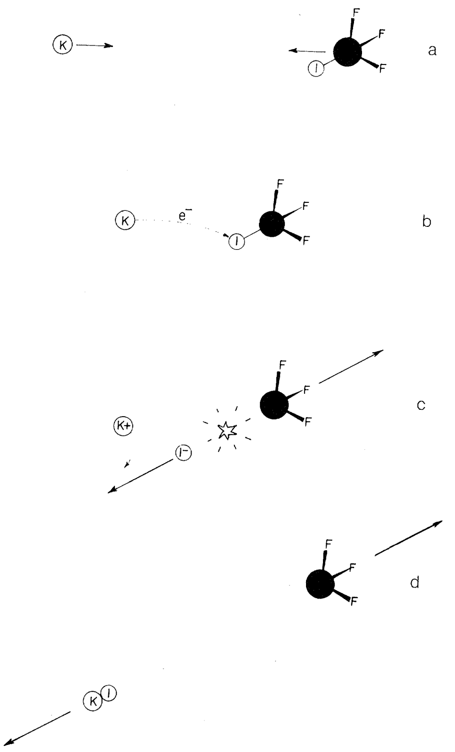


Fig. 10. Postulated electron jump model for the reaction $K + CF_3I$. (a) The K approaches the CF_3I, shown here in a heads configuration. (b) An electron from the easily ionizable K is donated to the electronegative CF_3I. (c) The negative ion dissociates, ejecting the I^- in the instantaneous direction of the C–I bond. The K^+ begins to move toward the I^-, and (d) the KI and CF_3 recoil.

ration consists of a K atom flying past the CF_3 end of the molecule, plucking off the I, and proceeding in the same direction. A schematic view of this mechanism is shown in Fig. 9.

The difference in behavior between CH_3I and the apparently anomalous CF_3I may be that the more electronegative CF_3I can participate in an electron transfer reaction (*22*). In this reaction, schematically shown in Fig. 10, the easily ionizable potassium atom donates an electron to the electronegative molecule. If the negative molecular ion is unstable it will immediately dissociate, sending the I^- species in the direction in which the C–I bond was "pointed" at the instant of dissociation, and the K^+ ion will tag along with the I^-. This mechanism predicts that in the tails configuration the I^- ion will be ejected forward because the C–I bond is pointed away from the incoming K. Likewise, in the heads configuration, the I^- will be ejected backward, in the direction from which the K comes. When combined with detailed orientation distributions, this mechanism accounts quantitatively for the observed laboratory peaks (*23*). It also accounts nicely for the angular distributions observed with unoriented molecules, which can be regarded as a mixture of heads and tails (*24*).

Are the Molecules Really Oriented?

Molecules that are selected by the inhomogeneous field should be oriented if they make adiabatic transitions into the uniform field. We have determined (*4*) that they will make these adiabatic transitions by placing a test homogeneous field (at C in Fig. 4) between two focusing hexapole fields. If an electric field $\gtrsim 10$ volt/cm is maintained in C, molecules make adiabatic transitions in this region and are observed to be focused by field B. If the field in C is near zero, the molecules essentially lose their reference direction and become randomly oriented. This is observed because the wrong orientations are not focused by field B and a decrease in beam intensity is observed. We are thus quite confident that under our experimental conditions the molecules make adiabatic transitions and should be oriented. The reactive scattering results which show that reactivity depends on orientation tend to support this.

Nevertheless, strong electric fields exist in the apparatus, and we wish to demonstrate beyond doubt that the molecules are oriented. In order to do this, an additional, but well-shielded, uniform field (at E in Fig. 4) can be introduced between the high-voltage selecting field and the uniform field applied to the reaction center (*20*). The molecules will make adiabatic transitions and will be oriented in the scattering region if a weak field is applied in E. However, the experiments described above show that if the field is zero, the molecules will not make adiabatic transitions but will, instead, become randomly oriented. Figure 8 shows the result of this disorienting experiment. When the orientations are first selected and then randomized, the reactive scattering is intermediate in magnitude between heads and tails scattering and independent of the direction of the orienting field H, indicative of roughly equal contributions from both configurations. Thus, by being able to randomize the beam, we have shown that it was oriented in the first place.

The molecules are oriented before the collision and the results for CF_3I show that they do not turn to present their most favorable end to the incoming atom. If the atom is very close ($\lesssim 5$ Å), however, the molecule is no longer isolated and we cannot rule out on experimental grounds the possibility that it rotates in the course of the reaction. This, of course, is a possible explanation for the backward scattering from the tails configuration of the alkyl iodides, and further work is required to elucidate this possibility.

Summary

Beams of oriented molecules have been used to directly study geometrical requirements in chemical reactions. These studies have shown that reactivity is much greater in some orientations than others and demonstrated the existence of steric effects. For some reactions portions of the orientation results are in good accord with traditional views of steric hindrance, but for others it is clear that our chemical intuition needs recalibrating. Indeed, the information gained from simultaneously orienting the reactants and observing the scattering angle of the products may lead to new insights about the detailed mechanism of certain reactions.

Further work must be done to extend the scope and detail of the studies described here. More detailed information is needed on the CH_3I reaction and the CF_3I reaction. The effects of alkyl groups of various sizes and alkali metals of various sizes are of interest. In addition, reactions where a long-lived complex is formed should be studied to see if orientation is important. Finally, it would be of interest to apply the technique to the sort of reactions that led to our interest in the first place: the S_N2 displacements in alkyl halides where the fascinating Walden inversion occurs.

References and Notes

1. K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, ed. 2, 1965).
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3. By orientation we mean the relation between the molecular geometry and some axis. By contrast, polarization and alignment with respect to some axis refer to angular momentum distributions, the former depending on the magnitude and sign of the components of the angular momentum in the field direction, M_J, the latter only on the sign.
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