Accordingly, the *c* series is assigned to a progression from the same upper state to the ground state levels $(0v_21)$.

Differences between the *a* and *e* series range from 738 to 720 cm^{-1} in very good agreement with the C–Cl mode of CClBr; the decrease comes from the anharmonic term X_{12} which is approximately -5 ± 2 cm^{-1}. The *e* series is assigned to the progression terminating in $(1v_20)$ levels. The *c* and *e* series energies, relative to the *a* series, confirm that the carrier of the fluorescence spectrum is CClBr.

The short *d* series of four members are spaced another quantum of the C–Br mode above the *c* series. The *d* series is attributed to the $(0v_20) \rightarrow (0v_22)$ fluorescence and it provides an X_{33} estimate of -1 cm^{-1}.

The *b* series is spaced approximately 190 cm^{-1} higher energy from the *c* series. This energy is appropriate for the excited state bending mode spacing. Therefore, the *b* series is assigned to the "excited state" progression $(0(v_2 + 1)0) \rightarrow (0v_21)$ counterpart to the *c* progression $(0v_20) \rightarrow (0v_21)$. The six lower energy *b* bands may in fact belong to a different progression than the four higher energy *b* bands; the present data are incapable of ruling out this possibility.

Two unlabeled bands at 14,372 and 14,113 cm^{-1} may also belong to CClBr since they exhibit the correct spacing, but without more members, this short "series" cannot be identified. Likewise weak bands on the low energy tail at 12,730, 12,680, 12,470, and 12,430 cm^{-1} may belong to other progressions of CClBr which cannot be defined without additional data.

The fact that the fluorescence spectra of the CX$_2$ species show long, strong progressions in the bending mode indicates a large change in valence angle between the ground and excited electronic states. The valence angles for the ground (105°) and excited (122°) electronic states of CF$_2$[14] are indicative of the geometries of these states for the heavier CX$_2$ species.

It is interesting to speculate on the failure to observe a fluorescence for CI$_2$. CI$_2$ is probably produced by the iodocarbon analogs[16] of reactions 1 and 2. However, CI$_2$ could be photodecomposed by the laser excitation. If the analogous electronic band for CI$_2$ were between 5682 and 6471 Å or to the red of 6500 Å, the presently available krypton plasma laser lines could not excite the fluorescence.

Conclusions

CBr$_2$ and CClBr have been synthesized by matrix reaction of CBr$_4$, CClBr$_3$, and CCl$_2$Br$_2$ with alkali metal atoms. Fluorescence spectra excited with 5682 Å krypton ion laser light have revealed two progressions in the ground state bending mode for CBr$_2$ (196 cm^{-1}) which emanate from two different bending mode levels of excited CBr$_2$; these emitting levels cannot be definitely assigned. The CClBr spectrum was only observed using the CCl$_2$Br$_2$ precursor suggesting nearly equal reactivities of chlorine and bromine with alkali metal atoms. Owing to the lower symmetry of CClBr, its fluorescence spectra were more complex than the CBr$_2$ spectra. Progressions in the CClBr ground state bending mode (257 cm^{-1}) were observed with and without combinations of the C–Br and C–Cl stretching modes.

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Steric Hindrance in Potassium Atom-Oriented Molecule Reactions. Methyl Iodide and *tert*-Butyl Iodide

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Abstract: The reaction of K atoms with oriented CH$_3$I or *t*-C$_4$H$_9$I molecules has been studied via the crossed molecular beam method. Oriented molecules are produced by passing a molecular beam through an inhomogeneous electric field which rejects unwanted orientations. The remaining molecules are oriented with respect to a weak electric field and can be reversed in the laboratory by changing the direction of the applied field. The reaction is studied for impact at the two ends of the molecule and for both reactions the iodine end is most reactive. A simple model is used to interpret the results and suggests that the hindering size which can be ascribed to the R groups is only roughly compatible with van der Waals radii.

Very few gas phase bimolecular chemical reactions proceed on every gas kinetic-collision. Most reactions have an activation energy which (presumably) restricts reaction to those collisions with energy greater than the activation energy, E_a. But counting only those collisions with energy greater than E_a still gives a rate faster than the rate of almost any chemical reaction. To account for this discrepancy between theory and fact the notion was advanced that only certain orientations of the reagents were effective in promoting reaction, and the "steric factor", ρ, was introduced as the fraction of gas-kinetic collisions which had the right orientation to react.

The qualitative aspects of the steric factor are both intuitive and useful. One routinely invokes the notion that reaction is localized on only one portion of a molecule and that bulky groups adjacent to the reaction site may inhibit reaction. Quantitatively, however, there has been no satisfactory basis for understanding steric factors. In a few instances[2a] ρ lies in the range 0.1–1.0 and seems intuitively acceptable, but in other cases incredibly small values of ρ cast doubts on the use one may make of geometric arguments. Unfortunately, kinetic data cannot be obtained with sufficient precision to enable an unambiguous determination of ρ nor to study the effect on ρ of subtle variations in molecular structure. For these reasons the steric factor has often been relegated to the dust bin as a "fudge" factor and alternative approaches to theories of kinetics have been taken.[2b]

With the development of techniques for studying chemical reactions in crossed molecular beams, one is essentially able to study the reactions of *isolated* molecules, and these molecules may be prepared in a variety of initial states. In particular, it is possible to orient the molecule prior to reaction and several reports of reactions using oriented molecules have now appeared. The earliest of these[3] were performed on CH_3I and showed, in agreement with chemical intuition, that reaction took place preferentially on the I end. Subsequent investigations were concerned with in-depth studies of the $Rb + CH_3I$ reaction[4] and with studies of the $K + CF_3I$ reaction which showed behavior at odds with chemical intuition.[5] It should be noted that this approach does not yield steric factors, but rather it is capable of yielding much more detailed information, how does reaction probability vary with orientation, from which steric factors may be obtained. This appears to be a crucial item in modeling potential enery surfaces.[6]

In this article we describe the reaction of K atoms with oriented CH_3I and $t\text{-}C_4H_9I$ molecules which were briefly reported in a preliminary communication.[7] The comparison of the two molecules is of interest, partially on intrinsic grounds, and partially because an earlier study[8] of the reactivity of unoriented alkyl iodides found almost no difference in behavior when the R group was changed. It might be argued that this is not surprising because the transition state is K- - -I-R and hence the R group should not affect the reaction. But the early evidence demonstrated that a long-lived complex was not formed so the assumptions of transition state theory are not valid. Nevertheless, our results partially support that naive picture because for both molecules reaction takes place preferentially on the I end, although some reaction can still occur when the molecule is approached from the backside. In order to assess the effect of the size of the R group on reactivity, a simple model is introduced which can be averaged over the (different) orientation distributions of the two molecules.

This model requires the *tert*-butyl group to have a radius comparable to the van der Waals radius, but the methyl group radius, while smaller than *tert*-butyl, is larger than the van der Waals radius. The steric factors predicted by this model are 0.5 for CH_3I and 0.42 for t-BuI and roughly support the earlier observations.

Experimental Section

The apparatus is schematically shown in Figure 1. While several new features have been added, it is similar in concept to that described earlier.[5] Each of the four chambers in the figure is differentially pumped.

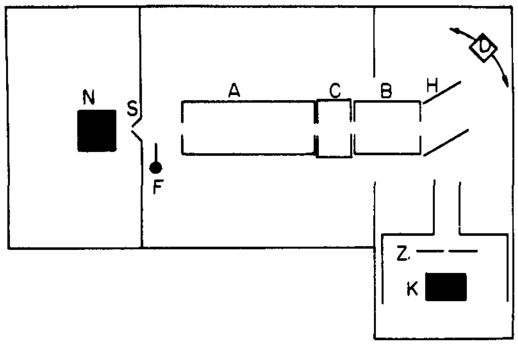

Figure 1. Schematic diagram of apparatus. Beams of alkyl halides are formed by hydrodynamic expansion from the nozzle (N) collimated by the skimmer (S) and can be interrupted by the beam flag (F). The electric deflection field (ACB) acts as a filter to pass molecules with certain orientations. The K atom beam effuses from oven K, is collimated by Z, and reacts with the oriented molecules in the tilted uniform field H. The rotating detector D measures the angular distribution of product.

Potassium atoms effuse from a single chamber Monel oven and 13.5 cm away intersect the gas beam at right angles. The gas beam is formed by hydrodynamic expansion from a 0.2 mm diameter nozzle and is collimated by a 0.7 mm diameter skimmer. The alkyl iodide sources are well-outgassed liquids held near room temperatures which yield driving pressures of a few hundred Torr. The gas beam is passed through an inhomogeneous electric hexapole field 58 cm long which serves to select molecules for which cos θ is negative, where θ is the classical angle between the dipole moment of the molecule and the electric field. (For symmetric top molecules cos θ is given by a combination of quantum numbers, $\cos\theta = MK/J(J+1)$.) These state-selected molecules pass into a region of uniform electric field (~90 V/cm) created by two parallel plates which are tilted ~30° with respect to the gas beam so the field is parallel to the average relative velocity vector. The two beams cross in this region of uniform field so molecules are oriented with respect to the incoming K atoms. The direction of alignment can be reversed by reversing the polarity of the two plates. Holes are cut in the plates to pass the beams.

Reactive scattering of KI is distinguished from the nonreactive scattering of K atoms by ionizing the particle flux on the surface of one of two hot wires. One of these (W) ionizes both K and KI. The other (a Pt-W alloy) ionizes only K atoms. The ions formed are focused onto a Bendix 306 electron multiplier and the current pulses from the multiplier are counted. Because the K atom ionization efficiency was different on the two wires it was necessary to measure the relative ionization efficiencies using the scattering from a nonreactive beam. CH_3OH was used for this purpose because it could be focused and could therefore be substituted for the alkyl halide beam. When the nonreactive scattering measured on the Pt-W filament was corrected for this ionization efficiency, subtraction of signals from the two wires then gives a measure of the KI produced. Details of this procedure and of the rest of the apparatus may be found elsewhere.[9]

Interpretation of the reactive scattering experiments requires knowledge of the distribution of orientations in the state-selected beam. Direct measurement of this distribution is possible by determining the deflection of a state-selected beam in an inhomogeneous electric field, but this measurement is complicated by also being velocity sensitive. Consequently, no experimental determination has yet been made of the orientation distribution and this distribution has instead been calculated using techniques previously described.[10] The transmission of molecules in a given range of cos θ is evaluated by numerically integrating over the incident velocity distribution and position of entrance in the field. The final distribution of orientations is then the product of the initial distribution and the probability of transmission. The final velocity distribution can be found by a similar technique. By integrating over either the final velocity distribution or orientation distribution, one obtains the total transmitted beam intensity which can then be compared with experiment[10] to an accuracy sufficient to determine the dipole moment to ~1%.

Unfortunately, this calculation requires knowledge of the incident velocity distribution and of the distribution of initial states. In the previous investigation[10] gas effused from a room temperature source so the velocity distribution could be assumed to be the modified Maxwell–Boltzmann distribution, and the distribution of rotational states (which characterizes the orientation) can be calcu-

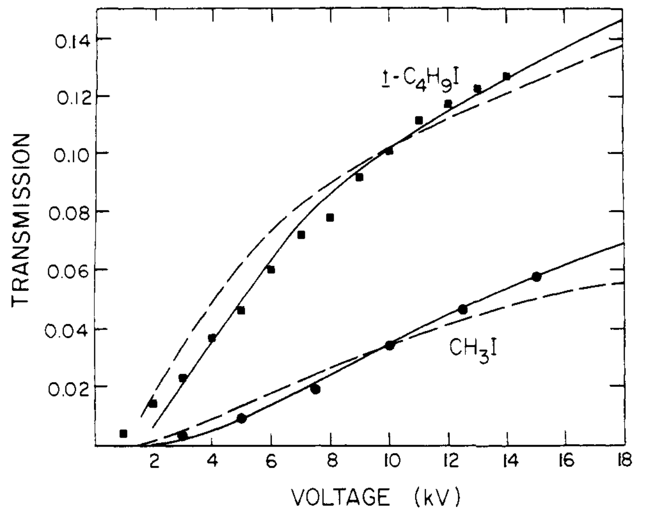

Figure 2. Calculated curves and experimental points for total transmission of beam through electric hexapole field. Dashed lines are calculated assuming $M = 3.5$, solid lines are for $M = 5$. Curves are normalized to experiment at 10 kV and different curves show sensitivity of calculations to the Mach number. (This is assumed to be 5 for MeI and *t*-BuI in subsequent calculations.)

lated from equilibrium statistical mechanics. But it is well known that when gas hydrodynamically expands from a nozzle, the velocity distribution narrows and shifts to a higher peak value[11] with a concomitant decrease in the internal temperature.[12,13] Previous studies of the characteristics of nozzle beams have largely been confined to atomic and diatomic molecules, and it was not clear what Mach numbers we could expect for polyatomics and what rotational temperatures would result from the expansion (if indeed rotational level population could be characterized by only one temperature). In order to better characterize the nozzle beam, the velocity distribution was measured using time-of-flight (TOF) techniques.[9] Although the signal-to-noise ratio for the TOF measurements was less than desired, measurements for several gases (but never for the alkyl iodides) and several operating conditions indicated that Mach numbers were obtained in the range from about 3.5 to 5.

The theoretical gas temperature for such an expansion is given by $T_N = T[1 + (\gamma - 1)M^2/M]^{-1}$, where M is the Mach number and γ is the heat capacity ratio C_p/C_V. Such a range of Mach numbers therefore leads to a wide range of internal temperature as well as to a range of speeds. Fortunately, none of the calculations[14] were found to be sensitive to the rotational temperature (rotational temperatures of 150 and 300°K produced computational results identical to 0.1%).[15] This made possible a separate, finer determination of the velocity distribution by fitting calculated transmission curves to experimental points. As shown in Figure 2, the experimental transmission for MeI and *t*-BuI can be very well fit using an appropriate Mach number. The close agreement here inspires confidence in the experimentally unmeasured orientation distribution.[16] These distributions, together with the distribution in the unselected beam, are shown in Figure 3.

Results

Angular distributions of reactively scattered KI were determined separately for the "heads" and "tails" configurations of each molecule and are shown in Figure 4. In both cases it was determined that most reaction occurred at the *negative* end of the molecule.[17] This is assumed to be the iodine end.

Verification that the molecules are indeed oriented is obtained by destroying the orientation. The classical angle that the dipole moment makes with the field is $\theta = \arccos MK/J(J + 1)$, and a small electric field must be maintained in order to provide an axis of quantization so that M is defined. If the electric field is zero, all M states are degenerate and the slightest perturbation (from internal molecular fields or from other molecules passing nearby) will be sufficient to mix the M states which result in a randomization of the molecular orientation.[18] The reactivity of such randomized molecules could then be expected to be intermediate between the reactivity of either the heads or tails configuration, and this is the case as shown in Figures 4 and 5. While the reaction must be carried out in the presence of an electric field, the *magnitude* of the field is immaterial as long as it is sufficient to prevent disorientation of the molecules. The *direction* of the field, of course, determines the direction of orientation. Because of ever-present stray fields, the direction and magnitude are coupled in that the magnitude of the applied field must be sufficient that the vector resultant of the applied field and any stray fields must, to a good approximation, be in the direction of the applied field. The influence of the uniform field on the reactive scattering is shown in Figure 5 where the ratio of heads and tails reactive scattering signals is plotted versus field strength. For $|E| \gtrsim 50$ V/cm, the ratio is constant, indicating that the magnitude is both sufficient to prevent randomization and sufficient to outweigh the direction of stray fields. At low voltages the ratio tends to one, showing either that the molecules become disoriented[5] or that stray fields are predominant. In either case, our operating point of 90 V/cm was sufficient to define and maintain the orientation.

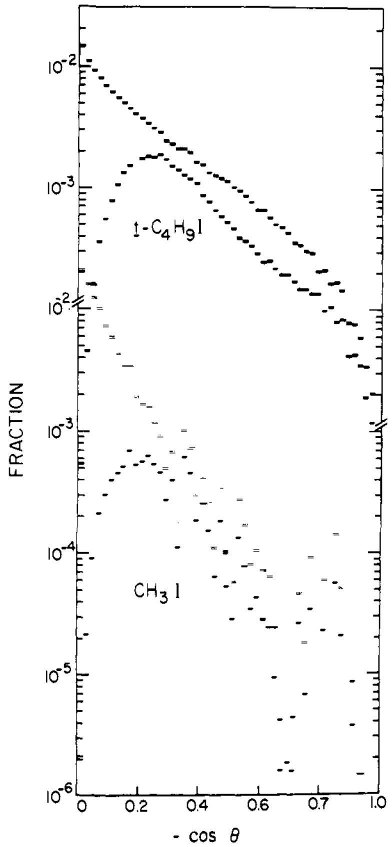

Figure 3. Calculated distribution of molecular orientation. Ordinate is the log of the fraction in an increment of (cos θ) of 0.02. (a) *tert*-Butyl iodide: top curve denotes orientations present in gas, bottom denotes orientations in state-selected beam. (b) Methyl iodide: top curve (open bars) denotes gas, bottom (light bars) denotes state-selected beam. (a) and (b) have been displaced two log units for clarity.

Discussion

Steric Hindrance. The data displayed in Figure 4 clearly demonstrate that the "heads" configuration is much more reactive that the "tails" configuration for both molecules. Unfortunately, each configuration represents a distribution of orientations which complicate interpretation of the data.

In order to gain some feeling for the effect of the orienta-

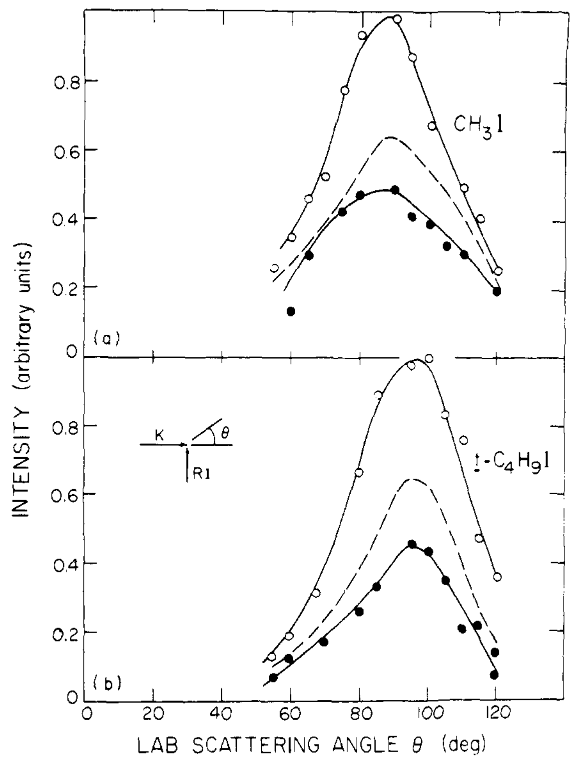

Figure 4. Angular distributions of reactively scattered KI from alkyl iodide molecules. Open points denote reaction from molecules oriented with the iodine end nearest the incoming K atom ("heads") and filled points denote reaction from molecules with the R end nearest the incoming atom ("tails"). Dashed curves are angular distributions from molecules which have been state selected, but are oriented randomly because of the absence of an electric field in the reaction center.

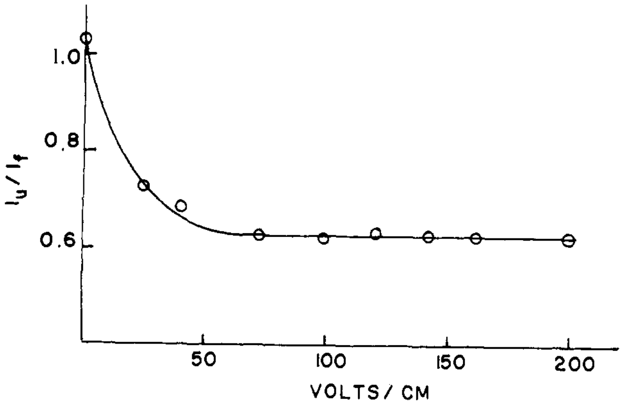

Figure 5. Ratio of signals from "tails" (I_u) and "heads" (I_f) configurations as a function of uniform field strength. This ratio should be independent of field strength except at low fields where the molecules may become unoriented.

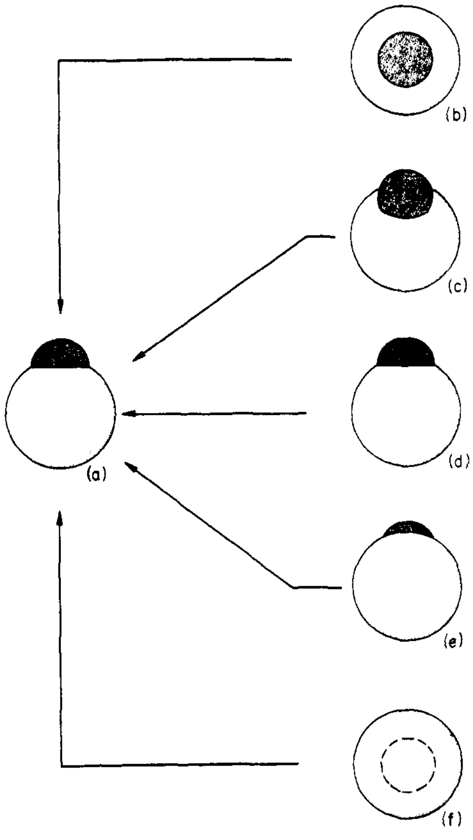

Figure 6. Hard sphere model used for interpreting results. A perspective side view (90° incidence) is shown in (a) and views for attack from other directions are shown in (b)-(f). Model parameters have been chosen so that the covalent radius of the I atom sphere (shaded) and center-to-center distances of the spheres are in the proportions given in Table I. The radius of the R sphere is allowed to vary to fit the data and is drawn to denote the steric size of CH_3 listed in Table I.

tion, it is necessary to adopt a simple physical model which can be averaged over the orientations present in the experiment. We earlier used a model which approximated CH_3I as two spheres of equal radii,[3a] and Beuhler and Bernstein[4] used as a model a partially reacting sphere in which the reactive and unreactive surface was separated by a plane passing through the sphere. We wish to maintain the flexibility of the Beuhler-Bernstein model but at the same time use a model which could be directly related to the qualitative expectations produced from space-filling molecular models, even though no experimental distinction can be made between these models. This model is schematically illustrated in Figure 6. We assume the R-I molecule to be composed of two spheres, one of fixed radius representing the I atom and the other of variable radius to represent the R group. The I atom radius is set equal to the covalent radius, r_c, the centers are separated by the average C-I bond length, and the radius of the R group is chosen to fit the experimental results. Each sphere is cut by a plane so that the two cut spheres may be placed smoothly together in the same fashion as the space-filling Fisher-Hirschfelder-Taylor models. The reaction probability for a K atom incident at arbitrary angle θ is assumed to be just the fraction of the I atom (cross-sectional area of πr_c^2) which can be seen from that angle. (Mathematically, the reaction probability is $(\pi r_c^2)^{-1}$ × area of the I atom projected on a plane normal to the incident velocity.) The view from the incoming K atom is shown for several orientations in Figure 6.[19]

The reaction probability as a function of incident angle calculated for various R group sizes is shown in Figure 7. These probabilities must be averaged over the orientation distributions shown in Figure 3. The ratio of reaction probabilities averaged over the "heads" and "tails" configurations is shown in Figure 8 for the two molecules for a variety of hindering group sizes. The experimental "head" to "tail" reaction probability is taken to be the ratio of the in-plane cross sections[20] (the area under the experimental angular distributions) and is also shown in Figure 8 for comparison. This ratio is predicted to be a very weak function of the voltage applied to the state-selecting field which is qualitatively confirmed by experiment.

The size of the R groups read from Figure 8 shows that the major difference between experimental results for MeI and *t*-BuI can be ascribed to the better degree of orientation which can be obtained for *t*-BuI (which is a more oblate top). On the basis of this rather arbitrary, but hopefully somewhat realistic, model the experimental results suggest

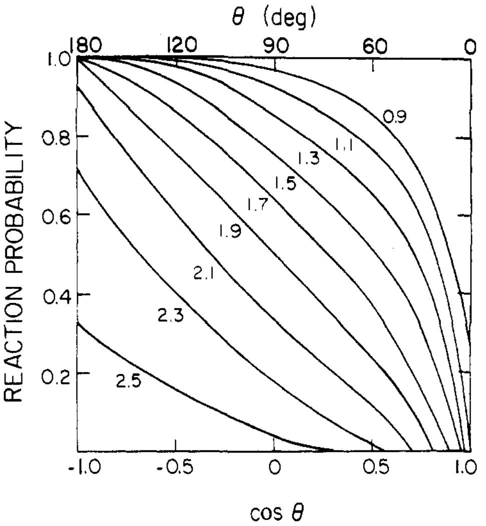

Figure 7. Reaction probability versus angle of attack for the model of Figure 6 for various size R groups measured relative to the covalent I atom radius.

that the sizes of the Me and *t*-Bu groups (radii of about 2.5 and 2.8 Å, respectively) are roughly compatible with chemical intuition. Using the sizes of R which best fit the beam experiments, we can furthermore predict the steric factor which one would expect for a gas phase experiment. The steric factor is the fraction of collisions which have the correct orientation, and we interpret that to be the fractional iodine area seen by the incoming K atom averaged over the distribution of orientations present in a gas. As shown in Table I, these steric factors are also roughly in agreement with chemical intuition.

Closer inspection of the steric radii, however, indicates that while the *t*-Bu group is larger than the Me group, it is not larger by very much. The van der Waals radius of the Me group is thought to be about 2.0 Å[21] which suggests that the value inferred from the oriented beam experiments may be too large.

What does "too large" mean? Does this reflect some uncertainty in the experimental parameters used in the calculation (such as the rotational temperature or the Mach number), or does this reflect a breakdown in the underlying assumption regarding the purely geometrical aspects of steric hindrance? Although we suspect the latter, there is presently insufficient data to rule out slight modifications of the model. Fortunately, however, the relative sizes of the two groups are relatively insensitive to the parameters used in the calculation. As mentioned earlier, calculations for both molecules were completely insensitive to the rotational temperature, and small changes in the Mach number resulted in only a minor variation of radius. (A change in M of 1.5 changes r by ~10%.)

Table I. Molecular Parameters

Covalent I atom radius, Å	1.33[a]
C–I bond length, Å	2.14[b]
van der Waals radii, Å	
Methyl	2.0[a]
tert-Butyl	2.7[c]
Hindering radii, Å	
Methyl	2.54[d]
tert-Butyl	2.76[d]
Steric factors, Å	
Methyl	0.50[d]
tert-Butyl	0.42[d]

[a] Reference 20. [b] C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill, New York, N.Y., 1955. [c] Estimated from the ratio of van der Waals b constants for methane and isobutane. [d] This work.

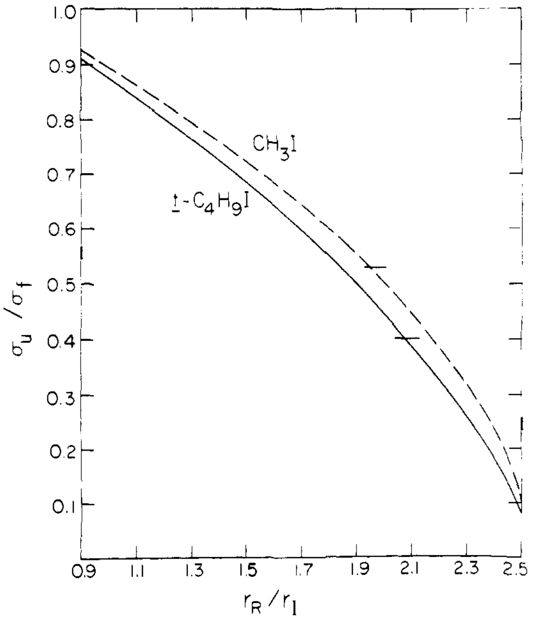

Figure 8. Calculated ratio of unfavorable (tail) to favorable (head) cross sections (σ_u/σ_f) for various R group radii, r_I, measured relative to I atom radius r_I. Experimental ratios are denoted by bars on each curve.

Reaction Mechanism. The potassium methyl iodide reaction has for some time been regarded as the prototype rebound reaction in which the newly formed KI recedes in the original direction of the incident alkali atom.[8,22] This experimental observation (for unoriented molecules) is entirely consistent with a simple physical picture in which the incident K strikes the closest end of the molecule and bounces back. If the nearest end is I the reaction occurs, but if it is methyl (or R) the atom bounces off without reaction.

The oriented molecule reaction displays the same features as the unoriented reaction; KI rebounds and the absence of product symmetry about the center of mass shows that a long-lived complex is not formed. These conclusions are obtained for reactions in either configuration, and the observed behavior for the heads configuration is entirely consistent with this simple model. In the tails configuration, however, the atom must pass the R group, react with the I, and then somehow the KI must depart in roughly the same direction as the incident K, presumably passing the R group on the way out. It is difficult to reconcile this with a hard sphere model of any kind.[4]

There is reason to suspect that other factors besides geometrical hindrance play a role in the orientational requirements for a reaction. As described earlier,[7] the reaction of K with oriented CF_3I is markedly different from the behavior described here; reaction occurs with roughly equal probability for the two configurations, but the scattered KI appears at different lab angles corresponding to backward scattering for heads and forward scattering for tails. This has been interpreted[5] as a long-range ionic–covalent curve crossing in which the alkali "donates" an electron to the CF_3I which then immediately dissociates. The fragments are ejected in whatever direction the CF_3I was originally oriented and this nicely accounts for appearance of product at different lab angles for the "heads" and "tails" configurations. The reactive scattering of the alkyl iodides, on the other hand, peaks at the *same* lab angle for *both* configurations which then suggests that reaction does not occur via a similar curve crossing, at least at large distances.

In order to explain how rebound scattering always occurs for MeI and *t*-BuI, one is immediately tempted to suggest that the molecule twists to somehow align itself with the incoming atom. This clearly does not occur at large distances, otherwise there would be no effect of the original orientation. It apparently does not occur at intermediate distances (~5 Å) because the CF_3I results clearly show that the initial orientation is retained, at least approximately, for such separations. But the partitioning of the reaction exoergicity between the products suggests[23] that most of the RI reactions can be correlated very nicely assuming an impulsive energy release of the type suggested for CF_3I, but somewhat weaker. This impulsive energy release could be reconciled with the oriented molecule experiments for RI (where orientation does not change the angular distribution) if the impulse were triggered at small distances where it is not really possible to identify the original molecule, let alone regard it as being oriented. A potential surface which accounts for all of these features has so far been elusive,[6] and should pose an interesting problem to the theorists.

Finally, it is interesting to compare the behavior of K + oriented CH_3I with the Rb + oriented CH_3I reported earlier.[4] For Rb + CH_3I, Beuhler and Bernstein were able to work with a more limited range of orientations, and a cautious extrapolation of their data to complete orientation suggested a reactivity ratio ≥ 3. A similar extrapolation of our data is not possible, but if the apparent ability of our model to interpret the results in terms of reasonable parameters is indicative of its accuracy, then the reaction with K would have a much larger reactivity ratio for perfect alignment. This perhaps suggests that a large atom tends to envelop the reacting molecule and minimizes the orientation requirements.

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(14) It is not known if experimentally changing the rotational temperature would affect any results.

(15) The rotational population, of course, is temperature sensitive, but the quantity of interest is the population of orientation states. The orientation is $\cos\theta = MK/J(J + 1)$ and both K and J are temperature dependent. For the alkyl iodides (prolate tops) high temperatures favor high values of both K and J, so the overall temperature dependence of $\cos\theta$ is not intuitively obvious.

(16) The recent experiments by M. P. Sinha, C. D. Caldwell, and R. N. Zare, *J. Chem. Phys.*, **61**, 491 (1974), emphasize the need for a more complete characterization of the orientation distribution. They showed that Na_2 molecules tend to align their planes of rotation to be parallel to the nozzle flow (angular momenta are therefore perpendicular to the flow). If this same hydrodynamic alignment occurred for symmetric top molecules, it would still be possible to separate laboratory orientations as we have discussed. It is possible, however, that the hydrodynamic alignment may change the distribution of states differently for methyl or *tert*-butyl iodide. This effect, as well as the uncertainty in velocity, can presently be assessed only by the fit to the total transmitted intensity.

(17) The hexapole field selects those orientbtions which have a high energy in an external electric field. The most reactive configuration of either molecule obtains when the field plate nearest the impinging K beam is made negative. Because the molecule is in a high energy state it will be aligned with its negative end closest to the negative plate. Consequently the negative end of the molecule is most reactive.

(18) Randomization also depends on the rapidity with which the field is changed.

(19) It is important to note that this is a rather simple but arbitrary model which is introduced to take into account the distribution of orientations and to see if the experimental steric effect can be interpreted solely on the grounds of hindrance by the R group. Although the numbers derived are reasonable, caution must be exercised in their use and interpretation. Other simple models could equally well be used, but there are no experimental grounds to distinguish one from another. It is furthermore unlikely that any simple model will account for all of the features of the reactive scattering. (See for instance ref 6.)

(20) The effect of orientation on the out-of-plane scattering has not yet been assessed. It is possible, but not necessarily likely, that this accounts for the anomalously large CH_3 hindering radius.

(21) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960.

(22) R. B. Bernstein and A. Rulis, *Faraday Discuss. Chem. Soc.*, **55**, 293 (1973).

(23) D. R. Herschbach, *Faraday Discuss. Chem. Soc.*, **55**, 233 (1973), and (for CF_3I) A. M. Rulis, B. E. Wilcomb, and R. B. Bernstein, *J. Chem. Phys.*, **60**, 2822 (1974).