Steric hindrance in potassium atom-oriented molecule reactions. Methyl iodide and tert-butyl iodide

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Accordingly, the c series is assigned to a progression from the same upper state to the ground state levels (0\(v_2\)).

Differences between the a and e series range from 738 to 720 cm\(^{-1}\) in very good agreement with the C-Cl mode of CClI\(_2\); the decrease comes from the anharmonic term \(X_{12}\) which is approximately \(-5 \pm 2\) cm\(^{-1}\). The e series is assigned to the progression terminating in \((1\nu_2)\) levels. The c and e series energies, relative to the a series, confirm that the carrier of the fluorescence spectrum is CCI\(_2\).

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 \((0\nu_2) \rightarrow (0\nu_2\) fluorescence and it provides an \(X_{13}\) 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 \((0\nu_3 + 1\nu_0) \rightarrow (0\nu_2)\) counterpart to the c progression \((0\nu_2) \rightarrow (0\nu_2)\). 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 CCI\(_2\)Br 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 CCI\(_2\)Br which cannot be defined without additional data.

The fact that the fluorescence spectra of the C\(_2\) 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 C\(_3\) species.

It is interesting to speculate on the failure to observe a fluorescence for CI\(_2\), CI\(_3\) is probably produced by the iodo-carbon 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\(_3\) and CCI\(_3\)Br have been synthesized by matrix reaction of CBr\(_3\), CCCI\(_3\), and CCl\(_3\)Br 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\(_3\) (196 cm\(^{-1}\)) which emanate from two different bending mode levels of excited CBr\(_3\): these emitting levels cannot be definitely assigned. The CCCI\(_3\)Br spectrum was only observed using the CCCI\(_3\)Br\(_2\) precursor suggesting nearly equal reactivities of chlorine and bromine with alkali metal atoms. Owing to the lower symmetry of CCCI\(_3\)Br, its fluorescence spectra were more complex than the CBr\(_3\) spectra. Progressions in the CCCI\(_3\)Br 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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**References and Notes**

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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-CH\(_3\)H\(_4\)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 reactants were effective in promoting reaction, and the “steric factor”, \(\rho\), 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, $\rho$ lies in the range 0.1–1.0 and seems intuitively acceptable, but in other cases incredibly small values of $\rho$ 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 $\rho$ nor to study the effect on $\rho$ 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.

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 were performed on CH$_3$I 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$_3$I reaction and with studies of the K + CF$_3$I reaction which showed behavior at odds with chemical intuition. 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 energy surfaces.

In this article we describe the reaction of K atoms with oriented CH$_3$I and t-C$_4$H$_9$I molecules which were briefly reported in a preliminary communication. The comparison of the two molecules is of interest, partially on intrinsic grounds, and partially because an earlier study 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$_3$I 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. Each of the four chambers in the figure is differentially pumped. 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 temperature.

![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.](image-url)

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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.)

Figure 3. Calculated distribution of molecular orientation. Ordinate is the log of the fraction in an increment of $\cos \theta$ 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" ($I_{L}$) 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.
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, 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 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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Covalent I atom radius, Å</td>
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</tr>
<tr>
<td>C–I bond length, Å</td>
<td>2.14b</td>
</tr>
<tr>
<td>van der Waals radii, Å</td>
<td>2.0c</td>
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<tr>
<td>Methyl</td>
<td>2.7c</td>
</tr>
<tr>
<td>tert-Butyl</td>
<td>2.54d</td>
</tr>
<tr>
<td>Hindering radii, Å</td>
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<td>Methyl</td>
<td>0.50d</td>
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<tr>
<td>tert-Butyl</td>
<td>0.42d</td>
</tr>
</tbody>
</table>


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.

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.3,22 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.

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 CF3I 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 interpreted5 as a long-range ionic–covalent curve crossing in which the alkali "donates" an electron to the CF3I which then immediately dissociates. The fragments are ejected in whatever direction the CF3I 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 Mel and t-BuI, one is immediately tempted to suggest that the molecule twists to somehow align itself with the in-
coming 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 CF₃I 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 that most of the RI reactions can be correlated very nicely assuming an impulsive energy release of the type suggested for CF₃I, 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, and should pose an interesting problem to the theorists.

Finally, it is interesting to compare the behavior of K + oriented CH₃I with the Rb + oriented CH₃I reported earlier. For Rb + CH₃I, 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.

Acknowledgment. We gratefully acknowledge the support of this research by the National Science Foundation.

References and Notes

(1) Alfred P. Sloan Fellow.
(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 θ = MK(1/Å + 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 θ is not intuitively obvious.
(16) The recent experiments by M. P. Sinha, C. D. Caldwell, and R. N. Zare, J. Chem. Phys., 61, 451 (1974), emphasize the need for a more complete characterization of the orientation distribution. They showed that Na₂ 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 fits to the total transmitted intensity.
(17) The hexapole field selects those orientations 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 8.)
(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 CH₃I hindering radius.