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Steric Hindrance in Molecular Beam Reactions

Sir:

Intuitive considerations of molecular geometry have for many years provided considerable insight into the rate and mechanism of many chemical reactions, and on a routine basis one invokes the qualitative notion that "bulky groups" can shield "reactive sites" or can interfere with the formation of a transition state. These notions regarding steric hindrance are sufficiently appealing and useful to warrant study by as direct observation of a steric effect was reported some time ago. Subsequent work has been mainly concerned with development of techniques and kinematic details. In this communication we wish to report on the reactivity of several oriented molecules which exhibit a wide range of behavior which is not always predicted by chemical intuition.

The experimental concept is unchanged from the early experiments and is discussed in detail in ref 3. Briefly, a beam of molecules is passed through a combination of electric fields which can select molecules in a range of orientation which can correspond to the reactive end pointing either toward the incoming reactive atom ("heads"), or away from the incoming atom ("tails"). The orientation may be reversed by changing the polarity of a weak electric field. The experimental observations are the product angular distributions resulting from either the "heads" or "tails" distributions.

Potassium atoms have been treated with CHJ, t-BuI, CFJ, and CClJH molecules to form KI or KCl. Typical results are shown in Figure 1. It is apparent that in general a significant difference in reactivity obtains for impact at different ends of the molecules. Furthermore, the existence of such a difference shows that these molecules do not turn to present their most favorable end prior to reaction.

The relative reactivities (the area under the curves) of the "heads" and "tails" configurations for methyl

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(12) A detailed mechanistic discussion will be presented in a forthcoming publication. We believe the mechanism involves a radical-like intermediate which opens stereoselectively as proposed by Paquette. Cfr recent papers by Goldstein13 and van Rantwijk.

(14) M. J. Goldstein and M. S. Benzon, ibid., 94, 5119 (1972).

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**Figure 1**: Laboratory angular distributions of reactively scattered KI (or KCl) for (a) CHJ, (b) t-BuI, (c) CHCl, (d) CFJ. Filled points denote reaction from the "heads" configuration in which the reactive end of the molecule points toward the incoming K atom; unfilled points denote reaction from the "tails" configuration. The results for different molecules have been normalized to have the same peak height. In all cases we observe the reactivity of un-oriented molecules to be intermediate between the extremes shown.

**Communications to the Editor**
iodide and tert-butyl iodide are consistent with a simple model composed of two spheres representing I and the R group. Other investigations \(^6\) with random orientations show that the product is KI in both cases. \(^4b,9\) These features for "heads" orientation the product scatters backwards in the CM configuration. Data given elsewhere strongly suggest that the product is scattered forwards in the CM for "tails" orientation. The lack of orientation dependence is not surprising since there are three potentially reactive sites and one would expect the small lone hydrogen atom to be rather inefficient in shielding the large chlorine atoms. Effects of substituents other than H have not yet been investigated.

The behavior of CF\(_3\)I is not in accord with "chemical intuition" and is consequently the most fascinating of the cases studied. Reaction occurs with roughly equal probabilities at either end, and again a long-lived complex is not formed. However, as shown in Figure 1, the scattered product is observed at significantly different scattering angles depending on orientation. For "heads" orientation the product scatters backwards in the center of mass system (CM) whereas the product is scattered forwards in the CM for "tails" orientation. The I\(^-\) ion is ejected exclusively in the ether bridge in the diaryl-substituted ozonides. Such observations have led to several additional suggestions \(^1,5^\text{-}14\) for the mechanism of ozonolysis all of which retain the proposal made by Criegee \(^15\) that ozonide can be formed by addition of a zwitterion or carbonyl oxide to a carbonyl group. One of these additional suggestions \(^1,5^\text{-}12\) includes the possibility that ozonide may also be formed by a route which is more complex than a simple zwitterion-carbonyl recombination reaction.

We have earlier \(^10,15\) attempted to obtain evidence for a nonzwitterion path to ozonide through the use of an \(^18\)O tracer procedure. This procedure assumes that operation of the zwitterion-carbonyl recombination mechanism will place the \(^18\)O label entirely in the ether bridge when ozonolysis is carried out in the presence of \(^18\)O-labeled aldehyde.

Finding of \(^18\)O in the peroxide bridge is then interpreted as evidence for a nonzwitterion path to ozonide. In our earlier work \(^10,16\) considerable evidence was found for peroxide bridge labeling in the cases of dialkyl-substituted ozonides. Using a similar technique, Fliszár and coworkers \(^17^\text{-}20\) have found that in the ozonolysis of phenylethlenes in the presence of \(^18\)O-labeled benzaldehyde the label is incorporated exclusively in the ether bridge in the diaryl-substituted ozonides obtained. In all of this earlier work, the assumption was made that the structure of the zwitterion has no contribution from forms such as

\[\text{O}^+\text{C} = \text{O} \longrightarrow \text{O}^+\text{C} = \text{O}^-\]

Fliszár and coworkers have now been able to rule out any contribution from structure 1 to ozonide formation based on a very elegant experiment involving the ozonolysis of an unsymmetrical olefin in alcohol solvent and analysis of the alkoxy hydroperoxides produced. \(^20\)

The possibility that incorporation of \(^18\)O in the peroxide bridge need not indicate a nonzwitterion path to ozonide formation based on a very elegant experiment involving the ozonolysis of an unsymmetrical olefin in alcohol solvent and analysis of the alkoxy hydroperoxides produced. \(^20\)

Ozonides from the Photooxidation of Diazo Compounds in the Presence of \(^18\)O Labeled Aldehydes and \(^18\)O\(_2\)

Sir:

One of the most puzzling aspects of the ozonolysis reaction is the apparent ability of olefin stereoch- emistry to affect the amounts and stereochemistry of the ozonide products. \(^1\text{-}8\) Such observations have led to

(4) G. Schröder, ibid., 95, 733 (1962).