physical data and infrared and nmr spectra. A typical product analysis is given in Table I. Although the yields of the various components may vary slightly from reaction to reaction depending on reaction time and temperature control, there is no major difference in the distribution of the products.

Table I. Reaction Products of Cumene with $NO^+PF_6^-$

Product	Yield, wt %
Benzene (**1**)	4.7
α-Methylstyrene (**2**)	2.4
Acetophenone (**3**)	2.2
2-Phenyl-2-propanol (**4**)	1.8
2,2-Diphenylpropane (**5**)	25.6
1,1,3-Trimethyl-3-phenylindan (**6**)	25.0
4b,9,9,10,10-Pentamethyl-4b,9,9a-10-tetrahydro(1,2-*a*)indan (**7**)	13.0
Residue (polymer) (**8**)	26.0

All products formed can be accounted for through the intermediate formation of the phenyldimethylcarbonium ion formed *via* hydride abstraction. Acetophenone and 2-phenyl-2-propanol are also known products from the radical decomposition of cumyl hydroperoxide, but their presence in low yield and the complete absence of any expected coupling products of the cumyl radical argue strongly against a free-radical process as a major pathway. An ionic hydride-abstraction mechanism is further supported by the observation that the nitrosonium ion reacts in a similar fashion with substituted cumenes like cymenes and halocumenes, but not with toluene or *t*-butylbenzene or their derivatives. Thus clearly the reaction is dependent on the presence of an easily abstractable tertiary hydrogen atom. This prerequisite is further supported by the observation that other substrates having easily abstractable hydrogen atoms, like tetralin, methylcyclopentane, diphenylmethane, triphenylmethane, allylbenzene, xanthene, cycloheptatriene, etc., also react readily with nitrosonium salts according to typical carbonium ion type reactions.

The general pattern of the reaction of substituted cumenes (like cymenes and halocumenes) with nitrosonium hexafluorophosphate is similar to that of cumene itself, although the reaction products are more complex.

The reaction of nitrosonium hexafluorophosphate with isopropylbenzenes is difficult to follow in a quantitative way, because carbonium ions formed in the course of the reactions and their deprotonation promote further reaction. When *p*-cymene was allowed to react, for example, with 0.25 equiv of $NO^+PF_6^-$ until the reaction ceases (1 hr), gas chromatographic analysis showed that 0.52 equiv of *p*-cymene had reacted. The reaction is thus nonstoichiometric. Competitive determinations of the over-all reactivity of cumene compared with cymenes and halocumenes shows only that methyl substitution increases the rate, whereas halogen substitution decreases the rates. The most striking observation is, however, the substantial difference in reactivity of the *meta*- and *para*-substituted cumenes compared with that of the *ortho* derivatives.

When a 1:1:1 molar mixture of *o*-, *m*-, and *p*-cymene was allowed to react with 0.33 mole equiv of $NO^+PF_6^-$ it yielded (according to capillary gas chromatography) a reaction mixture which contained only *o*-cymene, with no *p*-cymene and only traces of *m*-cymene present. The *para* and *meta* isomers react substantially faster than the *ortho* isomer. Similar observations were also made with haloisopropylbenzenes.

Reactions of mixtures of the isomeric isopropylbenzenes with NO^+ salts result in the depletion of the *meta* and *para* isomers, giving access of nearly pure *ortho* isomers. This observation explains the unusually high (>90%) yield of *o*-cymene in the isopropylation of toluene in the related alkylation work.[3] This effect is also evident, although to a lesser degree and decreasing strongly, F > Cl > Br, in the halocumene series.

The selective effect of nitrosonium salts in their reaction with isopropylbenzenes is considered to be due to their ability to abstract hydride ion without simultaneously causing electrophilic ring substitution.

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Observation of the Reactive Asymmetry of Methyl Iodide. Crossed Beam Study of the Reaction of Rubidium with Oriented Methyl Iodide Molecules

Sir:

Since the advent of crossed molecular beam kinetics,[1] dating from the work of Taylor and Datz, there has been considerable progress in the study of microscopic aspects of reactive collisions.[2] Continuing refinements of techniques have made it possible to extract more of the dynamical details of elementary reactions. As a step in this direction, the present communication reports a direct observation of the asymmetry in the reactivity of the two "ends" of a (polar) molecule; specifically, the ratio of the reactive cross sections of rubidium with methyl iodide for the two relative orientations

$$Rb + ICH_3 \xrightarrow{f} RbI + CH_3 \quad \text{"favorable"} \qquad (1)$$

vs.

$$Rb + H_3CI \xrightarrow{u} RbI + CH_3 \quad \text{"unfavorable"} \qquad (2)$$

The experiment consists of crossing a Rb beam with a beam of CH_3I which has been rotational state-selected by an electric six-pole field[3] and aligned with respect to the incident Rb beam[4] by an orientation

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(1) E. H. Taylor and S. Datz, *J. Chem. Phys.*, **23**, 1711 (1955).

(2) See "Molecular Beams," J. Ross, Ed., "Advances in Chemical Physics," Vol. 10, Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1966: (a) Chapter 4 by E. F. Greene, A. L. Moursund, and J. Ross; and (b) Chapter 9 by D. R. Herschbach.

(3) K. H. Kramer and R. B. Bernstein, *J. Chem. Phys.*, **42**, 767 (1965).

(4) More properly, the alignment should be with respect to the incident relative velocity vector. This imperfection (a misalignment of *ca.* 30°) has the effect of reducing the observed asymmetry.

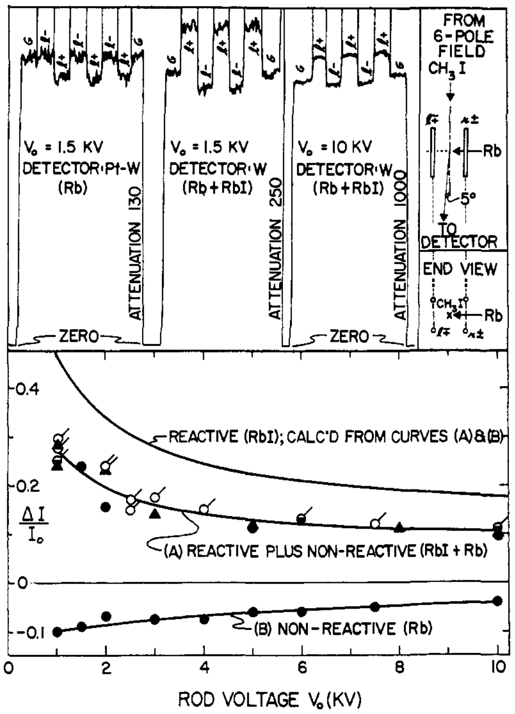

Figure 1.

field. From the fractional change, $\Delta I/I_0$, in the intensity of the RbI product (detected at 85° with respect to the Rb beam[5]) upon reversal of the polarity of the orienting field, the ratio of the reactive cross sections, σ_f/σ_u, may be obtained. Since the degree of alignment of the CH_3I in an orienting field is a function[6] of the hexapole rod voltage, V_0, the results require extrapolation to the limit of "perfect" alignment, *i.e.*, $V_0 \rightarrow \bar{V}_{th}$.

The apparatus was that of ref 3, with the following changes. The velocity selector was removed; a crossed-beam system and a goniometer mount for the detector assembly were introduced. A horizontal, flat-beam system was used, with horizontal, flat, in-plane detection. The CH_3I beam was modulated at 25 Hz; the Rb and RbI were detected by differential surface ionization. The electron-multiplier output from the quadrupole mass spectrometer was passed through a narrow-band amplifier and phase-sensitive detector to a recorder. The focused beam of CH_3I intersected the Rb beam within the "orienting field," placed immediately following the six-pole field. Voltages symmetrical around ground were applied; normally about 100 v was used (*e.g.*, $l = \pm 50$, $r = \mp 50$). The results were independent of the orienting voltage from 20 to 180 v.

Auxiliary experiments were carried out to establish the validity of the orientation effects observed. For an unfocused beam of CH_3I ($V_0 = 0$, direct-beam obstacle removed) there was no effect of reversal of the orienting field upon either the Rb or RbI current (*i.e.*, $\Delta I/I_0 \lesssim 0.01$).

A tracing of a sample recorder chart is shown (Figure 1). The symbol G indicates a grounded orientation field (I_0). The asymmetry data are plotted. It is of interest to note the significant "reverse asymmetry" of the nonreactive scattering, partly compensatory to the reactive effect. The upper curve is the asymmetry deduced for the pure reactive scattering (RbI), based on curves A and B and a reactive:nonreactive partitioning ratio of 2:1 (determined by auxiliary experiments).

Since all experimental imperfections would tend to reduce the observed reactive orientational anisotropy, the present results must be considered to yield a lower limit: $\sigma_f/\sigma_u \geq 1.5$. With a more nearly perfect "unfavorable" alignment (Rb–H_3CI), the reactive cross section may well be only a small fraction of the orientation-averaged cross section. Further work in this direction is in progress. Details of the experiments and analysis of results will be published elsewhere.

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(5) Herschbach and co-workers (*e.g.*, see D. R. Herschbach, *Discussions Faraday Soc.*, **33**, 149 (1962), and ref 2b) have shown that for the present reaction (a "rebound" type) the product is concentrated in the broad angular range 40–90° from the Rb beam.

(6) The degree of alignment[3] is $\langle \cos \theta \rangle$, where θ is the angle between the dipole moment and the electric field: $-\langle \cos \theta \rangle = \bar{V}_{th}/V_0$, where $\bar{V}_{th}$ is the velocity-averaged "threshold" voltage (here *ca.* 0.5 kv). Note that for $\langle \cos \theta \rangle = -1$, the negative end of the dipole is directed toward the negatively charged orienting plate.

Quasiclassical Trajectory Analysis for the Reaction of Potassium Atoms with Oriented Methyl Iodide Molecules[1]

Sir:

Beuhler, Bernstein, and Kramer[2] have recently reported preliminary results from a crossed beam study of the reaction of rubidium atoms with partially oriented methyl iodide molecules. They found that, in collisions with the I atom of CH_3I directed toward the incoming Rb, the reaction cross section for the formation of RbI is significantly greater than that in collisions with the reverse orientation of CH_3I. Since this observation represents the first microscopic determination of a "steric effect," its relation to our knowledge of the potential energy surface for the reaction is of considerable interest. In this communication we present some results obtained on this point by an extension to oriented molecules of quasiclassical trajectory calculations performed previously for the K–CH_3I exchange reaction[3] in the unoriented case.[4,5]

Prior to the work of Bernstein, *et al.*, the $M + CH_3I \rightarrow CH_3 + MI$ reaction in crossed beams composed of

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(1) Supported in part by a contract with the U. S. Atomic Energy Commission.

(2) R. J. Beuhler, Jr., R. B. Bernstein, and K. H. Kramer, *J. Am. Chem. Soc.*, **88**, 5331 (1966).

(3) Corresponding results to those of ref 2 are expected to hold for the K–CH_3I reaction. This expectation is confirmed by the work of P. R. Brooks and E. M. Jones on the K-oriented–CH_3I system (to be published); they used the method described in K. H. Kramer and R. B. Bernstein, *J. Chem. Phys.*, **42**, 767 (1965), and in ref 2.

(4) H. C. Blais and D. L. Bunker, *J. Chem. Phys.*, **37**, 2713 (1962); **39**, 315 (1963); **41**, 2377 (1964).

(5) (a) M. Karplus and L. M. Raff, *ibid.*, **41**, 1267 (1964); (b) *ibid.*, **44**, 1212 (1966).