

## Reaction of potassium atoms with oriented bromotrifluoromethane

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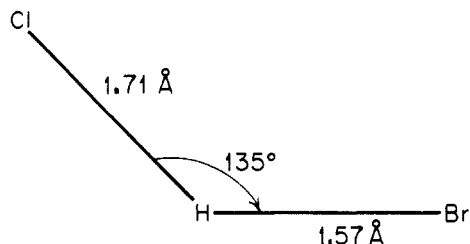


Figure 5. Nonlinear transition state for Cl + HBr.

An  $A$  factor for the reaction can be calculated by using Benson's methods,<sup>15</sup> assuming a tight transition state which is nonlinear (Figure 5). The entropy of Cl-H-Br can be calculated readily from the standard equation for translational, rotational, and vibrational entropy.

$$S = 40.2 \text{ (translation)} + 21.4 \text{ (rotation)} + 0 \text{ (vibration)} + 5.0 \text{ (1-D rotor)} + 1.4 \text{ (spin)} = 68.0 \text{ eu}$$

Therefore  $\Delta S^\ddagger = 68 - 47.5 - 39.5 = -19.0 \text{ eu}$ . This leads to an

$A$  factor of  $5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in very good agreement with our experimental results of  $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming a linear transition state would yield even a slower rate constant, there seems to be no way to bring the experimental results of Mei and Moore and Rubin and Persky into agreement with this calculation.

We see no evidence of a temperature dependence over the range 263 to 333 K. While our range was not as great as that of the two previous groups we could easily see a 30% change in rate constant over that interval as suggested by Rubin and Persky. We estimate that our reported rate constant is accurate to 15%, based on the prior established performance of the VLPR system.

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**Registry No.** HBr, 10035-10-6; Cl atomic, 22537-15-1.

## Reaction of K Atoms with Oriented CF<sub>3</sub>Br

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A beam of oriented CF<sub>3</sub>Br molecules is prepared by passing a randomly oriented beam through an appropriate series of inhomogeneous and homogeneous electric fields. An atomic K beam crosses the beam of oriented CF<sub>3</sub>Br and the angular distribution of the reactively scattered KBr is measured with a differential surface ionization detector. The "heads" orientation (Br end closest to incoming K) is about threefold more reactive than the "tails" orientation. The KBr is scattered backward in the "heads" orientation and forward in the "tails" orientation, qualitatively consistent with a "harpoon" type of mechanism in which the orientation affects either the electron jump or the breakup of the dissociating negative ion.

### Introduction

Proper orientation of reagents as a prerequisite for chemical reaction seems to be widely accepted on an intuitive level. Almost all theories of reaction rates include "steric factors" in one form or another.<sup>1</sup> However, a detailed understanding of these factors is still lacking. Experimentally, recent advances in molecular beam and laser technology<sup>2</sup> have made possible the direct observation of a variety of steric effects in several reactions.

Polarized laser radiation can be used to prepare beams of *polarized* molecules, which are molecules whose plane of rotation can be oriented with respect to a fixed axis. This technique has been applied, for example, to Sr + HF and "broadside" attack of the plane-of-rotation of HF is observed<sup>3</sup> to yield more SrF ( $J' = 2$ ) than "edge-on attack", suggesting a bent minimum energy configuration. Similarly, polarized light has been used<sup>4</sup> to produce atoms in which excited p- or d-orbitals are directed parallel or perpendicular to the relative velocity. In the case of Ca + HCl, the direction of the Ca\* p-orbital strongly influences the branching into two different CaCl\* states.

Electrostatic deflection techniques have been used to prepare beams of *oriented* molecules,<sup>2a,5</sup> which are molecules whose figure axes precess around a space-fixed axis. One "end" of the molecule can be distinguished from another, and can be pointed toward (or away from) an incoming atom so that chemical reactivity can be studied as a function of orientation. Examples of reactions studied

TABLE I: Operating Conditions

distances, cm	
K oven-scattering center	12
nozzle-scattering center	70
scattering center-detector	5
nozzle-skimmer	2.6
field length	54
temp, K	
gas nozzle	308
K oven	623
K nozzle	673
nozzle backing pressure, torr	110
hexapole voltage, kV	12
homogeneous field strengths, V/cm	80

using this technique are O<sub>3</sub> reacting with oriented NO,<sup>6</sup> K reacting with CH<sub>3</sub>I and CF<sub>3</sub>I,<sup>7</sup> and Rb reacting with CH<sub>3</sub>I.<sup>8</sup> The latter

(1) See, e.g.: Hammes, G. G. "Principles of Chemical Kinetics"; Academic Press: New York, 1978; Chapter 2.

(2) For recent reviews see: (a) Stolte, S. *Ber. Bunsenges. Phys. Chem.* **1982**, 86, 413. (b) Leone, S. *Annu. Rev. Phys. Chem.* **1984**, 35, 109.

(3) Karny, Z.; Estler, R. C.; Zare, R. N. *J. Chem. Phys.* **1978**, 69, 5199.

(4) (a) Rettner, C. T.; Zare, R. N. *J. Chem. Phys.* **1981**, 75, 3636. (b) Schmidt, H.; Weiss, P. S.; Mestdagh, J. M.; Covinsky, M. H.; Lee, Y. T. to be published.

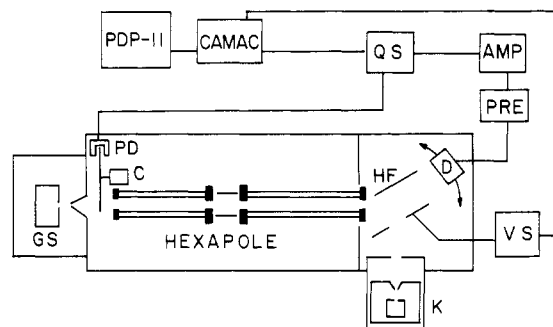
(5) Brooks, P. R. *Science* **1976**, 193, 11.

(6) (a) van den Ende, D.; Stolte, S. *Chem. Phys. Lett.* **1980**, 76, 13. (b) van den Ende, D.; Stolte, S.; Cross, J. B.; Kwei, G. H.; Valentini, J. J. *J. Chem. Phys.* **1982**, 77, 2206.

(7) Brooks, P. R.; McKillop, J.; Pippen, H. G. *Chem. Phys. Lett.* **1979**, 66, 144 and references therein.

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**Figure 1.** Schematic diagram of apparatus. GS, nozzle gas source; C, chopper; PD, photodiode assembly; HF, homogeneous orienting electric field plates; K, potassium atom source; D, detector; VS, voltage supply for homogeneous field; PRE, fast preamplifier; AMP, pulse amplifier/discriminator; QS, quad scalar. Relevant dimensions are given in Table I.

reaction has recently been probed in detail.

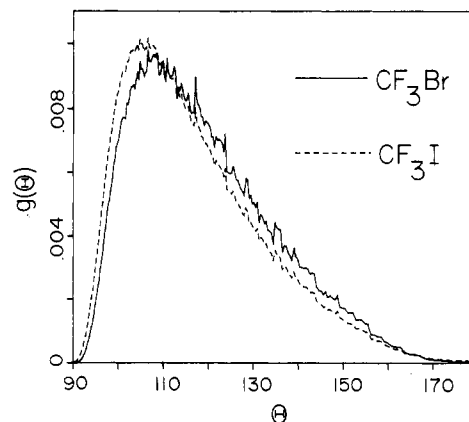
The  $\text{CH}_3\text{I}$  reactions are found to be qualitatively consistent with "chemical intuition": the alkali atom is most likely to react when the "heads" orientation (the I end) is approached, and for  $\text{Rb} + \text{CH}_3\text{I}$ , there is a sizable cone of no reaction<sup>8</sup> when the Rb approaches the "tails" end of the molecule. The product,  $\text{MI}$ , is scattered backward. In contrast,  $\text{CF}_3\text{I}$  appears<sup>5</sup> to be roughly equally reactive (to form  $\text{KI}$ ) when K approaches in either the heads (I end) or tails ( $\text{CF}_3$  end) orientations, but the products are backward scattered from the heads orientation and forward from the tails orientation. These observations are qualitatively consistent with an electron-jump model of reaction, and subsequent experiments on "sideways" orientations<sup>7</sup> have reinforced this interpretation.

The facility with which the electron is transferred to the oriented molecule is expected to depend on the electron affinity of the molecule. In order to assess the possible role played by the electron affinity, we have studied the reaction of K with oriented  $\text{CF}_3\text{Br}$ . This molecule has a smaller electron affinity<sup>9</sup> than  $\text{CF}_3\text{I}$ , and it was thought that a possible electron jump might be substantially different from  $\text{CF}_3\text{I}$ . We find a behavior somewhat intermediate between  $\text{CF}_3\text{I}$  and  $\text{CH}_3\text{I}$ .

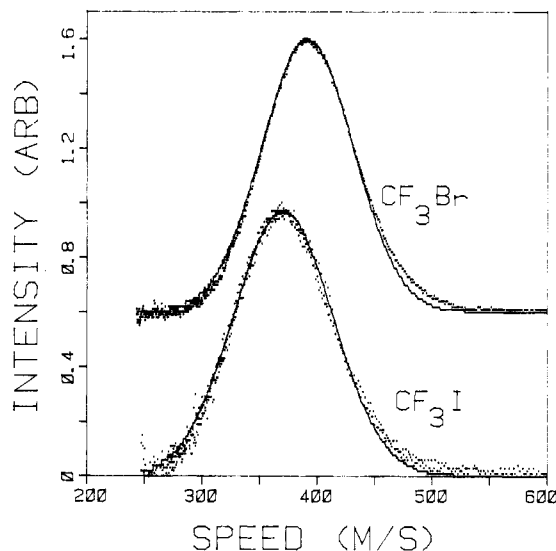
### Experimental Section

The apparatus is similar in concept to that used in previous investigations from this laboratory,<sup>7</sup> and is shown schematically in Figure 1. Relevant dimensions and operating parameters are shown in Table I.

Beams of  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$  are formed by supersonic expansion from a stainless steel oven with a 0.2-mm-diameter nozzle located in a separate cryopumped chamber. The beam is collimated with a 0.7-mm-diameter skimmer, modulated by a rotating wheel, and then enters an inhomogeneous hexapole electric field which transmits only molecules with negative values of  $\langle \cos \theta \rangle$ , where  $\theta$  is the average classical angle between the dipole moment and electric field.<sup>10</sup> (Quantum mechanically,  $\langle \cos \theta \rangle = MK/(J^2 + J)$ .) The state-selected molecules then enter a region of uniform electric field created by two parallel plates tilted at an angle of  $30^\circ$  with respect to the  $\text{CF}_3\text{Br}$  velocity. The molecules make



**Figure 2.** Distributions of orientation angles,  $\theta$ , where  $\theta$  is defined as  $\arccos(MK/(J^2 + J))$ . Curves are smoothed quantum mechanical results. (See ref 11.)



**Figure 3.** Experimental velocity distributions of supersonic  $\text{CF}_3\text{X}$  ( $\text{X} = \text{I}, \text{Br}$ ) beams as measured by the time-of-flight technique. The solid curves are calculated by using eq 1 and temperatures of 29 and 45 K for  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$ , respectively.

adiabatic transitions into this field where they are now oriented with respect to the relative velocity for  $\text{K} + \text{CF}_3\text{Br}$  collisions. ( $\text{CF}_3\text{I}$  was studied as a comparison and the field plates were not realigned to account for the different  $\text{CF}_3\text{I}$  speed, a correction of about  $2^\circ$ .) The direction of the molecule could be reversed by reversing the polarity of the uniform field.

The K beam was formed by effusion from a Monel oven and collimated with a 1-mm-diameter heated skimmer. The K beam passed through holes in the uniform field plates and intersected the  $\text{CF}_3\text{Br}$  ( $\text{CF}_3\text{I}$ ) beam at right angles in the region of uniform electric field. Scattered K and  $\text{KBr}$  ( $\text{KI}$ ) were detected by a surface ionization detector which rotated about the scattering center in the plane of the two beams. K and  $\text{KBr}$  ( $\text{KI}$ ) were detected by ionization on a single crystal W wire. It was empirically determined that best results for ionization of  $\text{KBr}$  were obtained if the wire were operated at 1525 K, which is cooler than normally used for detection of  $\text{KI}$  (1775 K). Nonreactively scattered K atoms were detected on a 92% Pt-8% W alloy wire operated at 1500 K. The atomic ionization efficiencies of the two filaments were normalized by measuring scattering from beams of 1,1,1-trichloroethane and methanol which can be focused in the electric field but which are not reactive. The product  $\text{KBr}$  ( $\text{KI}$ ) intensity was obtained as the difference between the count rate from the Pt filament and the count rate from the W filament (adjusted for different ionization efficiencies). The ions were detected by counting pulses from a Bendix Model 306 crossed-field multiplier. A PDP-11 computer collected the data and controlled the apparatus via a CAMAC interface.

(8) (a) Stolte, S.; Chakravorty, K. K.; Bernstein, R. B.; Parker, D. H. *Chem. Phys.* **1982**, *71*, 353. (b) Parker, D. H.; Chakravorty, K. K.; Bernstein, R. B. *Chem. Phys. Lett.* **1982**, *86*, 113. (c) Parker, D. H.; Chakravorty, K. K.; Bernstein, R. B. *J. Phys. Chem.* **1981**, *85*, 466 and references to earlier work listed therein.

(9) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 4360.

(10) The dipole moment is defined as pointing from the negative charge to the positive charge and the energy of interaction with an electric field is  $W = -\mu E \cos \theta$  (Debye, P. "Polar Molecules"; Dover: New York, 1945). But regardless of the sign convention used for the dipole moment and  $\cos \theta$ , the state selected molecules will be oriented in the uniform field with their positive end toward the positive field plate since they are in states which increase in energy in an electric field. See ref 5 and: Bernstein, R. B. "Chemical Dynamics via Molecular Beam and Laser Techniques"; Oxford University Press: New York, 1982.

A distribution of orientations (all with negative<sup>10</sup>  $\langle \cos \theta \rangle$ ) results from the state-selection process because the deflection in the field depends on both the rotational state and the speed of the molecules. Figure 2 shows distributions of  $\theta$  for  $\text{CF}_3\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ) which have been calculated<sup>11</sup> from the equations of motion through the field. These calculations require knowledge of the internal molecular temperature and the velocity distribution, so the velocity distribution was measured for the randomly oriented molecules incident on the hexapole field. For these measurements, the hexapole field was removed and the low-speed chopper was replaced with a 400-Hz wheel containing a narrow slit so that the beam could be pulsed and the velocity distribution measured by the time-of-flight technique. A small ionization gauge was used to detect the beam, and the pulses were averaged by using a Lecroy Model 2256A waveform digitizer. The velocity distributions are shown in Figure 3. The experimental distributions were fit to an expression of the form<sup>12</sup>

$$n(v) \propto \left( \frac{v}{v_s} \right)^2 e^{-[(v-v_s)/\alpha_s]^2} \quad (1)$$

where  $\alpha_s = (2kT_s/m)^{1/2}$ . The hydrodynamic flow speed,  $v_s$ , and the translational temperature,  $T_s$ , (29 and 45 K for  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$ ) were used as fitting parameters. The rotational temperature of the molecules is assumed equal to the translational temperature characterizing the velocity distribution.

## Results

Laboratory angular distributions for scattering from  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$  are shown in Figure 4. The results from  $\text{CF}_3\text{I}$  are in qualitative agreement with those found previously in this laboratory<sup>19</sup> and are included only for comparison with the  $\text{CF}_3\text{Br}$  results. These data represent averages of data taken on several different days. The larger error bars at small angles arise from the subtraction procedure used to determine the KX signal. (The KBr signal at  $40^\circ$  was typically only  $\sim 7\%$  of the total scattered flux, compared to  $\sim 70\%$  at  $90^\circ$ .) These data were taken by using a focusing voltage of 12 kV and arise from the  $\text{CF}_3\text{X}$  orientations shown in Figure 2. The heads configuration is the distribution of orientations which result when the uniform field plate nearest the K beam is positive; the tails configuration is that which results when the polarity of the uniform field is reversed. As discussed below, heads refers to orientations in which the X atom (I or Br) is closest to the incoming K atom, and tails refers to orientations in which the  $\text{CF}_3$  end is closest to the incoming K.

Figure 4 shows that an alkali halide molecule is formed in each reaction and that the angular distribution depends quite drastically on the orientation of the molecule. Unfortunately, two reaction products are possible in each case, KF and KX, and the surface ionization detector is unable to discriminate between the two possibilities. Nevertheless, we believe that each reaction proceeds to form KX (and not KF) for the following reasons:

(a) The C-F bond is stronger than either the C-I or C-Br bond (108 vs. 54 or 70 kcal/mol, respectively).<sup>13</sup> The classic Polanyi diffusion flame experiments<sup>14a</sup> showed no evidence of reactivity for the exothermic reaction of Na with  $\text{CH}_3\text{F}$ , and diffusion flame experiments on  $\text{Na} + \text{CF}_3\text{X}$  yielded<sup>14b</sup> mainly NaX with NaF formed only in secondary reactions with  $\text{CF}_3$  radicals.

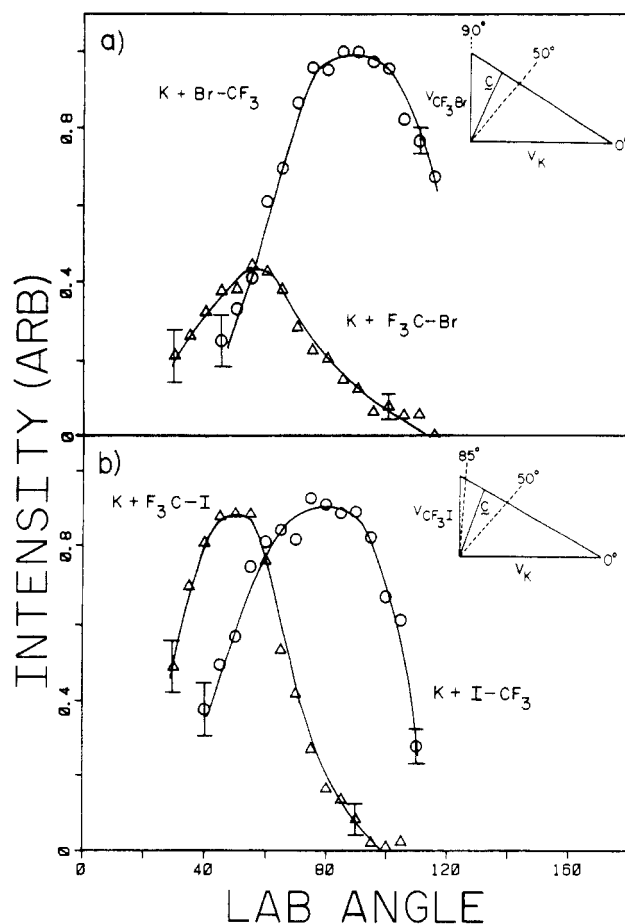
(b) Diffusion flame experiments from this laboratory<sup>14c</sup> on the  $\text{K} + \text{CF}_3\text{I}$  reaction showed that KI was the principal product and KF was formed in secondary reactions, and we concluded that  $\text{K} + \text{CF}_3\text{I}$  yields KI in either orientation of the molecule. Reactions with sideways oriented  $\text{CF}_3\text{I}$  molecules<sup>7</sup> (see Discussion) reinforce the conclusion that KI is the product.

(11) Strictly speaking, the distribution in Figure 2 is the distribution of molecules for which  $\langle \cos \theta \rangle = MK/J(J+1)$ , and is not the distribution of  $\cos \theta$ . This point is elaborated in ref 8a.

(12) Anderson, J. B. In "Molecular Beams and Low Density Gasdynamics"; Wegener, P. P., Ed.; Marcel-Dekker: New York, 1974.

(13) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502.

(14) (a) Polanyi, M. "Atomic Reactions"; Williams and Norgate: London 1932. (b) Reed, J. F.; Rabinovitch, B. J. *J. Am. Chem. Soc.* **1957**, *61*, 598. (c) Hardee, J. R.; Brooks, P. R. *J. Phys. Chem.* **1977**, *81*, 1031.



**Figure 4.** (a) Laboratory angular distribution of reactively scattered KBr from  $\text{K} + \text{CF}_3\text{Br}$ . (b) Laboratory angular distribution of reactively scattered KI from  $\text{K} + \text{CF}_3\text{I}$ . (O) heads orientation; ( $\Delta$ ) tails orientation. Smooth curves have been drawn through the points for clarity. Points shown are average values from several experiments. Representative error bars are drawn at small angles and at large angles. Inset nominal Newton diagrams show the lab angles where experimental intensity is maximum.

(c) The behavior of  $\text{CF}_3\text{Br}$  is similar to that for  $\text{CF}_3\text{I}$ , except that the "tails" configuration is less reactive. By analogy to the  $\text{CF}_3\text{I}$  case, we surmise that  $\text{K} + \text{CF}_3\text{Br}$  yields KBr in either orientation.

The hexapole electric field selects molecules in states for which the energy increases with applied field. In a uniform field the positive end of a state-selected molecule is thus closest to the positive field plate. The directions of the dipole moments of  $\text{CF}_3\text{X}$  are not known, but because of the high electron affinity of the F atom, we presume that the X ends of the molecules are positive. This assumption is consistent with the magnitude of the dipole moments<sup>15</sup> in various  $\text{CF}_3\text{Y}$  molecules. As Y is made more electropositive the dipole moment increases:  $\mu = 0, 0.5, 0.65, 1.0$ , and  $1.6$  D for  $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ , and  $\text{H}$ . Moreover, the reactive scattering itself strongly suggests that the positive end of  $\text{CF}_3\text{X}$  is the X end, since that end yields angular distributions which are strikingly similar to that from the I end of  $\text{CH}_3\text{I}$ . Our interpretation proceeds on the assumption that the positive end of each molecule is the X end.

The heads configuration for both molecules yields KX which peaks near  $90^\circ$  in the laboratory and which corresponds to backward scattering in the CM as shown by the nominal Newton diagrams in Figure 4. The tails orientation for both molecules yields KX which peaks near  $50^\circ$  in the laboratory and this corresponds to forward scattering in the CM. Unlike  $\text{CF}_3\text{I}$ , for which heads and tails seem to be roughly equally reactive, the heads end

(15) Nelson, Jr., R. D.; Lide, Jr., D. R.; Maryott, A. A. "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase"; *Nat'l Bur. Stand.* **1967**, NSRDS-NBS10.

of CF<sub>3</sub>Br is about threefold more reactive than the tails end.

Comparison of reactivity between CF<sub>3</sub>Br and CF<sub>3</sub>I was made on the basis of product count rate and crude flux measurements and also on the basis of stagnation pressures and the calculated hexapole field transmission. We roughly estimate the K + CF<sub>3</sub>I reactive cross section to be about 1.5 times that for K + CF<sub>3</sub>Br (17 Å<sup>2</sup> vs. 11 Å<sup>2</sup>). This estimate for CF<sub>3</sub>I agrees well with an earlier estimate of 15 Å<sup>2</sup> obtained from bulk gas-phase studies.<sup>14c</sup>

### Discussion

The reactivity of both the molecules studied is very sensitive to the molecular orientation, especially considering that the nominal orientation, shown in Figure 2, is really rather poor. This point should be emphasized: even though the molecules are not perfectly oriented, reaction still occurs. This suggests that most reaction events do not proceed via collinear geometry, and this seems to be the case with the other oriented molecules studied. Certainly collinear reactivity in the heads orientation is quite likely, but since noncollinear orientations greatly outweigh the collinear, it is expected that most reactions will proceed through noncollinear collisions. (Collinear tails orientations have been shown<sup>8</sup> to be nonreactive in CH<sub>3</sub>I.)

The angular distribution of reaction products from a *given* orientation in Figure 4 does not display symmetry about the CM and we conclude that long-lived complexes are not formed for either molecule in either configuration. Instead, when the X atom is nearest the incident K atom (heads), the product KX rebounds in the direction from whence the K came, and the KX is *backward* scattered and appears in the laboratory frame near 90° as is the case with heads (I end) scattering from CH<sub>3</sub>I. Scattering from the tails orientation of either molecule, on the other hand, is forward scattered, and is *not* analogous to CH<sub>3</sub>I.

This behavior can be rationalized on the basis of an impact parameter argument: for heads orientations the K may strike the X atom and product KX collide with the CF<sub>3</sub> moiety and rebound in the direction of the incident K atom. In the tails orientation, the molecule is not perfectly oriented and the obscuring CF<sub>3</sub> group may not completely shield the reactive site. Consequently, it can be expected that some trajectories incident at the CF<sub>3</sub> end may fly by the CF<sub>3</sub> group and strike the reactive X atom. Since the covalent radius of the I atom is larger<sup>16</sup> than that of the Br (1.33 Å vs. 1.14 Å), one might expect the Br to be more effectively shielded than the I and might expect the tails reactive cross section to be smaller than heads in CF<sub>3</sub>Br, as is observed.

**The Harpoon Mechanism.** The electron-jump or "harpoon" mechanism was introduced<sup>17</sup> to explain the anomalously large cross sections for alkali metal-halogen reactions and has been extended<sup>18</sup> to cover other reactions as well. The features of the model can be qualitatively seen<sup>18</sup> by considering the interaction between an alkali atom M and a halogen atom X. At large distances the interaction is that between neutral species and can best be described in terms of a covalent potential energy surface. But the binding of MX is clearly ionic, so at distances corresponding to the stable molecule, the system can best be described in terms of an ionic potential surface. The hypothetical reaction between M and X thus proceeds at long range via a covalent interaction, but at some distance,  $r_c$ , the interaction switches to an ionic interaction, and M donates its valence electron (the "harpoon") to X. The Coulombic attraction between M<sup>+</sup> and X<sup>-</sup> ensures reaction, so the cross section for reaction,  $\sigma_r$ , is approximately  $\pi r_c^2$  where

$$e^2/r_c \simeq I(M) - E(X) \quad (2)$$

where  $I(M)$  is the ionization potential of M and  $E(X)$  is the electron affinity of X.

For reaction with molecules the situation is a little more complicated. The surfaces for M-RX and M<sup>+</sup>(RX)<sup>-</sup> must again cross, but the details will depend on the nature of the R group, and the

appropriate electron affinity is the vertical electron affinity (evaluated at the bond distances which obtain when the electron jumps). The electron is expected to jump to the lowest unoccupied molecular orbital, which for many molecules is strongly antibonding. The molecular ion is thus likely to be formed in a repulsive state (or equivalently, high on the repulsive wall of a bound state) and the ion is expected to dissociate within one vibrational period in a manner strongly reminiscent of photodissociation.

In order to interpret our earlier results on the reactive scattering of oriented CF<sub>3</sub>I we postulated<sup>19</sup> that an electron transfer occurred, leaving the CF<sub>3</sub>I<sup>-</sup> ion in a repulsive state. The ion was expected to decompose in much less than a rotational period, so the I<sup>-</sup> ion was predicted to be ejected in the direction of the C-I bond which obtained at the instant of electron transfer. If the C-I bond were oriented such that the I were pointed toward (away from) the incoming K, the I<sup>-</sup> ion would be ejected backward (forward) and the K<sup>+</sup> ion would be expected to follow. This correctly explains the observed backward scattering for the heads orientation and forward scattering for the tails orientation. This model also qualitatively predicted the drastic difference in angular distribution when the molecules were oriented sideways.<sup>7</sup> From the sideways scattering results we tentatively concluded that the *probability* of electron transfer and subsequent dissociation of the ion are independent of the orientation of the molecule, but the *direction* in which the product is ejected depends directly on the orientation.

CF<sub>3</sub>Br exhibits both similarities and differences with respect to CF<sub>3</sub>I. The electron affinity of CF<sub>3</sub>Br is lower<sup>9</sup> (0.91 eV vs. 1.57 eV), and eq 2 predicts that the electron should jump at a shorter distance (4.2 vs. 5.2 Å), and  $\pi r_c^2$  is 55 vs. 85 Å<sup>2</sup>. The magnitudes of  $\sigma_r$  are only in rough agreement with our estimates for the reaction cross sections, 11 and 17 Å<sup>2</sup>, but the ratios agree almost exactly. The KBr angular distributions from CF<sub>3</sub>Br (backward for heads, forward for tails) are similar to that for KI from CF<sub>3</sub>I and is in nice agreement with the notion that the molecular ion will dissociate in the direction in which it is pointing at the instant of the electron jump. But the forward, tails scattering is attenuated in the CF<sub>3</sub>Br case, and this may result from several (presently indistinguishable) causes.

The probability of electron transfer (electron affinity) may be dependent on orientation. Even though the lowest unfilled orbital is mainly on the X atom, the electron is transferred to the entire molecule. At long range, as in the CF<sub>3</sub>I case, the molecule may appear as an electron acceptor regardless of orientation. But at shorter range, as for CF<sub>3</sub>Br, the electron transfer may be facilitated by having the Br closest to the incoming K, and reaction would thus be more probable in the heads orientation.

We should emphasize that the harpoon mechanism is a useful standard for comparison, but is a gross oversimplification for a very complicated process, especially at short range. Not only might the orientation affect the electron affinity, but also at close range the K<sup>+</sup> ion might affect the dissociation of the CF<sub>3</sub>Br<sup>-</sup>. Even if the electron affinity is not dependent on orientation, backside attack of the CF<sub>3</sub>Br may result in a nonreactive event just because the K<sup>+</sup> cannot get by the CF<sub>3</sub> moiety in time to react.

Trajectory calculations<sup>20</sup> to model alkali metal (M)-halogen (XY) reactions found that the strong forward scattering associated with these reactions arose from charge migration, where an initial M<sup>+</sup>...X<sup>-</sup> interaction was followed by migration to yield M<sup>+</sup>Y<sup>-</sup> + X. In addition, the forward scattered products formed in such encounters were found to have enhanced translational energy. If charge migration were important here, backside attack of CF<sub>3</sub>Br could give CF<sub>3</sub><sup>-</sup>-Br followed by charge migration to Br and forward scattering of the KBr, which might be expected to recoil with higher energy than backscattered KBr from the heads orientation. The diminished forward scattered intensity experimentally observed in the LAB might thus result not only from a real dynamic effect, but also from a kinematic effect whereby

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the CM cross sections for heads and tails scattering might be nearly equal, but the Jacobian factor  $(u/v)^2$  in the CM  $\rightarrow$  LAB transformation would favor a higher intensity in the lab for the slower backward scattered flux. Measurements on the product velocity distributions as functions of orientation may help to differentiate among these possibilities.

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## CONDENSED PHASES AND MACROMOLECULES

### Properties of the Vanadium Pentoxide Hydrogen Bronzes ( $\text{H}_{2x}\text{V}_2\text{O}_5$ )

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The electrochemical potential of an electrode containing the bronze  $\text{H}_{2x}\text{V}_2\text{O}_5$  at equilibrium state has been measured for  $0 < x < 1.7$  in order to characterize the intermediate phases.  $^{51}\text{V}$  NMR,  $^1\text{H}$  NMR, and EPR studies have shown that interaction between different cations ( $\text{V}^{5+}$ ,  $\text{V}^{4+}$ ,  $\text{V}^{3+}$ ) plays an important role in the stability of these phases. The  $\text{V}^{3+}$  ion seems to be stabilized in a  $3d_1 4s_1$  electronic configuration.

#### Introduction

A hydrogen bronze is an insertion compound of hydrogen within a host lattice, either an oxide or a chalcogenide, in which no formal chemical bond exists between the inserted proton and the anion. The vanadium pentoxide hydrogen bronze is formed at about 65 °C from a  $\text{V}_2\text{O}_5$  microcrystalline powder, coated with small Pt particles, in contact with gaseous molecular hydrogen, through hydrogen spillover. The final hydrogen content  $x$  is between 1.5 and 1.9 according to the residual pressure. This hydrogen bronze  $\text{H}_{2x}\text{V}_2\text{O}_5$  has been extensively studied.<sup>1,2</sup> It has been shown that the proton is localized and forms a hydride bond with the vanadium. The electrons are also localized, creating  $\text{V}^{4+}$  and  $\text{V}^{3+}$  paramagnetic centers. The exchange interactions between these two paramagnetic species and the small particle size are the origin of a transition between a frustrated superparamagnetic state ( $x < 1.65$ ) and an unfrustrated superparamagnetic state ( $x > 1.65$ ). Because of the amorphous structure of this bronze, the characterization of the final or eventual intermediate phases by X-ray crystallography or neutron diffraction was impossible. This paper aims to characterize intermediate phases in the range  $0 < x < 1.5$  by electrochemical methods and nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) techniques. At lower hydrogen content  $x \approx 0.25$  a phase has been recently described.<sup>3</sup>

#### Electrochemical Results

The electrochemical potential of the bronze  $\text{H}_{2x}\text{V}_2\text{O}_5$  has been measured for  $0 < x < 1.7$ . The electrochemical cell contains a solid electrolyte, which is a Nafion membrane. Nafion stands for perfluorosulfonic acid. It is the only solid proton conductor

working at room temperature. The electrodes are sheets made of Teflon and graphite mixed with the active materials. The reference electrode is the bronze  $\text{H}_{1.6}\text{MoO}_3$ , formed in acidic solution by nascent hydrogen, whose potential is about +0.1 V vs. NHE.<sup>4</sup> The counter electrode is the  $\text{MoO}_3$  oxide. The working electrode is the bronze  $\text{H}_{2x}\text{V}_2\text{O}_5$ , formed by hydrogen spillover and transferred into the cell under nitrogen atmosphere. The oxidation of  $\text{H}_{2x}\text{V}_2\text{O}_5$  is carried out stepwise. Each step begins with a galvanostatic discharge followed by relaxation toward the equilibrium state. At each step the value of  $x$  is determined by coulometry. The electrochemical potential of the bronze  $\text{H}_{2x}\text{V}_2\text{O}_5$  is plotted vs.  $x$  in Figure 1. According to the Gibbs phase rule, this diagram can be divided into several domains indicated by vertical dashed lines: Because the potential is invariant with respect to  $x$ , the first domain represents the coexistence of two solid phases,  $\text{H}_{x \approx 0}\text{V}_2\text{O}_5$  and  $\text{H}_{0.5}\text{V}_2\text{O}_5$  and  $\text{H}_2(\text{g})$ . In the second domain, there is a single solid phase  $\text{H}_{2x}\text{V}_2\text{O}_5$ , with  $0.25 < x < 0.5$ , and  $\text{H}_2(\text{g})$ . The slight increase of the electrochemical potential may be due to a modification of the lattice potential. In the third, the solid phases  $\text{H}_{1.1}\text{V}_2\text{O}_5$  and  $\text{H}_{1.5}\text{V}_2\text{O}_5$  coexist with  $\text{H}_2(\text{g})$ . The fourth domain is characterized by the existence of a single solid phase  $\text{H}_{2x}\text{V}_2\text{O}_5$  with  $0.65 < x < 1.1$  and  $\text{H}_2(\text{g})$ , the potential decreasing as  $x$  increases. Finally, the fifth domain expresses the coexistence of two solid phases which are  $\text{H}_{2.2}\text{V}_2\text{O}_5$  and  $\text{H}_3\text{V}_2\text{O}_5$  in equilibrium with  $\text{H}_2(\text{g})$ .

The reversibility of the system has been tested. The bronze  $\text{H}_{2x}\text{V}_2\text{O}_5$  with the highest value of  $x$  can be formed by hydrogen spillover from  $\text{H}_{x \approx 0}\text{V}_2\text{O}_5$ , obtained by electrochemical oxidation of  $\text{H}_{3.4}\text{V}_2\text{O}_5$ . All the hydrogen vanadium bronze phases are better oxidants than the reference  $\text{H}_{1.6}\text{MoO}_3$  electrode. This has also been shown for the CO oxidation.<sup>5</sup>

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