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states $|J|M\rangle = |111\rangle$ and $|212\rangle$, as for N₂O.⁹ However, there is a problem in assigning the relatively intense third peak in the focusing curves (consistently appearing with greater intensity than that of the $|111\rangle$ and $|212\rangle$ peaks), although a number of speculative explanations come to mind. Further work on OCS is in progress.

Figure 10 is a semilog plot of two focusing curves for BrCN. Because of the complexity of the Stark effect and the hyperfine problem for this molecule, no analysis of the structure in the focusing curve has yet been carried out. Further work on the cyanogen halides is in progress.

Concluding Remarks

As reported earlier,¹³ intense pulsed beams with essentially pure (>95%) rotational state selection have been obtained for prolate symmetric-top molecules. Partial state resolution [with some inevitable overlapping of peaks due to their $KM/(J^2 + J)$ degeneracies] is achieved in the case of oblate tops. Structured focusing curves are obtained for a variety of other polar polyatomic molecules, indicative of the potential for orientation of such molecules (even in the absence of knowledge of the state distribution in the oriented molecule beam). The strong focusing of BrCN suggests that beams of oriented cyanogen halide molecules can be used for crossed-beam reactive asymmetry experiments. Such experiments are now in the preliminary planning stage.²³

Acknowledgment. This research has been supported by NSF Grant No. CHE 83-16205, hereby gratefully acknowledged. The authors express their appreciation to Dr. S. Stolte of the Katholieke Universiteit, Nijmegen, for many valuable suggestions and informative discussions. R.B.B. acknowledges additional financial support, in connection with participation in the workshop (sponsored by the Institute for Advanced Studies of the Hebrew University of Jerusalem) from the US-Israel Binational Science Foundation. Thanks are also due to Prof. R. D. Levine and the Fritz Haber Center of the Hebrew University for organizing this exciting Workshop on Dynamical Stereochemistry.

Registry No. CH₃F, 593-53-3; CH₃CN, 75-05-8; CF₃H, 75-46-7; CCl₃H, 67-66-3; (CH₃)₃CCl, 507-20-0; H₃CCCl₃, 71-55-6; CH₂Cl₂, 75-09-2; CH₃NO₂, 75-52-5; CD₃OD, 811-98-3; NH₃, 7664-41-7; OCS, 463-58-1; BrCN, 506-68-3.

(23) Xu, Q.-X.; Bernstein, R. B., work in progress.

Molecular Beam Study of Steric Effects in the Reaction $K + HF (v = 1, j = 2) \rightarrow KF + H$

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HF molecules were optically aligned by use of linearly polarized infrared radiation generated by a color center laser tuned to the $R_1(1)$ line of HF. The state-specific integral cross section of the reaction K + HF (v = 1, j = 2) $\rightarrow KF + H$ was measured for the two different preparations of the approach geometry which result when the plane of polarization is positioned either parallel (σ_{\parallel}) or perpendicular (σ_{\perp}) to the most probable relative velocity of the reagents. At a translational energy of $E_{tr} = 0.46 \text{ eV}$ the resulting relative difference of the cross sections $(\sigma_{\parallel} - \sigma_{\perp})/\bar{\sigma}$ ($\bar{\sigma} = 1/2(\sigma_{\parallel} + \sigma_{\perp})$) amounts to $17 \pm 5\%$. This steric effect decreases with rising E_{tr} and reaches zero near 1.2 eV. The data strongly suggest that the reaction occurs via a collinear transition state.

Introduction

The probability that a reaction is initiated in a bimolecular collision depends not only on the energy of the reagents but also on their relative orientation. The most direct information on these geometric or steric properties of a reaction can be obtained from molecular beam experiments with polarized (oriented or aligned) molecules. The majority of such investigations exploit hexapolar fields¹ to generate molecular polarization but there exist for this purpose also powerful optical methods such as photodissociation,² saturated optical pumping,³ and excitation of ro-vibrational states by infrared radiation.⁴ In reactive scattering these optical techniques were applied as yet only in two studies: one on Xe* + IBr \rightarrow XeBr*(I) + I(Br)⁵ and the other on Sr + HF \rightarrow SrF + H.6

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In this paper we present the first results of an experimental investigation on steric effects in the reaction K + HF \rightarrow KF + H. The polarization (alignment) of reagent molecules was prepared optically by excitation of the v = 1, j = 2 state of HF (v, j denote the vibrational and rotational quantum numbers) by using linearly polarized infrared radiation. We have measured the relative state-specific integral reaction cross section for the two different preparations of the approach geometry which result when the plane of polarization is positioned either parallel (σ_{\parallel}) or perpendicular (σ_{\perp}) to the most probable relative velocity \vec{V} of the reagents. The relative cross section difference $(\sigma_{\parallel} - \sigma_{\perp})/\bar{\sigma} \ (\bar{\sigma} =$ $1/2(\sigma_{\parallel} + \sigma_{\perp}))$ was determined as a function of the reagent translational energy $E_{\rm tr}$ in the range $0.44 \le E_{\rm tr} \le 1.23$ eV.

Experimental Details

Molecular Beam Apparatus. The experiments were performed with a crossed molecular beam machine. Figure 1 shows a schematic diagram of the experimental arrangement. The K and the HF beams are generated by nozzle sources and intersect perpendicularly. The beams are collimated by conical skimmers which lead to an angular spread of 1.6° and 1.2° for HF and K, respectively. The velocity distributions of both beams are precisely

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Figure 1. Schematic diagram of the molecular beam experiment.

measured by time-of-flight analysis; the intensities are monitored by a mass spectrometer (HF) or a surface ionization detector (K). The products are detected by surface ionization; the Re ribbon used is housed in a separately pumped UHV chamber which can be rotated in the plane of the beams around the intersection volume.

For the optical preparation of specific v, j states the beam of a tunable color center laser (Burleigh Instruments) operated in the single mode intersects the HF beam 1.5 cm upstream from the scattering volume perpendicular to the scattering plane. The linear polarization of the laser beam is well conserved even after three reflections from gold-plated mirrors and transmission through a CaF₂ window. Thus rotation of the polarization plane can be simply achieved by the $\lambda/2$ plate which is mounted between CaF₂ window and HF beam (Figure 1).

If the laser is tuned for example to a transition frequency of the R branch of HF such as $R_1(1)$, a fraction of the molecules of around 1% of the relevant ground state is excited to the v =1, j = 2 state. Due to the long lifetime of these states of ~ 5 ms the loss of excited species on their way from the site of excitation to the reaction volume can be ignored completely. This is of course also the case with respect to the infrared radiation detector 43.5 cm further downstream. This device-a PbS element mounted to a gold-plated radiation collector-measures the small intensity of spontaneously emitted quanta ($\sim 10^{-9}$ W). The signal serves as a measure for the number density of excited molecules. Furthermore, it is used to optimize the tuning of the laser and to stabilize the frequency.

To label the products arising from reactions with state-prepared molecules the infrared beam is modulated with a mechanical chopper at a frequency of 117 Hz. With this labeling technique the products can be easily separated from the elastically scattered K atoms which are ionized on the Re ribbon with the same efficiency as KF. Prerequisite for separating the two fluxes in this way is that the elastic intensity has no modulated component. To verify the latter experimentally we benefit from the fact that, due to the extreme mass ratio of products, the angular distribution of KF in the laboratory coordinate system (LAB) is very narrow (fwhm $\sim 6^{\circ}$) and centered around the most probable center-ofmass angle Θ_{cm} (cf. Figure 1). In the close vicinity of this peak as well as at larger angles no modulated component of the elastic flux was observed. Therefore, we assume that also within the reactive region this component is absent and the entire modulated signal is due to reactive scattering.

The width of the product peak is dominated by the parent beam velocity distributions rather than by reaction dynamics. It is for this reason that the flux of KF measured for example at the peak angle Θ_{cm} represents the reaction probability or integral reaction cross section σ rather than the differential cross section.

As the fraction of excited molecules is missing in the ground state the modulated signal is in general proportional to the dif-



Figure 2. Transitions and final *m*-state population induced by linearly polarized $R_1(1)$ radiation.



Figure 3. Simplified classical view of the approach geometry after preparation of a v, j level with linearly polarized radiation (\vec{E} denotes the polarization vector): (a) $\vec{E} \parallel \vec{V}$, (b) $\vec{E} \perp \vec{V}$.

ference of the v = 1, j and v = 0, j - 1 (R₁(j-1) line) cross sections.⁷ But as the reaction is endothermic by 0.75 eV with a threshold energy close or equal to this value⁸ the v = 0, j - 1cross section vanishes for translational energies E_{tr} below 0.75 eV. Vibrational energy strongly enhances the reaction so that at $E_{\rm tr}$ = 1.23 eV, the highest energy considered in the present experiment, the v = 1 cross section is by orders of magnitude larger than that for $v = 0.^{7,8}$

The transition rate for the absorption of polarized light depends on the initial and final substates (m states) of the rotational levels. Figure 2 shows the transitions induced by linearly polarized $R_1(1)$ radiation. The *m* states refer to a quantization axis parallel to the polarization vector \vec{E} of the laser beam. In this frame the selection rule $\Delta m = 0$ holds which leads to unpopulated |m| =*j* states. As no saturation effects are observed at the typical laser power (300 mW/cm², bandwidth \lesssim 5 MHz), the final population of *m* states (alignment tensor component $A_0^{(2)} = -0.7^{\hat{9}}$) given in Figure 2 is proportional to the known transition rates.

The Approach Geometry. The relative orientation of the reagents of a three-center reaction (approach geometry) is adequately described by the angle of attack γ_a between the diatom axis and the relative velocity \vec{V} . For a rough illustration of the extent to which the approach geometry can be prepared optically we assume that only the most probable m state, m = 0, is populated, that is, \vec{j} is perpendicular to the polarization vector \vec{E} of the radiation. As for a Σ molecule j is always perpendicular to the axis the diatom rotates in a plane perpendicular to \vec{j} . For $\vec{E} \| \vec{V}$ (Figure 3a) the approaching atoms face the "narrow side" of the rotation disk, in this case the angle of attack γ_a is undetermined

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Figure 4. Polar diagrams of the probability distribution of the angle of attack, γ_a , after preparation of the v = 1, j = 2 level using linearly polarized $\mathbf{R}_1(1)$ radiation with $\vec{E} \parallel \vec{V}$ and $\vec{E} \perp \vec{V}$. In reality the distributions are somewhat less pronounced due to hyperfine interactions.

due to rotation. For $\vec{E} \perp \vec{V}$ (Figure 3b) the atoms face the "broad side" of the disk and γ_a is always 90° irrespective of rotation. In the present experiment integral cross sections for reactions with molecules in the v = 1, j = 2 state have been measured for both directions of the polarization plane and are denoted by $\sigma_{\parallel}(\vec{E} \parallel \vec{V})$ and $\sigma_{\perp}(\vec{E} \perp \vec{V})$.

For a quantitative determination of the γ_a distribution one has to incorporate the realistic populations of final *m* states (cf. Figure 4). It has been shown for optical excitation of a ${}^{1}\Sigma$ molecule that the probability for finding the axis pointing into the solid angle $d\Omega$ can be cast into the simple form⁴

$$P_{i}(\vartheta') \,\mathrm{d}\Omega = (4\pi)^{-1} [1 + A_{0}(j) P_{2}(\cos \vartheta')] \,\mathrm{d}\Omega \tag{1}$$

where ϑ' is the angle between the molecular axis and the z' axis (parallel to \vec{E} through the center of mass of the diatom as the origin of the coordinate system). If the frame is rotated by an angle β so that the new z axis is parallel to \vec{V} , the position of the diatom axis is then given by the polar angle γ_a and an azimut angle φ . Inserting the relation

$$\cos \vartheta' = \cos \gamma_a \cos \beta - \sin \gamma_a \cos \varphi \sin \beta \qquad (2)$$

into eq 1 and integrating over φ provides eventually the desired distribution of γ_a . For $\beta = 0$ and 90° one obtains the expression

$$P^{(j)}(\gamma_a) \, \mathrm{d}\gamma_a = 2\pi P_j(\gamma_a) \, \sin \, \gamma_a \, \mathrm{d}\gamma_a \tag{3}$$

with $A_0(2) = 1$ ($\beta = 0$) and $A_0(2) = -0.5$ ($\beta = 90^\circ$) for excitation by an R(1) line. Polar diagrams of both functions are depicted in Figure 4. For $\vec{E} || \vec{V} (\beta = 0^\circ) P^{(2)}(\gamma_a)$ is broadly distributed over the entire γ_a range with most probable angles at $\gamma_a = 41.8^\circ$ and 138.2° while it is sharply peaked at $\gamma_a = 90^\circ$ for $\vec{E} \perp \vec{V} (\beta = 90^\circ)$. The approach geometries are thus essentially the same as expected from Figure 3. Furthermore, γ_a is distributed symmetrically with respect to reflections of a line perpendicular to \vec{V} . It is near at hand to denote this property with the term "axis alignment" in analogy to the notation for symmetric distributions of angular momenta.

Due to the nuclear spin of hydrogen and fluorine the alignment of \vec{j} and of the axis described above are achieved only at the instant of excitation. The spin-rotation and spin-spin interactions couple all angular momenta together and \vec{j} precesses in a complicated way around the total angular momentum. These precessions lead to a loss of alignment. The depolarization by nuclear spin has been treated quantitatively by Altkorn et al.⁹ These authors found that for the j = 1 state of HF the loss of alignment is almost complete but already for j = 2 most of it (57.4%) is conserved. Consequently, the realistic γ_a distribution are somewhat less pronounced than those shown in Figure 4.

Preparation within a Stark Field. A more pronounced alignment of the rotor axis can be obtained by using a Stark field. Due to the relatively large dipole moment of HF the quadratic Stark effect causes level splittings of the order of 10 MHz already at moderate field strengths of around 20 kV/cm. With a Stark coupling energy ten times larger than the hyperfine interaction,¹⁰ nuclear spins and rotation are completely decoupled^{1b} and no spin-induced depolarization can occur. A measured Stark spectrum for the transition $v = 0, j = 1 \rightarrow v = 1, j = 2$ together with a level diagram is shown in Figure 5. The spectrum was obtained by recording the signal of the fluorescence detector while the laser was scanned in the single mode. Irradiating the molecules, for example, with the laser beam tuned to v_1 the j = 2, m = 0 state is populated. To exploit the resulting considerable alignment the quantization axis (Stark field) must be adiabatically rotated from the initial parallel direction to one perpendicular to the relative velocity. We are presently engaged in designing an adequate field structure.

Experimental Results

Our experimental results are shown in Figures 6 and 7. The temporal fluctuations of the σ_{\parallel} and σ_{\perp} measured with the laser tuned to the $R_1(1)$ transition are depicted in Figure 6. The data acquisition routine provides alternating data points for the plane of polarization parallel and perpendicular to the mean relative velocity. Residence time per data point is 200 s; the error bars refer to one standard deviation calculated from the accumulated number of pulses. At the collision energy $E_{tr} = 0.46 \text{ eV}$ (lower part of Figure 6) σ_{\parallel} is consistently larger than σ_{\perp} except for a few points. The average values of all corresponding data points over the total acquisition time of 73 min are given together with standard deviations on the right-hand side of Figure 6; they differ well beyond error margins and clearly manifest a significant steric effect. The result at $E_{tr} = 1.1$ eV, however, is quite different (upper part of Figure 6). The cross sections run mostly parallel and only for a few points $\sigma_{\parallel} - \sigma_{\perp}$ oscillates around zero. As a consequence the mean values of σ_{\parallel} and σ_{\perp} are equal within their error bars that is, the steric effect has disappeared.

The results of measurements carried out at various collision energies are depicted in Figure 7. The relative difference of cross sections is largest at the lowest collision energy (0.44 eV) which lies only slightly above threshold of the v = 1 reaction (0.24 eV) and declines monotonously with growing E_{tr} . At the highest energies near $E_{tr} = 1.1$ eV no significant steric effect has been found.

Discussion

For K + HF as well as for a series of other M + HX systems (M = Li, Na, K, Rb; X = F, Cl, Br, I) semiempirical potential energy surfaces (PES) have been calculated;¹¹ in addition, for Li + HF there exist also two ab-initio PESs.^{12,13} All PESs agree in one respect, the dependence of the barrier height V_b on the bond angle γ_b (cf. Figure 8) is rather weak and so is the anisotropy of the PES on the reagent side. Starting from $\gamma_b = 180^\circ$ to $\gamma_b \approx 40^\circ V_b(\gamma_b)$ is rather flat but beyond $\gamma_b \approx 40^\circ V_b$ increases strongly. Within the flat region the PESs behave differently and can be subdivided into two categories: one contains PESs with the minimal V_b at $\gamma_b = 180^\circ$ (collinear transition state) the other those with the minimum in a bent conformation (bent transition state). Semiempirical theory¹¹ predicts for K + HF a bent transition state with $\gamma_b = 65^\circ$. In the following we will attempt to show that our experimental results are in contradiction to this prediction.

The extent of a steric effect depends on to what degree the approach geometry is conserved on the way from the asymptotic region to the transition state. For reactive encounters with large impact parameters b, for example, an inspection of γ_a clearly shows

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Figure 5. Stark spectrum of the v = 0, $j = 1 \rightarrow v = 1$, j = 2 transition of HF. The *m* states refer to \vec{E}_{Stark} as the quantization axis. With $\vec{E} \perp \vec{E}_{\text{Stark}}$ the selection rule $\Delta m = \pm 1$ applies.



Figure 6. Relative reaction cross sections measured in alternating order for $\vec{E} \parallel \vec{V}(\sigma_{\parallel})$ and $\vec{E} \perp \vec{V}(\sigma_{\perp})$ at two collision energies. The mean values of the cross sections are given at the right-hand side of the diagram. The total data acquisition times for the latter are 73 min. Note the marked difference of σ_{\parallel} and σ_{\perp} for the majority of data points at $E_{tr} = 0.46$ eV. At the elevated energy $E_{tr} = 1.1$ eV there is obviously no significant difference.

that rotation of the HX molecule completely destroys the initial preparation. This quite obvious property was confirmed recently in a quasi-classical trajectory (QCT) study for $Li + HF.^{14}$ For central or near central collisions (small *b*), however, the situation is quite different. For a PES with negligible anisotropy (no torques



Figure 7. Energy dependence of the relative differences of cross sections $(\sigma_{\parallel} - \sigma_{\perp})/\bar{\sigma} \ (\bar{\sigma} = \frac{1}{2}(\sigma_{\parallel} + \sigma_{\perp})).$



Figure 8. Typical dependence of the barrier height V_b on the bond angle γ_b . E_1 and E_2 denote the energy available for surmounting the barrier at $E_{tr} = 0.46$ and 1.2 eV. The curve reflects closely $V_b(\gamma_b)$ of the system Na + HCl¹¹ for which the energy scale is in electronvolts.

are exerted on HF during the approach) the prepared γ_a distribution will transform into the same γ_b distribution (cf. Figure

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3). For a system with a realistic anisotropy the final γ_b distribution is of course altered. But using the "rotational sliding mass model"¹⁵ it can be easily demonstrated that due to the moderate anisotropy of the PESs of the M + HX-systems the range of γ_b still remains roughly the same as for γ_a .

Following these arguments one is led to the conclusions:

1. Steric effects for the present system arise from collisions with small b. As a consequence the ratio $(\sigma_{\parallel} - \sigma_{\perp})/\bar{\sigma}$ must be small in accord with the experimental results.

2. The finding $\sigma_{\parallel} > \sigma_{\perp}$ means that near central collisions are less likely reactive for a γ_a preparation which predominantly leads to $\gamma_{\rm b}$ near 90° $(\vec{E} \perp \vec{V})$ than for one providing no preferred $\gamma_{\rm b}$ $(\vec{E} \parallel \vec{V})$. This result can be easily rationalized if one assumes that the system exhibits a collinear transition state with a γ_b dependence of the barrier height like the one shown in Figure 8. Is E_1 the energy available for passing the barrier at a collision energy $E_{\rm tr}$

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= 0.46 eV then no reactions can occur for $\gamma_{\rm h}$ near 90° while for a widely distributed γ_b reactions can take place via near collinear conformations.

3. Figure 7 shows that the steric effect vanishes at $E_{\rm tr} \sim 1.2$ eV. This means that the corresponding energy E_2 is already sufficiently large to admit reactions via both the near bent and the near collinear conformations (cf. Figure 8). Then the different γ_a preparations lead to a reaction with the same probability.

Using these arguments one would predict for a reaction with a bent transition state that $\sigma_{\parallel} < \sigma_{\perp}$. No experimental data are available so far but the result of a recent QCT study for Li + HF¹⁴ based on a PES featuring a bent transition state¹³ is in accord with this prediction.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft (SFB 216, P5) is gratefully acknowledged.

Registry No. K, 7440-09-7; HF, 7664-39-3.

Isotopic Variants of the H + H₂ Reaction. 1. Total Reaction Cross Sections of the H + D₂ and H + HD Reactions as a Function of Relative Energy

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The total cross sections for the reactions $H + D_2 = HD + D$ and $H + HD = H_2 + D$ have been measured as a function of relative initial translational energy in the ranges 0.87 to 2.70 and 0.82 to 1.86 eV, respectively. The technique for measuring the rate constant exploits the fact that the atomic product and reactant have very similar absorption wavelengths and that nearly monoenergetic hydrogen atoms can be generated by photodissociation of particular small molecules. Detection of the hydrogen atoms was carried out by laser-induced fluorescence at such short times that single collision conditions prevailed. The measured cross sections are in excellent agreement with the classical trajectory calculations of Blais and Truhlar and Schechter and Levine. As a byproduct of these experiments it was shown by Doppler spectroscopy that at the wavelengths 248 and 193 nm the transition dipole moment for H_2S is perpendicular to the molecular plane and that almost all of the available energy in this photodissociation is released into translation.

The reaction $H + H_2 = H_2 + H$ (and its isotopic variants) is the central elementary chemical reaction. The elementary chemical reactions A + BC = AB + C are at the heart of theoretical reaction dynamics because of their simplicity. The subset of exchange reactions A + BA = AB + A have a special simplicity in that the potential surfaces are symmetrical with respect to reactants and products. $H + H_2$ is the only such system for which an accurate potential surface has been calculated.^{1,2} Although quantum mechanical calculations have so far been carried out only at energies near the threshold³⁰ extensive calculations have been carried out of the classical trajectories on the best potential surface.3-7,31

Ever since the early work of London⁸ an immense theoretical literature has been devoted to this reaction (see ref 9 for a review). Classical kinetic experiments have been carried out on isotopic versions of $H + H_2$ in which the temperature-dependent rate constant k(T) was measured.¹⁰ The corresponding energies are near the threshold for the reaction, that is, in the region 0.4 to 0.6 eV. More recently a new class of experiments have been carried out involving some degree of state selection. Differential reactive scattering cross sections have been measured for $D + H_2$ at 0.48, 1.0-, and 1.5-eV relative energies.^{11,12} The HD state distribution has been measured for the $H + D_2$ reaction at 0.98, 1.1-, and 1.3-eV relative energy by coherent anti-Stokes Raman scattering and by multiphoton ionization (MPI).^{13,14}

From these experiments we have learned that near threshold the reactive scattering for $D + H_2$ is backward in the centerof-mass system but at higher energies the scattering is mainly sideward. At least up to 1.3 eV the HD product of the $H + D_2$ reaction is mainly in the v = 0 state. The rotational distribution broadens and shifts to higher J values with increasing relative translational energy.

A minor failing of these superb experiments is that the total reaction cross section as a function of initial relative translational energy (E) cannot be easily measured. In general, there are major difficulties in measuring $\sigma(E)$ or k(E) for a given chemical re-

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