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Collision Dynamics of Alkali-Metal Atoms with Oriented Symmetric-Top Molecules

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Theoretical calculations based on the long-range dynamics of the harpoon model have been used to predict the effects of reactant orientation upon ionization yields and angular distributions of product MX for reactions of alkali-metal atoms M with oriented symmetric-top molecules of general formula CY3X, where X is a halogen and Y is H, F, or methyl. Large effects of orientation upon ionization yield near threshold are found to result from differences in the partitioning of kinetic energy between relative motion and center-of-mass motion, depending on whether the X- ion ejected by the unstable CY3X- ion is traveling in the same direction as the incoming M+ ion or the opposite direction. For most systems for which comparison is possible, excellent agreement is obtained with experimental data on the effect of orientation upon ionization yield. For ionizing collisions of fast K atoms with CH3I and CH3F, and for product angular distributions found with thermal K atoms and oriented CF3I and CF3Br, the theory is less successful and it appears that orientation-dependent short-range interactions must play a major role.

Introduction

Molecular beam studies of collisions of alkali-metal atoms M with oriented CY3X molecules, where X is Cl, Br, or I, comprise a number of measurements of angular distributions of the product MX from reactions of thermal alkali-metal atoms,1-10 and of the effect of orientation on ionization yields obtained with fast (5-30 eV) potassium atoms.11-13 Angular distributions of products have often been interpreted in terms of what chemists intuitively think of as sterically想到的，amounting to a substantial "cone of no reaction" for the case of a rubidium atom approaching a methyl iodide molecule on the side of the methyl group.8 An alternative, dynamic interpretation in terms of the harpoon mechanism has arisen from work at Rice University. In this alternative picture, the electron transfer proceeds independently of orientation, but the direction of the CY3X- axis at the instant the "harpoon" electron is transferred from the approaching metal atom fixes the direction in which the X- ion is ejected by the resulting unstable CY3X- ion. The direction of ejection of the X- in turn has a major influence on the direction in which the MX product is observed to be scattered. This same model has been used to interpret the results of measurements of the effect of orientation on ionization

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yields from collisions of fast potassium atoms with a number of oriented symmetric-top molecules. For these systems, the direction of ejection of \( X^+ \) relative to the incoming \( M^+ \) has been assumed to affect the ionization yield through its effect on the relative velocity, \( v \), in the Landau-Zener expression

\[
P = \exp[-4\pi^2H_0 \gamma^2/(\hbar |\Delta E|)]
\]

for the probability of curve-crossing at the intersection of the \( M^+ + X^- \) potential with the neutral \( M \) potential. When the \( X^- \) ion is ejected toward the incoming \( M^+ \) ion, the magnitude of the relative velocity \( v \) is much greater than when it is ejected in the same direction as the \( M^+ \) is traveling, so that \( P \), representing the probability that the system will remain on the diabatic potential curve leading to ions, is larger.

It seems likely that the two kinds of mechanism, which we will term \textit{steric} and \textit{dynamic}, represent ideal limiting cases and a real reaction system can be expected to show behavior which is intermediate between the two extremes. The interpretation in terms of ordinary steric effects emphasizes the short-range behavior of the system during a collision of \( M \) with \( CY_3X \), whereas the dynamic interpretation emphasizes the long-range features of the picture provided by the harpoon mechanism. The present paper gives the results of numerical calculations based purely on the dynamic model, the aim being to establish how well the experimental results can be accounted for on the basis of this model alone. The results show that, as might have been expected, the dynamic mechanism accounts for many but not all of the features of the experimental results. An interesting additional outcome of these calculations has been the identification of a second kind of dynamic mechanism which can lead to an orientation dependence of the ionization yield. The new mechanism depends on the circumstance that partitioning of the energy of the \( M^+, X^- \) system into kinetic energy of relative motion and kinetic energy of motion of the center of mass is strongly dependent on the direction of relative motion of \( M^+ \) and \( X^- \). If the two ions are moving in the same direction, the kinetic energy of the center of mass will be much greater than if the ions are traveling in opposite directions. Consequently, at collision energies close to the threshold for ion production, the kinetic energy of relative motion is more likely to be insufficient to enable the charges to separate, when they are traveling in the same direction, and the observed ionization yield will therefore be lower than when they are traveling in opposite directions. The present calculations show that this effect is likely to be more important when the mass of \( M \) is comparable with or larger than that of \( X \), and when species \( Y \) of the \( CY_3 \) group is the heavier \( F \) or \( CH_3 \) rather than \( H \).

Calculations

(a) Ionization Yields with Fast M Atoms. Data used in the calculations, and derived curve-crossing radii, are given in Table I. For these calculations the \( CY_3X \) molecule was regarded as a stationary target, oriented at some angle \( \theta \) with respect to the collision axis, and rotated by an angle \( \phi \) with respect to the plane of the collision (Figure 1). The distribution over \( \theta \) was calculated

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Angular relationships in the collision of a fast M atom with an oriented CY_3X molecule. The angle \( \theta \) is selected by the hexapole focusing system; \( b \) is the impact parameter.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Section through potential energy surfaces showing energy relationships and crossing radii \( R_l \) and \( R_2 \) in the M + CY_3X system.}
\end{figure}

TABLE I: (a) Data Used in Calculations and (b) Calculated Curve-Crossing Radii

(a) Data Used in Calculations

\begin{itemize}
\item Ionization potentials, \( eV \): Li (5.39), Cs (3.894), Ca (5.39)
\item Electron affinities, \( eV \): F (3.399), Br (3.656), I (3.060), CF_3Br (0.91), CF_3I (1.57), CH_3I (0.2)
\item Dipole moments, \( D \): CF_3Cl (0.50), CF_3Br (0.65), CF_3I (0.92), CH_3F (1.79), CH_3Cl (1.869), CH_3Br (1.822), CH_3I (1.62), t-BuCl (2.15), t-BuBr (2.21), t-BuI (2.13)
\item Dissociation energies, \( D_{el} \) kJ/mol: CF_3Cl (328), CF_3Br (276), CH_3Cl (349), CH_3Br (280), CH_3I (234), t-BuCl (328), t-BuBr (276), t-BuI (240)
\item CY_3-lifetimes: all 10^{-13} s
\end{itemize}

(b) Calculated Curve-Crossing Radii

\begin{itemize}
\item First-crossing radius \( R_1 \), Å: Li + CF_3I (3.77), CF_3Br (3.21), CF_3Cl (3.10), CH_3Cl (3.10), CH_3F (3.10), CH_3Br (2.94), CH_3I (2.91), t-BuCl (2.80), t-BuI (2.77)
\item Second-crossing radius \( R_2 \), Å: K + CF_3I (5.18), CF_3Br (4.19), CF_3Cl (4.00), CH_3F (4.00), CH_3Cl (3.74), CH_3Br (3.47), CH_3I (3.51), t-BuCl (3.47)
\item Dissociation energies, \( D_{el} \) kJ/mol: CF_3Cl (328), CF_3Br (276), CH_3Cl (349), CH_3Br (280), CH_3I (234), t-BuCl (328), t-BuBr (276), t-BuI (240)
\end{itemize}

\( * \) Reference 17. \( ^{a} \) Assumed values. \( ^{b} \) Reference 18.

for the species \( CY_3X \) with values of hexapole dimensions and other beam parameters chosen to correspond to the experimental system as previously described. The distribution over \( \phi \) was assumed to be uniform. For each \((\theta, \phi)\) combination the ionization cross section was calculated by summing the product of area and ionization probability over a range of impact parameters between zero and the first curve-crossing radius \( R_1 \). This radius was calculated as the intersection of the \( M^+ + CY_3X^- \) Coulomb potential with an essentially flat \( M + CY_3X \) neutral potential (Figure 2). The CY_3X^- ion was assigned an arbitrary lifetime \( \tau \), which was taken to be \( 10^{-13} \) s for the results reported here. Results obtained with assumed lifetimes between \( 10^{-11} \) and \( 10^{-14} \) s differed in detail but were qualitatively very similar.

The \( M^+ + CY_3X^- \) trajectory for each impact parameter was calculated on an uneven radial grid with a hard-sphere core located at some arbitrary minimum radius (typically 1.5 Å), and the trajectory was continued until either less than 1% of the negative ion remained to dissociate, or the second crossing radius \( R_2 \), given by the intersection of the \( M^+ + X^- \) Coulomb potential with a flat \( M + CY_3X \) potential (see Figure 2), had been reached. The kinetic energy of the \( X^- \) ion was calculated from the exothermicity \( \Delta E = E_{AX} - D_{el} \) of the \( CY_3X^- \) dissociation process (Figure 3), with no contribution from the kinetic energy of the incoming \( M \) atom. Such long-range energy transfer might occur as a result of polarization of the anion by the Coulomb field of the cation, but calculations in which an amount of the order of 15% of the
energy of a K atom was assumed to be transferred to the CY3X- in a way that did not differ qualitatively from those obtained with no energy transfer at long range, and this effect has been assumed negligible.

At each point on the radial grid, the fraction of CY3X- dissociated since the previous grid point was calculated, and the kinetic energy of the center of mass of the M+ and X- ions was found. This center of mass energy was then subtracted from the sum of the kinetic energies of the metal ion and the ejected X- to give the amount of energy remaining as kinetic energy of relative motion of M+ and X- at each point on the grid. For trajectories in which the kinetic energy of relative motion failed to exceed the energy of the M+ + X- dissociation limit (the majority of trajectories were in this category at energies close to the ionization threshold) the contribution to the ionization cross section was zero. For the remaining trajectories, an effective impact parameter for the M+ + X- collision was calculated from the initial velocity vectors of the ions at the time of dissociation of CY3X-, this quantity being needed to calculate the centrifugal energy contribution to the effective potential at R2. Trajectories in which the kinetic energy of relative motion failed to exceed the effective potential at R2 also made no contribution to the ionization cross section. For the remainder, the Landau-Zener crossing probability was calculated from the relative velocity of M+ and X- at R2, using the matrix element H12 given by the formula of Baede.\(^{(15)}\) Values of H12 given by Baede's formula were also used, with less justification, to calculate the crossing probability for M + CY3X forming M+ + CY3X- at R1. Because of the relatively small first-crossing radii, the calculated values of H12 were quite large and the corresponding transition probabilities were of the order of unity. Ideally, values of H12 for the first crossing would be calculated from the observed dependences of relative ionization cross-sections on collision energy, but this cannot be done on the basis of the available data because the experimental arrangement\(^{(12,13)}\) did not permit accurate measurement of the metal atom flux as a function of energy. Errors in the calculated first-crossing probabilities would affect the absolute values found for ionization cross sections but would not affect the calculations of relative ionization yields for different orientations of CY3X. The relative yield was expressed in terms of the quantity G, defined by

\[
G = \frac{(\sigma_{180} - \sigma_0)}{(\sigma_{180} + \sigma_0)}
\]  

where the subscript 0 denotes the orientation in which the CY3 group points towards the incoming M atom and the subscript 180 denotes the opposite orientation. With this definition the quantity G is always positive but is otherwise identical with G as defined in ref 12, where the subscripts related to the direction of the dipole moment of CY3X rather than to the direction in which the X- was ejected.

In order to assess the relative importance of the various possible reasons for the calculated values of G to differ from zero, the program kept count of the number of trajectories which failed to reach the M+ + X- dissociation limit, the number of trajectories which failed to reach the second crossing radius, and the number of trajectories in which the Landau-Zener crossing probabilities at the second curve-crossing differed by more than 20% between the two orientations.

(b) Product Angular Distributions. In these calculations, the velocity distributions of both the CY3X beam and the thermal beam of M atoms were taken into account. As before, the experimental distribution over the orientation angle \(\theta\) was used, \(\theta\) being defined with respect to the relative velocity vector of M and CY3X (Figure 4). The acceptance angle of the MX detector was assumed to be small enough that only products traveling in the plane of the collision need be considered, so that for each value of \(\theta\) with given orientation there were two possible velocity vectors for the ejected X- ion, corresponding to the two intersections of a cone of apex angle 2\(\theta\) with the plane of the collision. In the very simple calculations to be discussed here, the M+ ion was assumed to proceed undeflected and there was no integration over impact parameter. The direction of the velocity vector of the MX product in the laboratory frame was calculated from the resultant of the M+ and X- momenta in this frame, using the trigonometric relationships implicit in Figure 4, and converted to a deflection angle \(\alpha\) relative to the M+ velocity vector.

Results and Discussion

Experimental and calculated values of \(G\), as defined in eq 3, are shown in Figure 5 as a function of metal atom energy for collisions of potassium atoms with CY3X where X = Cl, Br, and I. For CF3Cl the agreement between theory and experiment is seen to be remarkably good, a result that is probably fortuitous in view of both experimental error and the uncertainty in such quantities as the CF3Cl electron affinity and the CF3-Cl- bond energy and lifetime. Nevertheless, the qualitative agreement between theory and experiment shown by the relative magnitudes of \(G\) values for X = Cl, Br, and I is certainly significant and can be taken as implying that the dynamic mechanism does play a major role in deciding the value of \(G\) for these systems. The
chloride and methyl bromide, but very poor for methyl iodide. For methyl iodide, the calculated departure of ionization yield are seen to be much more pronounced than for potassium, and to persist to much higher metal atom energies. At higher energies the total ion signal is larger, so that the signal-to-noise ratio for measurements of G should be much better than zero found at relatively high energies are possibly attributable to the presence of a significant number of lower energy K atoms in the fast atom beam, which was formed by charge exchange of K+ in a cloud of neutral K. They might also be due to short-range effects which are not included in the model. The usual kind of steric effects, which are specifically excluded from the dynamic model, could lead to a dependence of ionization yield on orientation because they inhibit the formation of MX in one orientation and not the other, and formation of MX competes with production of ions. However, the direction of any steric effect would be expected to be similar to that found for the Rb + CH3I system, which is such that more MX, and therefore fewer ions, should be formed when the X- ion is ejected toward the incoming K+ ion, and this is opposite to the observed effect of orientation on ionization yield.

Calculated and experimental G values for collisions of potassium atoms with tertiary butyl halides are shown in Figure 6. Experimental data is lacking for tertiary butyl iodide. For methyl iodide, the calculated departure of G from zero arises mainly from differences in Landau-Zener crossing probabilities, which is such that more MX, and therefore fewer ions, should be formed when the X- ion is ejected toward the incoming K+ ion, and this is opposite to the observed effect of orientation on ionization yield.

Figure 7. Experimental (squares) and calculated (circles) values of G for K + CH3Cl (unfilled points), K + CH3Br (half-filled points), and K + CH3I (solid points).

Calculated and experimental G values for collisions of potassium atoms with methyl halides are shown in Figure 6. Experimental data is lacking for methyl iodide. For methyl iodide, the calculated departure of G from zero arises mainly from differences in Landau-Zener crossing probabilities.

Figure 8. Calculated values of G for Cs + CF3Cl (unfilled points), CF3Br (half-filled points), and CF3I (solid points).

Figure 9. Calculated values of G for Cs + CH3Br (half-filled circles), CH3I (solid circles), t-BuCl (unfilled diamonds), t-BuBr (half-filled diamonds), and t-BuI (solid diamonds).

in marked contrast to all the other results considered so far. The experimental results for methyl fluoride13 are not shown here. According to the model we are using, with no long-range energy transfer, there should be no F- produced from methyl fluoride because the CH3-F bond energy exceeds the electron affinity of F- and the CH3F- ion should therefore be stable (Figure 3). Attempts were made to model the K + CH3F system by allowing long-range transfer of an energy-dependent fraction (typically 20% near threshold) of the K atom energy to the CH3F, but it proved impossible to reproduce the experimental results on the basis of such a model. Thus, in order to account for an orientation-dependent ion production in collisions of CH3F with K atoms, it appears to be necessary to postulate the transfer of kinetic energy from the K atom to the CH3F as the result of a short-range collisional interaction in which steric effects are important. It is noteworthy that the experimental ionization cross sections for the K + CH3F system were very small,16 which suggests that the short-range mechanism is important only when the dynamic mechanism is either inefficient, as for K + CH3I, or ineffective, as for K + CH3F.

Predicted G values for Cs colliding with CF3Cl, CF3Br, and CF3I are shown in Figure 8. The effects of orientation on ionization yield are seen to be much more pronounced than for potassium, and to persist to much higher metal atom energies. At higher energies the total ion signal is larger, so that the signal-to-noise ratio for measurements of G should be much better with Cs than with K, and experiments with cesium should therefore provide a better test of the theory. Significant differences in

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the experimental data, the general form of the results is found to be qualitatively correct, with approach from the bromine or iodine end of the molecule leading to scattering at larger angles, and the ratio of the peak scattering cross sections is reproduced quite well for the bromide, although not for the iodide. However, quantitative agreement with the experimental angular distributions is poor, in that the peak scattering angles are about 30° too small, and this is undoubtedly a result of the failure of the model to take account of short-range interactions of the kind that lead to large-angle scattering.

Thus it would appear that the dynamic theory is much better at predicting the outcome of experiments with high-energy metal atom beams than with beams of thermal energy but, even at high energies, there are cases such as $K + CH_3F$ where the experimental results cannot be understood without invoking collisions in which steric effects operate at short range. In an attempt to include some of the short-range behavior of the collision system, product deflection angles were also calculated by a more elaborate procedure in which detailed trajectories were calculated for $M + CY_3X$ collisions over the range of impact parameters from zero to the first crossing radius $R_1$, and the deflection angle of $M^+$ was included in the calculation of the direction of the resultant $MX$ velocity vector. (For a given impact parameter there were then two possible deflection angles for $M^+$, because the approach of $M$ to $CY_3X$ could occur on either side of the collision axis in Figure 1.) The more elaborate calculation was expected to lead to larger predicted product deflection angles but so far the improvement in agreement with experiment has not been significant, even with a core radius of several angstroms and an assumed lifetime of $10^{-11}$ s for the $CY_3X^-$ ion. Clearly this is not a simple problem and more work is required.

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