Role of impact parameter in branching reactions

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We have measured the angular and velocity distributions of the ionic products formed in the reactions

\[ \text{Kr}^+ + \text{CH}_4 \rightarrow \text{KrH}^+ + \text{CH}_3 \quad (\Delta E_0 = -0.3 \text{ eV}) \]  
\[ \rightarrow \text{KrCH}_3^+ + \text{H} \quad (\Delta E_0 = -0.6 \text{ eV}) \]  
\[ \rightarrow \text{KrCH}_2 + \text{H}_2 \quad (\Delta E_0 = -1.3 \text{ eV}) \]

as a function of collision energy between 0.57 and 9.7 eV in the center of mass (c.m.). The beam instrument (single beam-collision chamber configuration with product velocity and angular analysis) used in this study has been described. 4

In all cases the product velocity vector distributions were asymmetric with respect to the center of mass, indicating that over the energy range studied these reactions are dominated by a direct mechanism (i.e., occur on a time scale less than or at most comparable to one rotational period). 5 Typical product velocity vector distributions, displayed as Cartesian contour maps, 6 are shown in Fig. 1 for Reactions (1) and (3). The KrCH3+ distribution (not shown) is very similar to that for KrCH2+.

Especially striking is the contrast between the velocity vector distributions for Reactions (1) and (2). The H-atom abstraction product (KrH+) is scattered into the forward hemisphere over a relatively small range of angles. The product recoil velocity is high, approaching that predicted by the spectator stripping model, 7 and product internal excitation is correspondingly low. On the other hand, the displacement products (KrCH2+ and KrCH3+) undergo large-angle scattering and are formed with internal excitation approaching that required for dissociation of the ionic product.

Direct reactions, in general, exhibit a correlation between impact parameter and scattering angle, with glancing collisions causing little angular deflection and nearly head-on collisions producing large-angle scattering. 8 The present results, therefore, clearly imply that the opacity functions (reaction probability as a function of impact parameter) are significantly different for these two types of reactions; i.e., abstraction is favored by moderately large impact parameters, whereas displacement is most likely in small impact parameter collisions. Similar conclusions have been obtained in trajectory studies 9 of the reactions of hot T atoms with CH4, but the present results appear to provide the first experimental evidence for such behavior.

This interpretation of the observed scattering patterns is also consistent with the need to conserve angular momentum and the difficulty of doing so in reactions yielding products whose reduced mass for relative translational motion (\(\mu'\)) is much less than that of the reactants (\(\mu\)). For the abstraction process, \(\mu' \approx \mu\). Hence, large amounts of angular momentum (\(L\)) can be accommodated in the orbital motion of the products and reaction can occur even when \(L\) and, consequently, the impact parameter are large. The displacement processes, however, yield products with \(\mu' \ll \mu\). Apparently, this restricts reaction to those encounters which have little angular momentum (i.e., small impact parameters). 10

These results support the suggestion 11 that factors such as the impact parameter and the angle of collision determine the reaction channel followed in direct reactions, as opposed to the usual minimum energy considerations which govern branching ratios in reactions proceeding via a long-lived complex. 12

![FIG. 1. Probability distributions \(P_C(\omega, \theta)\) for KrH+ and KrCH2+ produced in the reaction of Kr+ with CH4 at the collision energy \(T = 1.38 \text{ eV} \text{ (c.m.)}\). The product ion intensities, each normalized to 100 at the position of maximum intensity, are shown relative to the Cartesian system. Arrows represent the scattering angle with respect to the center of mass (marked c.m.).](image-url)
A more complete account of this work is in preparation.

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The reaction exothermicity is based upon the value $D_0(Kr^+ - H^+)=4.38$ eV reported by J. D. Payzant, H. I. Schiff, and D. K. Bohme, J. Chem. Phys. 63, 149 (1975).

Based upon the value $D_0(Kr^+ - CH_3)=5.03$ eV derived from the value of 10.37 eV for the heat of formation of KrCH$_3$ reported by D. Holz and J. L. Beauchamp, Science 178, 1237 (1971).

Based upon the assumption that $D_0(Kr^+ - CH_3)=D_0(Kr^+ - CH_4)=$ 5.03 eV. This assumption seems reasonable when the Br–C bond strengths in the isoelectronic molecules CH$_3$Br and CHBr$_3$ are compared.


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NOTES

Pressure dependence of the molecular rotational correlation times of benzene and pyridine

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Classical theories for the molecular dynamics of liquids predict that the molecular rotational correlation time is proportional to viscosity at a particular temperature. Measurements of the nuclear spin-lattice relaxation times of deuterated benzene and pyridine have shown that their rotational correlation times are much less dependent on pressure than their respective viscosities. The origin of this discrepancy most probably lies in the sixfold or near sixfold symmetry of the two molecules. Motion about the symmetry axis disturbs the surrounding environment very little and thus is coupled weakly to viscosity. This argument has been successfully used to qualitatively account for the degree of coupling in a series of substituted benzenes.

In this note we show how recent measurements on the rotational motion of benzene can be used to quantitatively predict the pressure dependence of the rotational correlation times of benzene and pyridine.

By depolarized Rayleigh light scattering and $^{13}$C NMR spin-lattice relaxation measurement, Bauer et al., have determined the viscosity dependence of rotational correlation times about individual molecular axes for a number of simple aromatic compounds. For benzene they found that at room temperature

$$\tau_s = 0.8 + 3.5 \theta \text{ psec}$$

(1)

where $\tau_s$ and $\tau_0$ are the correlation times for motion about an axis perpendicular and parallel to the symmetry axis, respectively, and $\eta$ is the viscosity in centipoise. The second equation displays explicitly the concept that a molecule does not interact effectively with its environment during a rotation about its symmetry axis. These equations also agree with results for the rotation of acetonitrile and the internal rotations in toluene and trifluoroacetoxy where in each case motion about a symmetry axis was found to be independent or very nearly independent of viscosity.

The rotational correlation times determined from spin-lattice relaxation measurements of deuterated benzene are a complex function of motions about axes both parallel and perpendicular to the symmetry axis. For a symmetric top molecule such as benzene where the electric field gradient relaxing the deuterium nucleus is perpendicular to the symmetry axis, this correlation time, called the "effective" correlation time is given by

$$\tau_{eff} = \frac{1}{\frac{1}{\tau_s} + \frac{1}{\tau_0}}$$

(3)

where $D$ is $1/\tau_s$ and $D_0 = 1/\theta\tau_s$. Combining Eqs. (1), (2), and (3)