

LETTERS TO THE EDITOR

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area. (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1975 for a fuller description of Letters to the Editor.

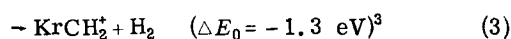
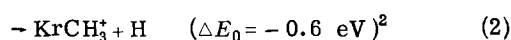
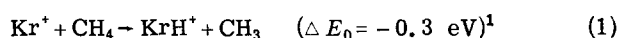
COMMUNICATIONS

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



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 KrCH_3^+ distribution (not shown) is very similar to that for KrCH_2^+ .

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 (KrCH_2^+ and KrCH_3^+) 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 studies⁹ of the reactions of hot

T atoms with CH_4 , 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 (μ') is much less than that of the reactants (μ). 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 suggestion¹¹ 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

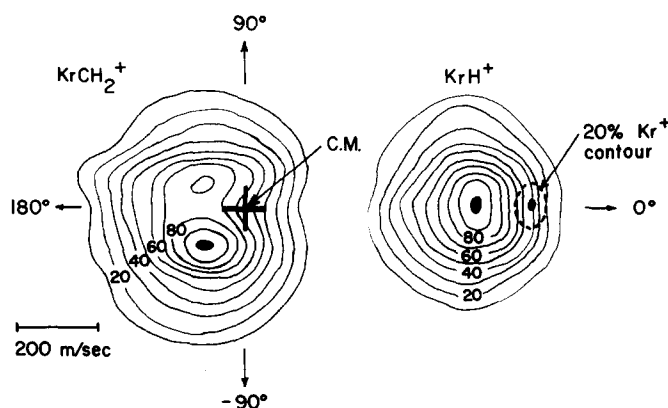


FIG. 1. Probability distributions $P_C(u, \theta)$ for KrH^+ and KrCH_2^+ produced in the reaction of Kr^+ with CH_4 at the collision energy $T=1.38 \text{ eV}$ (c.m.). The product ion intensities, each normalized to 100 at the position of maximum intensity, are shown relative to the Cartesian system. Arrows represent the scattering angle with respect to the center of mass (marked c.m.).

A more complete account of this work is in preparation.

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¹The reaction exothermicity is based upon the value $D_0(\text{Kr}-\text{H}^*) = 4.38$ eV reported by J. D. Payzant, H. I. Schiff, and D. K. Bohme, *J. Chem. Phys.* **63**, 149 (1975).

²Based upon the value $D_0(\text{Kr}^+-\text{CH}_3) = 5.03$ eV derived from the

value of 10.37 eV for the heat of formation of KrCH_3^+ reported by D. Holtz and J. L. Beauchamp, *Science* **173**, 1237 (1971).

³Based upon the assumption that $D_0(\text{Kr}^+-\text{CH}_2) = D_0(\text{Kr}^+-\text{CH}_3) = 5.03$ eV. This assumption seems reasonable when the Br-C bond strengths in the isoelectronic molecules CH_2Br and CH_3Br are compared.

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⁵D. R. Herschbach, *Discuss. Faraday Soc.* **33**, 149 (1962).

⁶R. Wolfgang and R. J. Cross, *J. Phys. Chem.* **73**, 743 (1969); P. M. Hierl, Z. Herman, and R. Wolfgang, *J. Chem. Phys.* **53**, 660 (1970).

⁷A. Henglein, K. Lacmann, and G. Jacobs, *Ber. Bunsenges, Phys. Chem.* **69**, 279, 286, 292 (1965).

⁸See, for example, R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Clarendon, Oxford, 1974), pp. 76-77.

⁹T. Valencich and D. L. Bunker, *J. Phys. Chem.* **61**, 21 (1974), and references cited therein.

¹⁰D. G. Truhlar, *J. Chem. Phys.* **51**, 4617 (1969); B. H. Mahan, *Acc. Chem. Res.* **3**, 393 (1970).

¹¹R. Wolfgang, *Ann. Rev. Chem.* **16**, 15 (1965); *Prog. Reaction Kinetics* **3**, 97 (1965).

¹²See Ref. 8, pp. 211-227.

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.^{1,2} Measurements of the nuclear spin-lattice relaxation times of perdeuterated benzene³ and pyridine⁴ 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.⁴ 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 ¹³C NMR spin-lattice relaxation measurement, Bauer *et al.*,⁵ have determined the viscosity dependence of rotational correlation times about individual molecular axes for a number of simple aromatic compounds.⁵ For benzene they found that at room temperature

$$\tau_1 = 0.8 + 3.5\eta \text{ psec} \quad (1)$$

$$\tau_{\parallel} = 0.7 \text{ psec}, \quad (2)$$

where τ_1 and τ_{\parallel} are the correlation times for motion about an axis perpendicular and parallel to the symmetry axis, respectively, and η 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 acetonitrile⁶ and the internal rotations in toluene⁷ and trifluorotoluene⁸ 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 perdeuterated 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 by⁹

$$\tau_{\text{eff}} = \frac{1}{6D_1} + \frac{3}{2D_1 + 4D_{\parallel}}, \quad (3)$$

where $D_1 = 1/6_1$ and $D_{\parallel} = 1/6_{\parallel}$. Combining Eqs. (1), (2)