

Crossed beam reaction of atomic chlorine with n-pentane: primary vs. secondary H atom abstraction dynamics

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We present a study of the dynamics of the reaction $\text{Cl} + \text{C}_5\text{H}_{12} \rightarrow \text{HCl} + \text{C}_5\text{H}_{11}$, probed using undulator radiation to effect soft ionization of the pentyl radical product. The study of chemical reactions in crossed molecular beams allows one to investigate chemistry under well-defined conditions:¹ the use of crossed supersonic molecular beams provides reagents in very low rotational states and yields a precisely defined collision energy rather than a Boltzmann average. Moreover, these studies are performed under single collision conditions, ensuring that the measured product velocity distributions directly reflect the energy released in the reaction. In addition, since the approach direction of the molecular beams is well-defined, the product scattering angles with respect to this direction can be used to reveal important dynamical information.

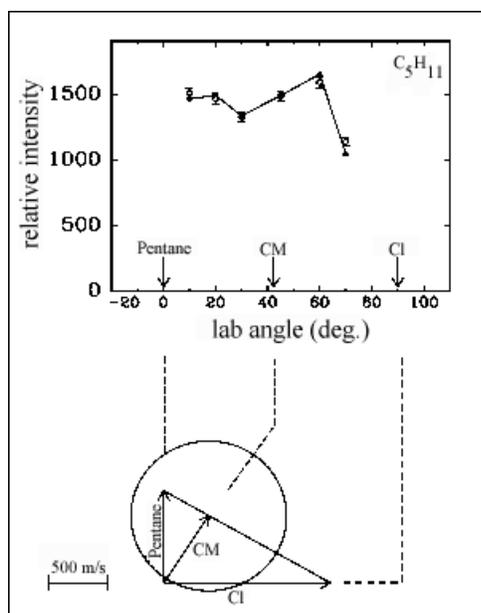


Figure 1. Laboratory angular distribution (top) and Newton diagram (bottom) for reaction of Cl + n-pentane at a collision energy of 16.4 kcal/mol. The circles with error bars are experimental points, the squares with connecting lines are the result of the simulation described in the text. The circle superimposed on the Newton diagram represents the maximum energetically allowed for formation of the 1-pentyl radical.

Free radical abstraction of hydrogen atoms in saturated hydrocarbons are reactions of great importance in combustion, and the differing propensities for reaction of terminal, or *primary*, H atoms vs. *secondary* H atoms, as well as the different dynamics underlying these two processes, are important to a detailed understanding of combustion chemistry. We have used reaction of Cl atoms with saturated hydrocarbons as a first step toward a detailed investigation of these abstraction reactions. Our initial studies focused on the slightly exoergic reactions of Cl with propane (C_3H_8)^{2,3}, with probe of the C_3H_7 product using tunable undulator radiation. These studies showed differing dynamics for the forward and backward scattered products. The former were ascribed to facile abstraction of the secondary H atoms, while the latter were believed to result from more strongly coupled collisions involving the terminal H atoms. Here we extend these studies to reaction of Cl with n-pentane, where the different energetics are used to explore these underlying trends in the reaction dynamics.

In these studies, conducted on Endstation 1 of the Chemical Dynamics Beamline 9.02, a beam of chlorine atoms seeded in helium gas is crossed at 90 degrees by a beam of n-pentane, and the reactively scattered C_5H_{11}

is probed using photoionization by tunable undulator radiation, with the resulting ions mass-selected by means of a quadrupole mass filter. The yield of pentyl radicals is recorded as a function of the neutral time-of-flight (by means of a pseudo-random chopper) and the angle between the molecular beams and the detector. Fig. 1 shows the laboratory angular distribution for the reaction along with the result of a forward convolution simulation from which we infer the

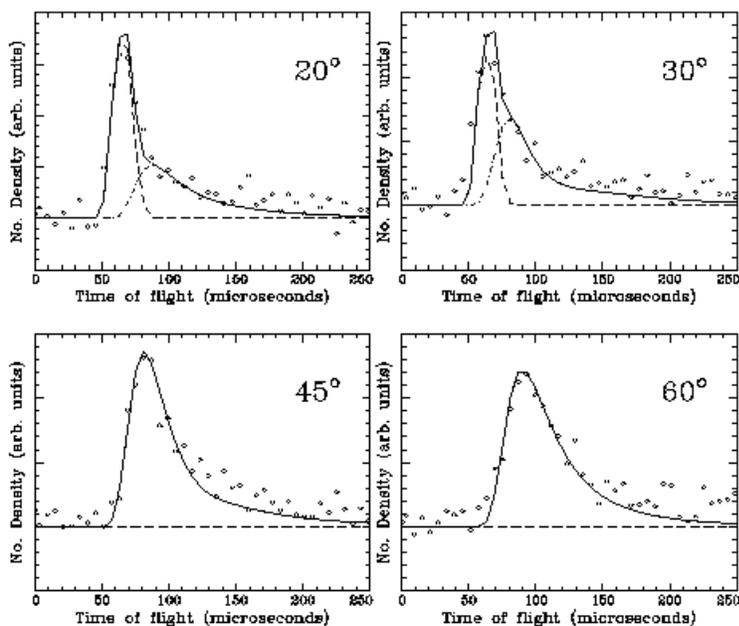


Figure 2. Time-of-flight spectra for $m/e=71$, pentyl, recorded with 10 eV probe photon energy at the indicated laboratory angle. The points represent experimental data, the solid line is the result of the simulation.

Also shown in Fig. 3B are energy thresholds corresponding to the formation of the 1-pentyl and 2-pentyl radicals. The translational energy release in the forward direction (channel one) extends beyond the energetic limit for abstraction of one of the primary H atoms, thereby excluding the possibility of formation of the 2-pentyl radical for this channel.

It is also interesting to note that the translational energy release for this channel extends very nearly to the energetic limit, implying formation of 1-pentyl radicals and HCl with no internal energy.

Although these trends are similar in Cl-pentane and Cl-propane, both showing forward scattered distributions near the thermodynamic limit along with slower backscattered distributions, the magnitude of the difference in translational energy release for the two components in the pentane case is quite striking. In both cases, it is likely that the backscattered distribution arises from abstraction of the primary rather than secondary H atoms, which involves an entrance barrier and the need for low-impact parameter, near-collinear

center-of-mass translational energy and angular distributions (the double differential cross sections) for the reaction. Fig. 2 shows typical time-of-flight which are important to an accurate determination of the translational energy distributions. The center-of-mass distributions obtained from fitting the experimental data in Figs. 1 and 2 are shown in Fig. 3. The scattering distributions have been decomposed into two components: channel 1 is the forward scattered component (Fig. 3A), also associated with a much larger translational energy release (Fig. 3B) while channel 2 is the backward scattered component, found to have a much lower translational energy release.

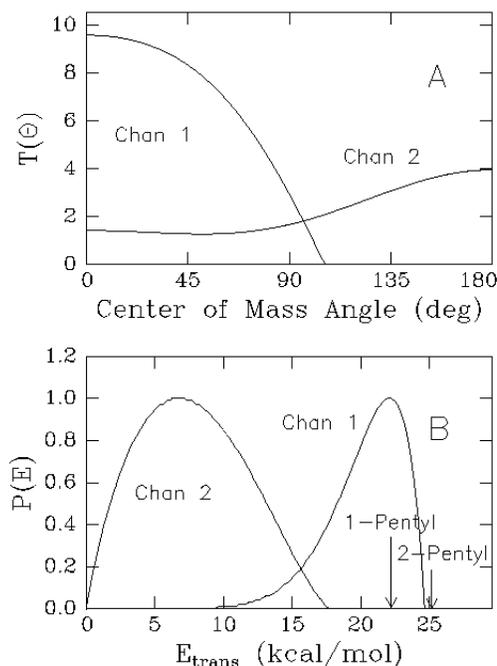


Figure 3. A. Center-of-mass angular distributions derived from the experimental data. B. Center of mass translational energy distributions inferred from the data.

Cl-H-C geometries to overcome this barrier. However, the energetics are not so distinct for these two systems, so the differences must be solely owing to the different dynamics arising from the momentum transfer to the extended carbon skeleton in the low impact parameter collisions.

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under contract No. DE-ACO3-76SF00098.

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