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Chemical Sciences Division

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The Dynamics of Hydrogen Abstraction Reactions: Crossed-beam reaction Cl+n-C$_5$H$_{12}$→ C$_5$H$_{11}$+HCl

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Abstract

We present a crossed molecular beam study of the dynamics of the metathesis reaction Cl + n-C$_5$H$_{12}$ → HCl + C$_5$H$_{11}$ at a collision energy of 16.8 kcal/mol. The experiments were conducted on the Chemical Dynamics Beamline at the Advanced Light Source, using tunable undulator radiation to effect soft ionization of the pentyl radical product. Laboratory angular distributions and time-of-flight spectra at many laboratory angles were used to obtain the center-of-mass translational energy and angular distributions. These distributions were found to be strongly coupled, with the forward scattered pentyl radical formed extremely cold, while the backscattered radicals were formed leaving nearly 15 kcal/mol in internal energy in the products. These results are contrasted with recent studies on the analogous reaction with propane, suggesting in this case direct involvement of the carbon skeleton in the collision process.

I.   Introduction

Metathesis reactions, in which a single atom is transferred from a stable molecule to an atom or radical, are the only truly bimolecular (i.e. bimolecular in both directions) gas phase reactions.[1] Those involving hydrogen atom transfer arguably represent the most important subclass of this vast body of reactions, particularly for combustion dynamics. Free radical abstraction of hydrogen atoms in saturated hydrocarbons, for example, are reactions of great importance in combustion, and the differing propensities for reaction of primary, secondary, or tertiary H atoms, as well as the different dynamics underlying these pathways, are important to a detailed understanding of combustion chemistry. These processes have come under increasing scrutiny in recent years as experimental innovations have allowed more direct probing of the dynamics.

An important pair of papers by Andresen and Luntz in 1980[2] reported experimental and theoretical studies of the reaction dynamics of $O(^3P)$ with a variety of saturated hydrocarbons chosen to underscore distinct trends in the reaction dynamics for primary, secondary or tertiary H atom abstraction. They measured OH product state distributions from these reactions using laser-induced fluorescence (LIF) and compared the results to classical trajectory calculations employing triatomic model surfaces with empirical LEPS potentials. The trends they observed for the OH rotational state distributions have been confirmed in all subsequent studies of H abstraction dynamics, viz., all the newly formed hydride products, regardless of the identity of the hydrocarbon or the attacking atom, are formed rotationally cold. This was ascribed to the importance of a collinear O-H-C transition state in these reactions. In addition, they found that the more exothermic the process (exothermicity increases in the sequence primary < secondary < tertiary), the greater the yield of vibrationally excited OH product, with tertiary H atom abstraction preferentially populating v=1. They argued that this arises from a shift in the nature of the surfaces from repulsive to attractive across the series, with the more product-like transition state for primary H abstraction favoring vibrationally cold products while the more reactant-like transition state for the tertiary H abstraction yields greater vibrational excitation.

Studies of the dynamics of chlorine atom reactions with hydrocarbons were stimulated in the early 90's when it was realized that these reactions represent a possible termination step for the chlorine-atom catalyzed ozone destruction cycle in the stratosphere. Theoretical studies[3,4] mapped features of the transition state for the methane reaction, while an experimental dynamics study in 1990 considered reaction of Cl with deuterated cyclohexane[5]. In the latter case, using time-resolved infrared absorption probe of the DCl product, Flynn and coworkers observed cold rotational distributions of the DCl, and efficient coupling of the initial collision energy into product translational energy. They framed the dynamics in a simple 'spectator' picture in which the hydrocarbon radical does not participate in the reaction and little momentum is transferred in the collision. They also invoked a collinear transition state to account for the cold rotational distributions in the DCl product. Koplitz and coworkers[6] used selective deuteration to investigate the site propensities for reaction of Cl with propane, using state-resolved resonant multiphoton ionization (REMPI) to detect the HCl or DCl products. They concluded that the middle carbon site (with secondary H atoms) was significantly more reactive than the terminal carbons.

A pioneering series of papers from the Zare laboratory[7-10] reported studies of Cl reaction with both vibrationally excited and ground state methane molecules, using their 'photoloc' technique to provide state-resolved differential cross sections for these reactions. Reaction of Cl atoms with vibrationally excited methane was found to be quite facile, showing the characteristic cold rotational distribution but predominantly forward scattered HCl, especially for the vibrationally excited HCl product. In addition, although all rotational distributions were relatively cold, for the vibrationally excited HCl product, the higher J values were associated with greater backscattering. A significant steric effect was also reported, with reaction yielding HCl (v=1) favored by perpendicular approach of the Cl atoms to the excited C-H stretch. Their results for reaction with ground vibrational state methane showed strongly backscattered, rotationally cold distributions. They rationalized this in terms of a hard-sphere model in which reaction is only possible for small impact parameter collisions. They also argued that the association of low rotational excitation with a collinear TS, as adduced by Andresen and Luntz in the O(^{3}P) reactions

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and Flynn and coworkers for the Cl-C$_6$D$_6$ reaction, is strictly appropriate only when there is impulsive energy release in the reaction. For the Cl-methane case, this is only applicable for the backscattered products. For the forward-scattered HCl, which is the dominant product from reaction of vibrationally excited methane, the cold rotational distributions were attributed simply to stripping-like mechanism involving large impact parameter collisions.

Varley and Dagdigian have reported an extensive investigation of the reaction dynamics of Cl with simple hydrocarbons[11-13] using a technique similar to the 'photoloc' method employed in Zare's experiments. In this work, state-resolved differential cross sections were obtained for the HCl product from reaction with a number of hydrocarbons including methane, propane, isobutane, and selectively deuterated propane. They observed backscattered HCl from the isobutane reaction, and vibrational population ratios that were similar for propane and isobutane, in contrast to the O(^{3}P) results of Andresen and Luntz. Their results for the partially deuterated propane showed abstraction of the D atoms (as the primary substituents) led to sideways scattered DCl product, while abstraction of the H atoms (the secondary substituents) led to a more isotropic angular distribution, yet still favoring the backward direction. It must be noted that their collision energies were very broad, and extended to very high energies, owing to the crossed-flow conditions. It is also important to recognize that the distributions obtained in these experiments as well as the 'photoloc' experiments, are largely blind to internal energy in the undetected product. Often the assumption is made that the undetected product is internally cold. We will see below that this may be far from the truth in some cases.

We have used reaction of Cl atoms with saturated hydrocarbons as a step toward a detailed investigation of these metathesis reactions. Our initial studies[14] focused on the slightly exoergic reactions of Cl with propane (C$_3$H$_8$), with probe of the C$_3$H$_7$ product using synchrotron radiation. The use of tunable undulator radiation, offering a unique combination of universality and selectivity in product detection, enables us to probe the doubly differential cross sections for the hydrocarbon radical fragment. The propane

studies suggested different 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, in an effort to examine the underlying trends in the reaction dynamics, in particular allowing us to probe the role of the extended carbon skeleton in these reactions.

II.   Experimental

These experiments were performed using a rotatable source molecular beam apparatus on the Chemical Dynamics Beamline[15] at the Advanced Light Source at Lawrence Berkeley National Laboratory. The apparatus has been described in detail elsewhere[16]. Briefly, a molecular beam of the hydrocarbon reagent, n-pentane, crosses a chlorine atom beam and the reactive scattering products are detected by a quadrupole mass spectrometer. The two molecular beam sources are fixed at 90° and the whole source chamber is rotatable to allow data collection at angles of -20° to 110° between the pentane beam and detector. The significant feature in the experimental setup is the use of the VUV undulator radiation for photoionization probe of the neutral scattering products, in place of the conventional electron impact ionizer. The spectrum of the undulator radiation consists of a fundamental peak of roughly Gaussian energy profile with a FWHM of 2.5%, and a series of harmonics of diminishing intensity extending beyond n=15. The energy of the fundamental may be tuned continuously over a range from 5 to 30 eV. The harmonics are suppressed as described below. Under typical operating conditions, the time structure of the undulator radiation is 35 ps pulses at 500 MHz; for our purposes it may be considered a continuous source. The photon flux at full storage ring current is greater than 10^{16} photons/sec. It is focused to a diameter less than 0.5 mm in the detector region.

For the reactive scattering studies on pentane with atomic chlorine, the pentane molecular beam was prepared by bubbling helium through n-pentane (Aldrich, HPLC grade) held at -40°C, where it has a vapor pressure of about 19 Torr, with a total stagnation pressure of 150 Torr, yielding a 13% beam. The continuous pentane beam was

expanded through a 0.25 mm stainless steel nozzle held at 200°C to inhibit cluster formation, into a source chamber maintained at 1.0×10^{-4} Torr. The mean velocity of the pentane beam was 1215±61 m/s. After collimation by two skimmers separated by a region of differential pumping, the pentane beam was crossed by the continuous beam of atomic chlorine, generated by thermal dissociation of Cl_2 diluted in helium. A mixture of 5% Cl_2 (Matheson, HP grade) in He (Matheson, HP grade) was used. The pyrolytic molecular beam source[14] consists of a high density graphite nozzle with a 0.15 mm opening and a resistively heated silicon carbide front plate. The nozzle tip is heated to about 1500 °C providing dissociation of a large fraction of the Cl_2. The mean velocity of the chlorine beam was 2120±282 m/s.
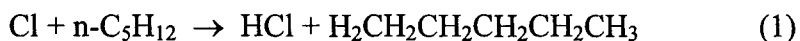
The cross-correlation method[17] was used for velocity measurements for both reactant beams as well as the reactive scattering products. A 17.8 cm diameter cross-correlation wheel with two identical 255-bit pseudorandom sequences of open and closed slots was used in front of the detector entrance to modulate the incident flux. The wheel was spun at 326.8 Hz resulting in a nominal resolution of 6 μsec in the TOF. The neutral flight length from the wheel to the photoionization volume is 11.9 cm. For velocity analysis of either molecular beam, the beam being analyzed was placed on line with the detector axis, the aperture at the entrance to the detector was set to 0.075 mm, and the photoionization energy was set to 14.5 eV with argon in the gas filter. The argon gas filter filled at 30 Torr eliminates the undulator harmonics above 15.0 eV.

Detection of the scattered C_5H_{11} reaction products was accomplished using 9.5 eV photoionization radiation with a MgF_2 filter that has transmission cutoff at about 11 eV, thus removing any residual radiation above that energy. The ionization potential (IP) of n-pentane is 10.35 eV, while for the pentyl radical it is 7.7 eV. By using a photoionization energy of 9.5 eV there is almost no background from dissociative ionization of the C_5H_{12} reactant. The quadrupole was set at a mass resolution of about 1.0 amu to maximize transmission for products at m/e 71 ($C_5H_{11}^+$). A multichannel scaler triggered by the chopping wheel was used to record TOF at various laboratory scattering angles, defined with respect to the pentane beam. Signals were averaged for 1-3 hours at each angle and laboratory angular distributions were obtained by integration of the TOF

spectrum for each angle. The center-of-mass translational energy and angular distributions were obtained by the forward convolution technique[18].

III. Results

The reaction of chlorine atoms with n-pentane proceeds via either primary or secondary H atom abstraction:

$$Cl + n\text{-}C_5H_{12} \rightarrow HCl + H_2CH_2CH_2CH_2CH_2CH_3 \qquad (1)$$

$$Cl + n\text{-}C_5H_{12} \rightarrow HCl + H_3CHCH_2CH_2CH_2CH_3 \qquad (2)$$

$$Cl + n\text{-}C_5H_{12} \rightarrow HCl + H_3CH_2CHCH_2CH_2CH_3 \qquad (3)$$

Throughout the remainder of this paper, reactions 2 and 3 will be considered together since they both represent secondary H atom abstraction and are energetically indistinguishable. Fig. 1 shows the energetics of these reactions. The heat of formation (ΔH_f^o (298.15)) of the 2-pentyl radical, 10.71 kcal/mol, is taken from reference 19, while the energy differences between this and the 1- and 3- pentyl radicals were taken from reference 20. We have chosen the slightly lower value for the heat of formation of the 2-pentyl radical based upon reference 19 owing to a significantly more favorable fit to our experimental results. Barriers for these two pathways are unknown, but rate constant measurements and analogy to smaller hydrocarbons suggest no barrier for the secondary H atom abstraction pathways, and a very small barrier for the primary abstraction channel.

The Newton diagram for the reaction is shown in Fig. 2, along with the measured laboratory angular distribution. The maximum available energy for the 2-pentyl radical product from this slightly exothermic reaction gives the recoil limit circle indicated. Also shown in conjunction with the measured angular distribution is the simulated distribution resulting from the best fit to all of the data. The inherently coupled nature of the angular and energy distributions can be inferred directly from inspection of the angular

distribution: the forward scattering extends beyond the beam in the forward direction, nearly to the recoil limit. The backscattered distribution, in contrast, drops sharply at a lab angle of 60°, well before the translational energy limit. This is confirmed by the time-of-flight distributions shown in Fig. 3. These distributions serve to constrain the simulations from which the translational energy and angular distributions are obtained.

Although it was impossible to obtain a satisfactory fit to the data with a single uncoupled translational energy (P(E)) and angular distribution (T(Θ)), excellent fits were obtained simply by decomposing the center-of-mass distributions into two components shown in Fig 4. The first, shown as 'channel 1', is exclusively forward scattered, and shows a translational energy distribution peaking at the limit of the available energy. In fact, improved fits could be obtained by allowing the exothermicity of the reaction to increase an additional 0.5 kcal/mol beyond that shown in Fig. 1, implying a heat of formation for the 2-pentyl radical of 10.2 kcal/mol. However, since the fitting approach is not unique and this difference is small, we do not feel justified in arguing for a lower heat of formation for the 2-pentyl radical. In contrast to channel 1, channel 2 shows a broad but predominantly backscattered distribution, with a vastly different translational energy release. The average energy release obtained for channel 1 is $<E>_1= 20.4$ kcal/mol, which is 92% of the available energy (E_{avail}), while for channel 2 it is $<E>_2=7.7$ kcal/mol, which is 35% of E_{avail}. The branching fractions are 58% for channel 1 and 32% for channel 2.

As in any forward convolution simulation of crossed-molecular beam results, the fit obtained is not unique. Nevertheless, the velocity-flux contour map we obtain, shown in Fig. 5, does faithfully reproduce the measured distributions. However, for the forward-scattered products in particular the decomposition into two components is somewhat arbitrary, and driven by the fit to the backscattered distribution.

IV. Discussion

The dynamics for the forward-scattered channel obtained from the fit are largely consistent with previous studies of Cl-hydrocarbon reaction dynamics. The P(E) peaks at

the maximum energy available for formation of the isoenergetic 2-pentyl (butyl-1-methyl) or 3-pentyl (propyl-1-ethyl) radicals, with an average of only 1.8 kcal/mole remaining in rotation and vibration of the products. The bulk of the forward scattered distribution appears at translational energies exceeding the limit for formation of the 1-pentyl radical (see the limits in Figs. 4B and 5). Abstraction of primary H atoms is thus ruled out for channel 1; however, there is little here to suggest any different propensities for abstraction of the hydrogen atoms from the 2- or 3- carbons.

The results for this channel are reminiscent of those reported by Flynn et al. for the Cl-cyclohexane[5] reaction, and identified by others in propane[11-13] and even for vibrationally excited methane[7-10]. That is, the products are formed with very little internal energy. As mentioned in the Introduction, many have attributed this to a collinear transition state; yet the correlation between forward scattering and a collinear transition state is problematic. Zare and coworkers considered several possible mechanisms that could reconcile these, but finally suggested an alternative interpretation of the dynamics[7]. They argued that if the reaction is not in the impulsive limit, then a cold product rotational distribution need not imply a collinear transition state. They considered the relative speed of the H and Cl at the time of the collision to estimate the anticipated rotational excitation. A related view of the collision dynamics can be obtained by asking what the appropriate impact parameter is for the collision. In fact, one may consider a hierarchy of impact parameters: that between the Cl and the whole molecule, which determines the overall angular momentum; that between the Cl atom and the carbon to which the abstracted H is attached, or even that between the Cl and H atoms. The most appropriate choice depends on the magnitude of the barrier, the tightness of the transition state and the particular feature of the dynamics under consideration. For example, collisions that have a large impact parameter with respect to the pentane center-of-mass (most collisions, obviously) may nevertheless exhibit small impact parameters with respect to the abstracted H atom. If there is no barrier for reaction even for a perpendicular C-H-Cl geometry, then the reaction may proceed with no momentum transfer whatsoever, other than that associated with change in the H atom motion. The orbital angular momentum will be largely unchanged, yielding forward

scattering in a 'spectator-stripping' mechanism. Calculations[21] have indicated a collinear transition state for the closely related Cl-propane reaction, but the question really is how tight the transition state is; we suggest the coincident observation of a cold rotational distribution with forward scattering argues for a fairly loose transition state.

The dynamics for channel 2, the backscattered distribution, diverge dramatically from previous work on H abstraction dynamics in hydrocarbons, even differing significantly from our own studies of the analogous Cl-propane reaction. The P(E) for channel 2 peaks at 6.8 kcal/mol, with an average release of 7.7 kcal/mol, a fractional energy release of only 35%. This may be compared to results for Cl-propane, for which the fractional energy release for the backscattered component ranged from 52% at 11.5 kcal/mol collision energy to 48% at the highest 31 kcal/mol collision energy. This means that an average of 15 kcal/mol remains in internal degrees of freedom of the products. State-resolved studies for propane have shown only a small yield of vibrationally excited HCl product[12,13], so it is unlikely that this accounts for much of the energy. Furthermore, we anticipate little difference between the HCl energy content from propane or pentane, since the energetics are virtually the same for both reactants. The likely repository of the bulk of this energy is thus in the hydrocarbon fragment; the question is whether it is in rotation or vibration. One significant difference between n-pentane and propane is the average impact parameter: the long n-pentane molecule naturally will yield abstraction of primary H atoms a considerable distance from the center of mass of the molecule. One might expect this to lead to greater rotational excitation for the pentane case. However, these large impact parameter (b) collisions will also yield fairly large exit impact parameters (b') so that little of the necessary conversion of orbital to rotational angular momentum may occur. Large rotational excitation in general requires small impact parameters for effective coupling of the initial linear momentum into rotational excitation. It is only for these close collisions that we can achieve the required large value of (b-b'). Certainly some measure of enhanced rotational excitation is plausible in the case of n-pentane, but for this to account for an increase to 65% of the available energy seems unlikely.

On the other hand, plausible reasons for greater vibrational excitation in the case of pentane vs. propane are readily apparent. There are many more vibrational modes for n-pentane (45 vs. 27), and perhaps more significantly, many more involving the low-frequency C-C-C bends. For these modes, with vibrational frequencies on the order of 800 cm^{-1}, the half-period is roughly 20 fs. We can compare this to the collision time under the conditions of the experiment: for an effective interaction region of 0.5 X at 2400 m/s we estimate a collision time of 21 fs, a remarkable match to the vibrational period. The combination of the higher density of states and the excellent match between the collision time and the bending mode vibrational period greatly favors coupling between the collision energy and the internal modes of the hydrocarbon. This suggests that in pentane we are seeing the direct participation of the extended carbon backbone in the reaction.

A final question concerns the nature of the two different channels. In our previous work on the propane reaction, we argued for the association of the forward-scattered distribution with the abstraction of secondary H atoms, while the backscattered product was associated with primary H atoms. It is even clearer in the pentane case, since the bulk of the forward scattered products are formed at translational energies well exceeding that possible for production of the 1-pentyl radicals, that the forward scattered products are indeed the result of secondary H atom abstraction. The question remains for the backscattered products: Are they preferentially associated with primary H abstraction? Although attempts were made to discriminate between these two radical isomers based upon their ionization potentials, we found no significant differences in the angular distributions as a function of probe photon energy. However, the vastly different internal energy distributions for the forward and backward scattered products may account for the absence of any significant differences, and would make interpretation of such an effect problematic in any case.

Although there is no direct evidence indicating a connection between the predominantly backscattered 'channel 2' and the primary abstraction channel, several lines of evidence point this direction. Firstly, the maximum energy release shown in Fig.

4B, and apparent in the contour map in Fig. 5, extends well below the limit of the available energy for production of the higher energy isomer. This distribution came directly from the best fit to the laboratory data and was in no way enforced. Secondly, there is the total branching between forward and backward scattered products. For the propane reaction, the fraction scattered forward of 90° was very close to 50% of the total. Assuming simply a limiting case association of forward scattering with secondary H abstraction we find, effectively, three times higher reactivity of the secondary vs. primary H atoms. For pentane, then, we expect the fraction forward scattered to increase from 1/2 to 3/4, since there are three times the number of secondary H atoms, if this limiting assumption is a good one. Indeed, if we look only at the fraction of the total scattered in the forward direction, in the same way we considered the propane case, we find a value of 74%, a remarkable agreement. If we compare the fraction of the total scattered into 'channel 1', then the value is 64%. If we make the association between channel 1 and secondary H abstraction, and channel 2 and primary H abstraction, this implies roughly a 1.8-fold higher reactivity of the secondary H atoms. However, we cannot directly compare this to the propane results since the distributions were decomposed differently. These values, on the order of 2- to 3-fold higher reactivity of secondary vs. primary H atoms, are consistent with those reported by Koplitz et al.[6] as well as Varley and Dagdigian[13] for selectively deuterated propane.

We may also consider the role of the transition state and the collision dynamics in an attempt to understand the nature of the backscattered component. Given a small enough barrier for primary H abstraction, virtually any direct encounter between Cl and a primary H atom could be reactive if the transition state is sufficiently loose. That is, even considering only the relative energy between Cl and H, we find under our conditions an effective collision energy of 0.7 kcal/mol or about 250 cm^{-1}. Collisions that possess a zero Cl-H impact parameter but achieve a perpendicular geometry at the transition state still have a relative energy of at least 250 cm^{-1}. If the barrier is lower than this, then the scattering distribution directly reflects the geometry of the transition state rather than the need for translational energy along the line-of-centers. The broad, predominantly backscattered distribution we see in 'channel 2', thus implies a tighter

transition state for this channel than for channel 1. Taken together these points argue convincingly for the association of the slower, preferentially backscattered product with abstraction of primary H atoms, while the very fast, forward scattered product is unambiguously associated with secondary H abstraction.

These translational energy distributions argue for a bit of caution on the part of those employing the photoloc technique and other methods relying on state-resolved measurements of one of the fragments to extract the speed and angular distributions for the reaction. These studies are generally blind to internal energy in the undetected fragment. Moreover, the reconstruction of the product distributions require some assumptions about the unmeasured fragment. If these assumptions are in error, then the derived distributions are inaccurate. Usually the assumption is made that the undetected fragment is internally cold, although in at least one case this issue was considered explicitly[8]. As we have seen, for the forward-scattered products in the pentane and propane case, this is a fairly accurate assumption. For the backscattered distributions, however, this is grossly incorrect. The implications of this for the inferred distributions are not clear, but these issues should be considered for any quantitative analysis of the photoloc-type experiments.

V.   Conclusion

We have studied the dynamics of the metathesis reaction Cl + n-C₅H₁₂ 6 HCl + C₅H₁₁ at a collision energy of 16.8 kcal/mol using the crossed molecular beam technique. The experiments were conducted on the Chemical Dynamics Beamline at the Advanced Light Source, using tunable undulator radiation to effect soft ionization of the pentyl radical product. The center-of-mass translational energy and angular distributions obtained from the experiments were found to be strongly coupled, with the forward scattered pentyl radical formed extremely cold, while the backscattered radicals were formed leaving nearly 65% of the available energy in internal energy in the products. These results are contrasted with recent studies on the analogous reaction with propane, suggesting in this case direct involvement of the carbon skeleton in the collision process.
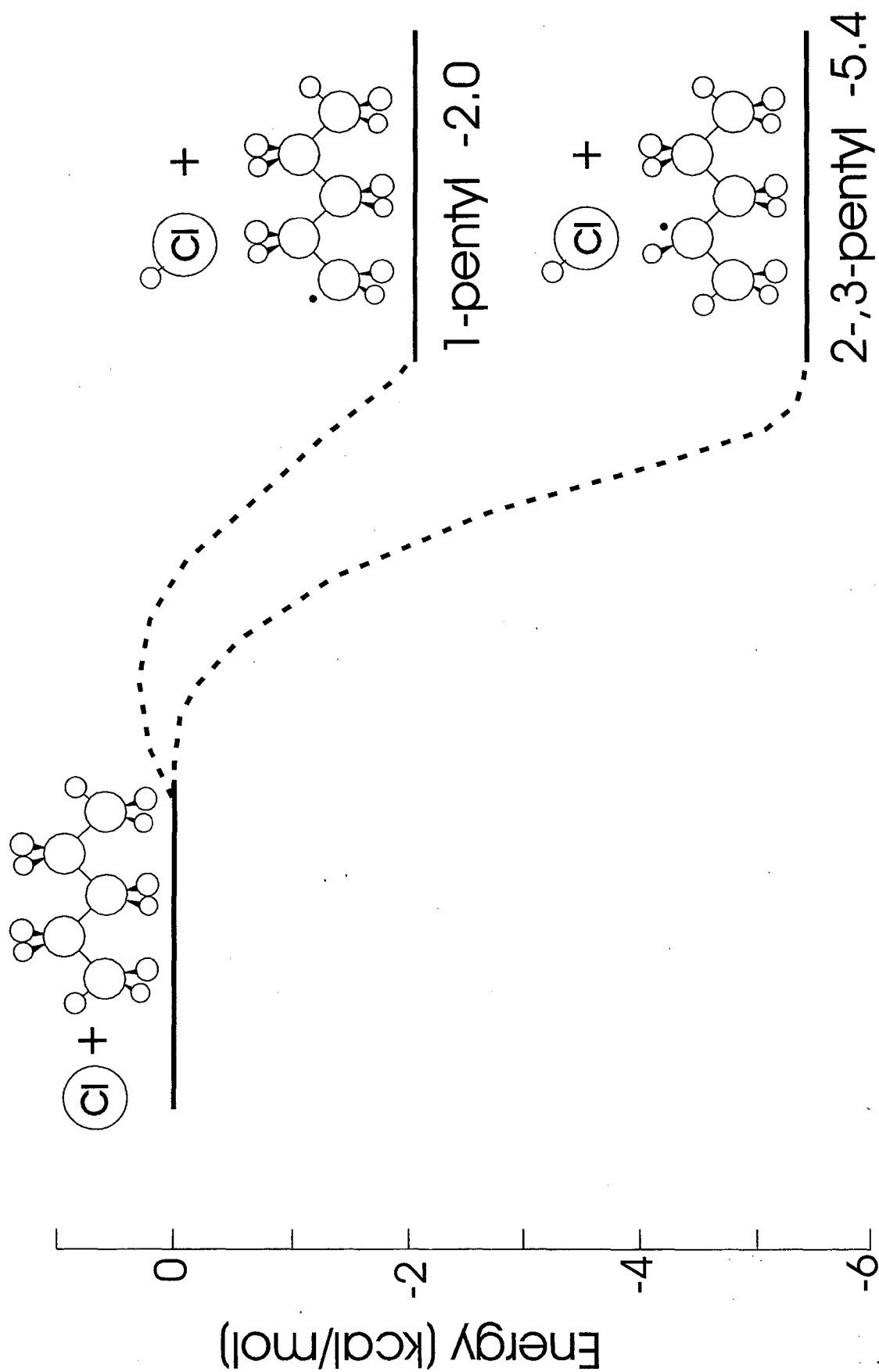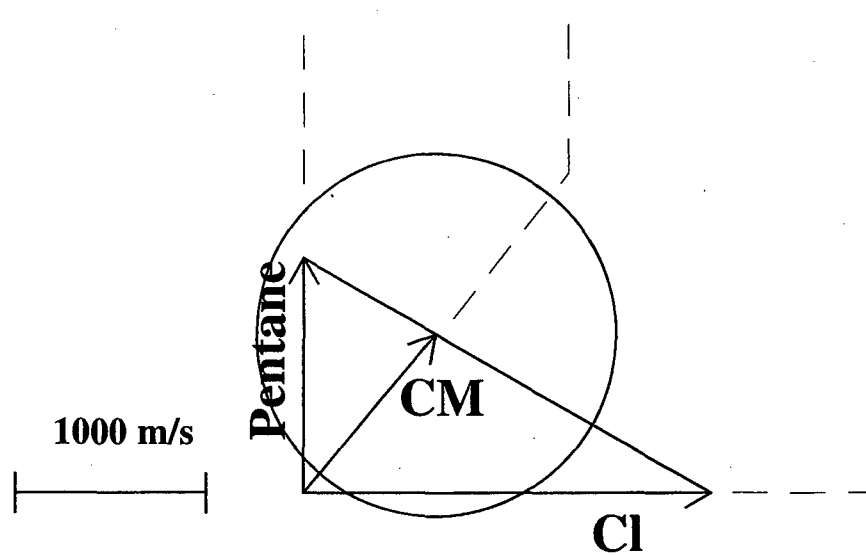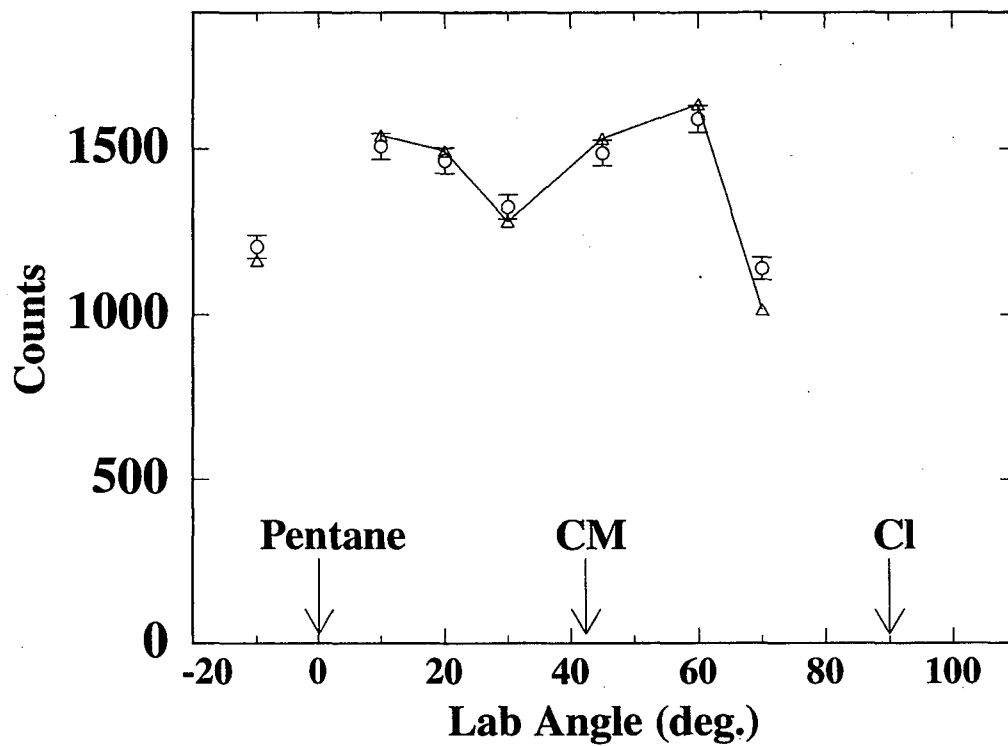
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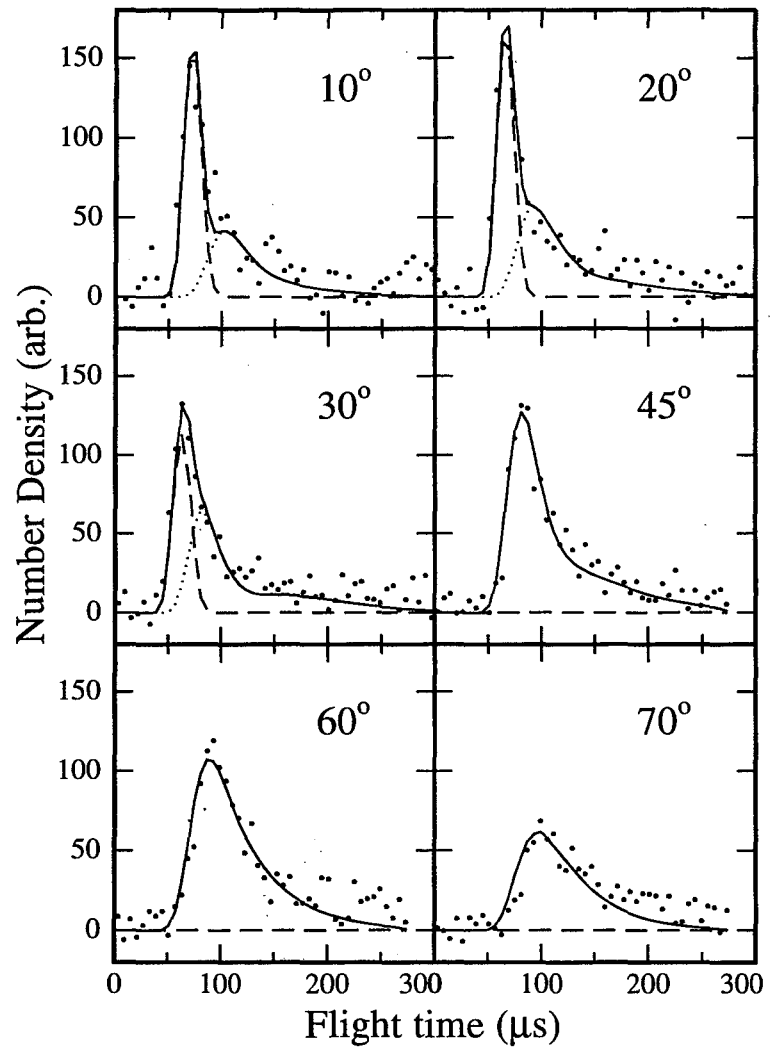[21] A. Bottoni and G. Poggi, *J. Mol. Struct.,* **337,** 161 (1995).
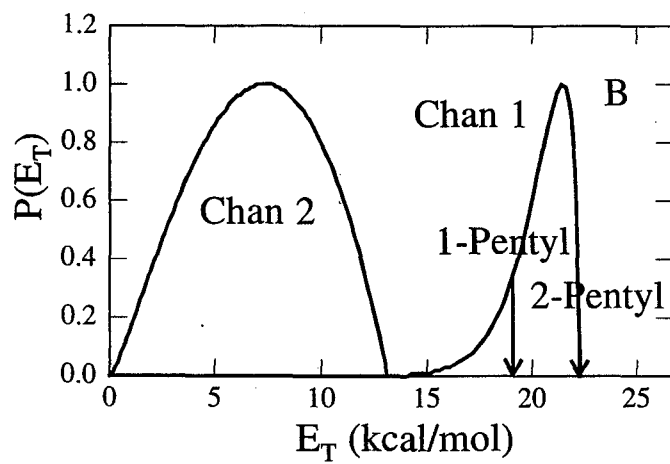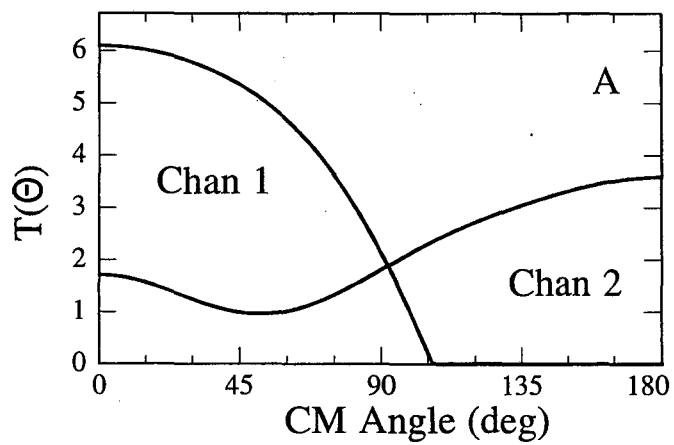
Figure Captions

1. Schematic energy diagram for the reaction Cl + n-C$_5$H$_{12}$ 6 HCl + C$_5$H$_{11}$.

2. Laboratory angular distribution for C$_5$H$_{11}$ product (top) and Newton diagram (bottom) for the title reaction. The circle on the Newton diagram represents maximum recoil limit for production of 2- or 3-pentyl radicals. Circles on the angular distribution are experimental data, open triangles are the best-fit simulations. The connecting line is included to guide the eye.

3. Time-of-flight spectra for m/e 71 (C$_5$H$_{11}^+$) from the title reaction at the indicated laboratory scattering angles (defined with respect to the pentane beam). The filled circles are experimental points, the dashed line represents the contribution to the fit from 'channel 1', the dotted line that from 'channel 2' and the solid line represents the total simulation using the distributions in Fig. 4.

4. Center-of-mass angular (A) and translational energy (B) distributions obtained from the fit to the data in Figs. 2 and 3. Arrows mark translational energy limits for production of indicated product isomers.

5. Velocity-flux contour map for the title reaction. Inner circle shows recoil velocity limit for the 1-pentyl radical; outer circle indicates corresponding limit for 2- or 3-pentyl radicals. The contour line spacing is twice as dense for the lowest 25% of the distribution to reveal the channel 2 contribution more clearly.
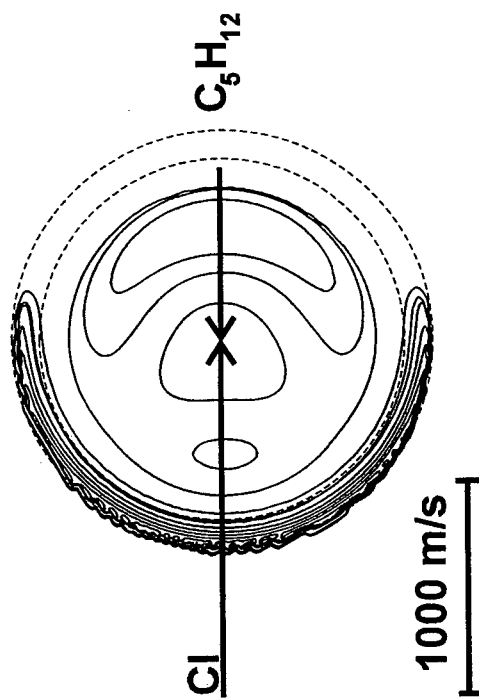
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Energy (kcal/mol)

Cl +

1-pentyl -2.0

2-,3-pentyl -5.4

Cl +

Cl +

0

-2

-4

-6

C_5H_{12}

Cl

1000 m/s