Communication

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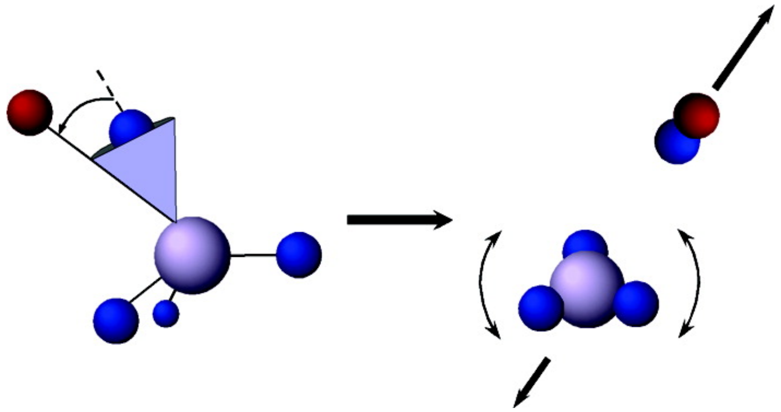

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A Reinterpretation of the Mechanism of the Simplest Reaction at an sp^3-Hybridized Carbon Atom: H + CD_4 → CD_3 + HD

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The H + CD_4 reaction is the prototypical abstraction reaction occurring at an sp^3-hybridized carbon atom. It also plays a role in combustion chemistry[1] and has features that distinguish it from well understood triatomic reactions. Furthermore, as the simplest six-atom system, it has served as a testing ground for new theoretical methods.[2−4] For many years, the H + CD_4 → HD + CD_3 reaction was believed to proceed via a rebound mechanism.[2] In this process, reaction occurs when the incoming H atom is directed along the central C−D bond, yielding an HD product that recoils in the backward direction while the CD_3 fragment goes forward to conserve linear momentum (as viewed in the center of mass frame where backward is measured with respect to the incoming H atom). Indeed, calculations presented in this work using the most recent global CH_5 potential energy surface[4] (EG PES) support this view. In addition, the rebound picture is consistent with the known behavior of the H + D_2 → HD + D reaction[5] and many other H abstraction reactions with collinear transition states. In contrast to the expected behavior, recent experiments[6] indicated that at a center of mass (com) collision energy (E_{coll}) of 45.0 kcal/mol the CD_3 product is backward scattered. Here, we report a combined experimental and theoretical effort that explains this observation and yields new insight into the reaction mechanism.

The H + CH_4 → CH_3 + H_2 reaction is nearly thermoneutral [$\Delta H(0\ K) = -0.02$ kcal/mol][7] but has a large classical barrier to reaction.[8] Many recent experimental studies[9] have addressed the kinetics, but the small reaction cross-section has made state-to-state resolved dynamics experiments difficult, and few exist.[6,10] For experimental reasons, we have examined the H + CD_4 reaction.

Using the photoloc technique,[11] we measure the center of mass differential cross-section (DCS) of the $CD_3(\nu{=}0)$ products for $E_{coll} = 27.8$ kcal/mol. These results are compared with results from quasi-classical trajectory (QCT) calculations integrated with two different interaction potentials: EG[4] and UB3LYP/6-31G** (B3LYP).[12] The former is the best currently available analytic PES, and the latter involves a direct dynamics QCT calculation with energy and forces generated on the fly. Figure 1 shows the comparison of the experimentally determined DCS at $E_{coll} = 27.8$ kcal/mol and the comparable quantities calculated from the EG and B3LYP surfaces. Our experiments indicate that the CD_3 products scatter on average sideways and backward, with $\langle \cos\theta \rangle = -0.07 \pm 0.10$, where θ is the scattering angle of the CD_3 product in the com frame. These results are in very good agreement with B3LYP calculations, while the EG surface predicts predominantly forward-scattered CD_3, implying a direct reaction with a large contribution from a rebound mechanism.

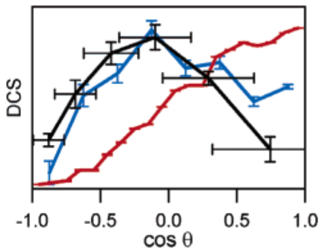

Figure 1. Differential cross-sections versus the center of mass scattering angle, θ, for the $CD_3(\nu{=}0)$ products of the H + $CD_4(\nu{=}0)$ → HD + CD_3 reaction at $E_{coll} = 27.8$ kcal/mol. Experimental results (black) and theoretical calculations obtained on the EG (red) and B3LYP (blue) potential energy surfaces are shown. Forward scattered with respect to the incident H atom is $\cos\theta = 1$, whereas $\cos\theta = -1$ is backward scattered. Both experiment and B3LYP contradict the previous assumption that the reaction proceeds via a rebound mechanism.

The absolute reaction cross-section derived from the time-consuming direct dynamics calculations also agrees quantitatively with previous measurements,[10] while the corresponding EG result is a factor of 3 too high. The B3LYP PES also contains information about the H + CD_4 → HCD_3 + D exchange channel that would be extremely difficult to include in an analytical PES. However, at the energies of the current experiments, the exchange channel is not open; therefore, we can rule out a previous speculation[6] that the observed angular distributions result from a competition between abstraction and exchange at low impact parameters.

In Figure 2a, we plot the average value of $\cos\theta$ as a function of the impact parameter obtained from calculations on the EG and B3LYP surfaces. The impact parameter b is defined as the distance of closest approach if the reagents were to follow straight line paths during the collision. The standard deviation, which in this case is a measure of the range of $\cos\theta$ that arises for a particular impact parameter, is also given. The observed behavior is very similar to that predicted from a simple hard sphere model. In this model, the scattering angle is uniquely related to the impact parameter by $\cos\theta = 1 - 2b^2/d^2$, where d is the hard sphere collision diameter. A fit to the data yields a value of d that is similar to the sum of the C−D (1.09 Å) and H−D (0.7 Å) bond lengths. Additionally, at both collision energies, the curves obtained from calculations on the EG and B3LYP surfaces are in nearly perfect agreement! Therefore, the subtle differences between these potentials, which lead to dramatic differences in the DCS (Figure 1), play little role in determining the average scattering angle for a given impact parameter.

Figure 2b displays the calculated opacity functions $bP(b)$ for the two different surfaces at $E_{coll} = 27.8$ kcal/mol. $P(b)$ is multiplied

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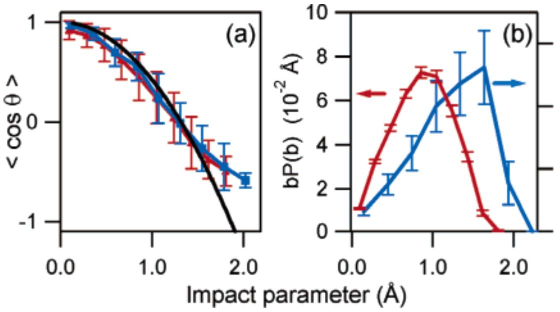

Figure 2. (a) Correlation between the average scattering angle and the impact parameter as obtained from the EG (red) and B3LYP (blue) surfaces at $E_{\mathrm{coll}} = 27.8$ kcal/mol. The standard deviation is calculated from the trajectories that fall within each impact parameter bin and is plotted for the red and blue curves. The correlation expected for hard sphere scattering (black) is also shown for $d = 1.86$ Å. (b) Opacity functions (expressed as $bP(b)$ vs b). The arrows attached to each curve point to the reference axis. The B3LYP surface's preference for larger values of b bias the angular distribution in the backward hemisphere.

by the impact parameter b to account for the fact that as b increases there is a larger area in the range b to $b + \mathrm{d}b$, and thus these values of b should receive a larger statistical weight.[13] Clearly, more reactive collisions occur at large impact parameters on the B3LYP surface than on the EG surface. For the EG surface, no reactive collisions occur beyond 1.85 Å, whereas for the B3LYP surface, the reactive region extends to 2.12 Å. This fact is particularly striking when compared with the sum of the C−D and H−D bond lengths (1.8 Å).

We attribute the observed angular distributions for the two PESs to the difference in opacity functions. The contribution of larger impact parameter reactive collisions on the B3LYP surface, which from Figure 2a we know preferentially lead to backward-scattered methyl fragments, biases the angular distributions in the sideways and backward directions. Clearly, a mechanism operates on the B3LYP surface that extends the range of impact parameters that lead to reaction, which is unexpected for a direct reaction like H + CD_4 that has a large barrier.

We propose that a wide cone of acceptance around the C−D bond, that is, the range of H−D−C angles in the transition state, leads to the observed opacity functions. The larger cone of acceptance is readily demonstrated by examination of the H−D−C (D is the abstracted deuterium atom) bending-energy curves at the abstraction saddle point. These curves are generated by varying the H−D−C angle ($\varphi_{\mathrm{H-D-C}}$) while freezing all other coordinates at their saddle point values. The analytical EG curve increases much more rapidly with bending angle (higher anisotropy) than does the B3LYP curve, which is in good agreement with high-quality ab initio calculations. For instance, the energy difference between the collinear saddle point ($\varphi_{\mathrm{H-D-C}} = 180°$) and one in which $\varphi_{\mathrm{H-D-C}} = 90°$ is 40.6 kcal/mol on the EG PES, but only 28.8 kcal/mol according to B3LYP PES. The B3LYP energy is in good agreement with CCSD(T) calculations with complete basis set extrapolation (26.5 kcal/mol). The lower anisotropy of a surface in the area near the transition state indicates a more flexible transition structure or a broader cone of acceptance, allowing the H−D−C angle to deviate further from the collinear minimum energy path. On such surfaces, we find that the contribution from sideways/peripheral reactive collisions at large impact parameters is greatly enhanced. Also, we find that nearly collinear collisions at small impact parameters are less probable, as the flexible structure is less effective in "steering" the trajectory to a linear structure as the barrier is surmounted. Therefore, the wider cone of acceptance shifts the maximum in the opacity function [plotted as $bP(b)$ in Figure 2b] to larger values of b. It is specifically this feature that gives rise to the unexpected angular distributions.

We find that the wider cone of acceptance results because the saddle point is closer to the product valley on B3LYP [the C−D bond distance is 1.41 Å at the B3LYP saddle point versus 1.33 Å on EG and 1.40 Å on CCSD(T)/cc-pVTZ]. The larger C−D bond results in a more fluxional transition structure due to less steric hindrance between the HD and CD_3 fragments. This is analogous to what is found[14] for CH_5^+, which is quite loosely bound (fluxional), with an overall geometry in which H_2 forms a nonclassical three-center two-electron bond with CH_3^+, in the same way that H_2 bonds sideways to metal centers in metal dihydrogen complexes.[15] In our system (CD_4H), the CD_3 and HD fragments are not strongly bound, but a similar argument leads to a transition structure in which the C−D−H bond angle is not restricted to 180°.

This work elucidates the detailed mechanism of the prototypical abstraction reaction at a carbon center, which is found to be contrary to the previously predicted behavior. The now classic 1966 review by Herschbach[16] states that "the preferred direction of recoil of the products is strongly correlated with the magnitude of the total reaction cross section, σ_r, which varies from <10 Å^2 for rebound reaction to >100 Å^2 for stripping." The present study on the H + CH_4 reaction with $\sigma_r < 0.2$ Å^2 represents a clear exception to this. We have identified subtle features of the multidimensional PES that give rise to the unexpected dynamical behavior and shown that comparisons of full dimensional theoretical calculations to state resolved scattering experiments are now possible for lightweight six-atom systems.

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References

(1) Warnatz, J. In *Combustion Chemistry*; Gardiner, J. W. C., Ed.; Springer-Verlag: New York, 1984; p 197.
(2) (a) Bunker, D. L.; Pattengill, M. D. *J. Chem. Phys.* **1970**, *53*, 3041. (b) Raff, L. M. *J. Chem. Phys.* **1974**, *60*, 2220.
(3) (a) Jordan, M. J. T.; Gilbert, R. G. *J. Chem. Phys.* **1994**, *102*, 5669. (b) Bowman, J. M. *Theor. Chem. Acc.* **2002**, *108*, 125. (c) Althorpe, S. C.; Clary, D. C. *Annu. Rev. Phys. Chem.* **2003**, *54*, 493. (d) Kerkeni, B.; Clary, D. C. *J. Chem. Phys.* **2004**, *120*, 2308. (e) Wu, T.; Werner, H. J.; Manthe, U. *Science* **2004**, *306*, 2227.
(4) Espinosa-Garcia, J. *J. Chem. Phys.* **2002**, *116*, 10664.
(5) Althorpe, S.; Fernandez-Alonso, F.; Bean, B.; Ayers, J.; Pomerantz, A.; Zare, R.; Wrede, E. *Nature* **2002**, *416*, 67.
(6) Camden, J. P.; Bechtel, H. A.; Zare, R. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5227.
(7) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; Mcdonald, R. A.; Syverud, A. N. *J. Phys. Chem.* **1998**, ref data 14, supplement 1.
(8) A value of 14.8 kcal/mol was calculated at the CCSD(T) level with complete basis set extrapolation using CCSD(T)/cc-pVTZ geometries.
(9) (a) Bryukov, M. G.; Slagle, I. R.; Knyazev, V. D. *J. Phys. Chem. A* **2001**, *105*, 3107. (b) Sutherland, J.; Su, M.; Michael, J. *Int. J. Chem. Kinet.* **2001**, *33*, 669.
(10) Germann, G.; Huh, Y.; Valentini, J. *J. Chem. Phys.* **1992**, *96*, 1957.
(11) Simpson, W. R.; Orr-Ewing, A. J.; Rakitzis, T. P.; Kandel, S. A.; Zare, R. N. *J. Chem. Phys.* **1995**, *103*, 7299.
(12) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(13) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University: London, 1987.
(14) Marx, D.; Parrinello, M. *Science* **1999**, *284*, 59.
(15) Kubas, G. J. *Metal Dihydrogen and s-bond Complexes: Structure, Theory and Reactivity*; Kluwer Academic/Plenum Publishers: New York, 2001.
(16) Hershbach, D. R. *Adv. Chem. Phys.* **1966**, *10*, 319.

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