Reaction Dynamics at a C Atom

Dynamics of the Simplest Reaction of a Carbon Atom in a Tetrahedral Environment**

*Jon P. Camden, Hans A. Bechtel, and Richard N. Zare**

Reactions occurring at a carbon center are one of the most important and useful classes of reactions in chemistry. The simplest reaction at a carbon atom with a tetrahedral environment is that of an H atom with methane, and understanding this prototypical reaction has implications for a number of fields ranging from organic and combustion chemistry to fundamental reaction dynamics. Consequently, it has been the subject of numerous experimental studies[1] exploring the kinetics and isotope effects of both the forward and reverse reactions. Recent theoretical work includes new potential energy surface calculations,[2–6] direct dynamics studies,[7] calculation of isotope effects,[8] and new quantum scattering methods[9] that have been reviewed by Althorpe and Clary.[10]

Herein we report the first study of the nascent CD_3 products from the H + CD_4 reaction. This isotope combination was chosen for experimental reasons because this arrangement allows for the detection of all possible reaction products: CD_3, HD and D. We also examined the CH_3 products from the H + CH_4 reaction and find that it shows very similar behavior[11] to that reported herein for the H + CD_4 reaction. By using the well-established photoloc technique,[12] we find that at a collision energy of 1.95 ± 0.05 eV the CD_3 products are produced in their ground vibrational state or have one quantum of excitation in the low-frequency umbrella-bending mode (ν_2). In addition, the CD_3 products are sideways/backward scattered [$\langle \cos\theta \rangle = -0.20 \pm 0.09$] with respect to the incident H-atom direction. This result stands in stark contrast with the benchmark H + $D_2 \rightarrow$HD + D bimolecular exchange reaction in which the D atom is scattered in the same direction as the incoming H atom, thus indicating a rebound mechanism.[13] The H + D_2 reaction is a logical choice for comparison with the H + CD_4 abstraction reaction because they are both nearly thermoneutral and have similar classical barriers.[14,15] We propose two possible explanations for the unusual angular distribution of the CD_3 products: (1) a stripping mechanism is more important at this energy than a rebound mechanism, and (2) a competition between abstraction and exchange diminishes the probability for abstraction at small impact parameters.

Hot-atom chemistry has established the existence of the abstraction and exchange channels by using T atoms from nuclear recoil experiments[16] and photolytic sources.[17]

Equation (1) and Equation (2) are close to thermoneutral

$$H + CD_4 \rightarrow CD_3 + HD \quad \text{Abstraction} \qquad (1)$$

$$H + CD_4 \rightarrow D + CHD_3 \quad \text{Exchange} \qquad (2)$$

but have very different classical barrier heights (0.65 and 1.65 eV respectively).[14] Since the early hot-atom studies, experimental probes of the dynamics have been rather sparse. Valentini and coworkers[18] examined the abstraction channel by measuring the rovibrational state distributions of the HD product from H + CD_4 at 1.5 eV by using coherent anti-Stokes Raman spectroscopy (CARS). They found that the total cross section for reaction is 0.14 ± 0.03 Å^2, from which it is concluded that the maximum impact parameter for reaction is less than 1 Å. More than 95% of the HD products were formed in $v = 0,1$; 84% of the initial reagent translational energy was channeled into translation of the products while only 9% of the available energy went into HD rotation and 7% into vibration. In a complementary study, Bersohn and coworkers[19] examined the exchange channel by detecting the D-atom products from the H + $CD_4 \rightarrow$D + CHD_3 reaction at a collision energy of ~2 eV. The absolute cross section for exchange was measured to be 0.084 ± 0.014 Å^2 and the average D-atom kinetic energy was 86 ± 7% of the collision energy. They concluded that the exchange channel proceeds through an S_N2-type inversion mechanism and suggested that trajectories of small impact parameter lead to either exchange or abstraction depending on the orientation of the incoming H atom with respect to the C–D bond.

Figure 1 displays the REMPI (resonance enhanced multiphoton ionization) spectrum of the CD_3 products in the region of the 0^0_0, 1^1_1 and 2^1_1 bands, corresponding to ground state, symmetric stretch (ν_1), and umbrella-bending (ν_2) excited methyl radical fragments, respectively. This spectrum is dominated by the large Q-branch members of the 0^0_0 band; however, some members of the S and O branches (N ≤ 9) of the 0^0_0 band are also apparent. The position of the Q branch

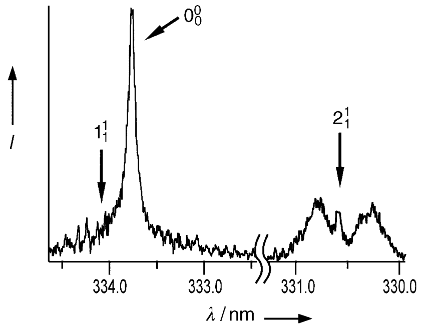

Figure 1. (2+1) REMPI spectrum of CD_3 products from the H + CD_4 reaction. Arrows indicate the positions of the 0^0_0, 1^1_1 and 2^1_1 bands of the CD_3 ($3p_z$–X) transition.

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[*] Prof. R. N. Zare, J. P. Camden, H. A. Bechtel
Department of Chemistry
Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-723-9262
E-mail: zare@stanford.edu

[**] The authors (J.P.C. and H.A.B) thank the National Science Foundation for Graduate Fellowships. We also thank Davida J.A. Brown and Andrew E. Pomerantz for useful discussions and critical comments on this manuscript. This work was supported by the National Science Foundation under Grant Number NSF-CHE-02-42103.

DOI: 10.1002/ange.200352642
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for the CD_3 1_1^1 band is indicated by the arrow in Figure 1. No products were observed on this transition within the signal-to-noise ratio of our experiment. In contrast, the 2_1^1 band is observable and has roughly the same integrated area as the 0_0^0 band. Although a quantitative determination of the branching ratios between these three states is difficult because the $3p_z$–X REMPI transitions are not fully characterized, we can draw several qualitative conclusions: 1) the reaction does not significantly populate the energetically allowed symmetric stretch of CD_3 ($\nu_1 = 1$), 2) the major product channels are the ground state and umbrella-bending mode CD_3 ($\nu_2 = 0,1$), and 3) the reagent translational energy is converted mostly into translational energy of the products.

Many ab initio calculations of the transition-state geometry exist for both the abstraction and exchange channels.[4] These calculations serve as a starting point to understand the methyl radical internal-state distributions. In a simple picture of the reaction dynamics, one expects excitation of those internal modes of the products that are stretched in the transition state. The nonreactive C–D bond lengths change little among the reactant CD_4 (1.091 Å), the C_{3v} saddle point (1.080 Å) and the product CD_3 (1.079 Å), thus suggesting no excitation of the stretching mode (ν_1) is to be expected in the methyl radical product, in agreement with the REMPI spectrum. The relaxation of the sp^3-hybridized C of methane to the sp^2-hybridized C of the methyl radical predicts the presence of CD_3 ($\nu_2 = 1$), also in agreement with the REMPI spectrum. There is clearly more at work than this model; nevertheless, it gives a reasonable account of the overall dynamics. Furthermore, we caution that the significant population of CD_3 ($\nu_2 = 1$) observed in these experiments suggests that a simple pseudo-diatomic picture of methane as (CD_3)–D, in which the methyl radical acts as a spectator, is insufficient to understand fully the dynamics.

Figure 2 shows the CD_3 differential cross section (DCS), which is a measure of the angular distribution of the products in the center-of-mass frame, averaged over all HD quantum states; the DCSs for CD_3 ($\nu = 0$) and for CD_3 ($\nu_2 = 1$) are the same within the experimental resolution. The reaction has an obvious preference for sideways/backward scattering of CD_3 with respect to the incident H-atom direction. The average scattering angle is unambiguously in the backward hemisphere, $\langle \cos\theta \rangle = -0.20 \pm 0.09$ with the spread in values resulting from the unknown internal energy deposited into the HD coproduct, shown by the shaded region of Figure 2.

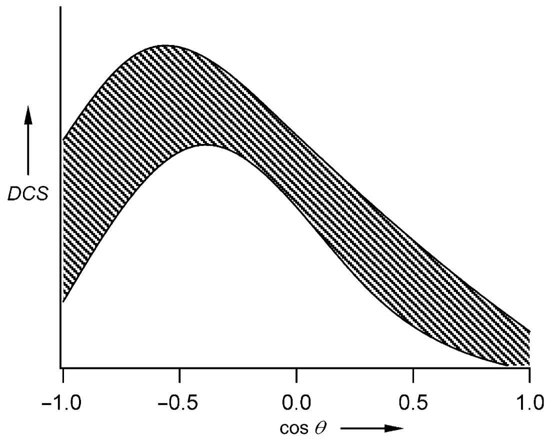

Figure 2. Differential cross section of the CD_3 products as a function of the cosine of the center-of-mass scattering angle θ. The uncertainty in the experimental measurements is indicated by the shaded region.

This result is unexpected in light of previous trajectory calculations. Polanyi and co-workers[20] studied the dynamics over a range of energies (2–18 eV) by using a three-atom model, in which methane was considered to be a pseudo-diatomic species R–D (R = CD_3). In all cases, the reaction was direct and concerted. At the energy of the current experiment, the CD_3 product was forward-scattered and had an average scattering angle of $\langle \cos\theta \rangle = +0.5$, thus indicating a rebound mechanism. Raff,[21] and Valencich and Bunker[22] extended the treatment to full dimensionality and also found that the abstraction channel occurs through a rebound mechanism at similar energies ($\langle \cos\theta \rangle = +0.28$ and $\langle \cos\theta \rangle = +0.57$, respectively, at 1.73 eV). These theoretical results are in sharp contrast to our experimental findings, which are illustrated in Figure 3. As these early attempts showed, this system is a challenge from a theoretical perspective because of the large number of degrees of freedom and the need to consider all hydrogen atoms as equivalent.[23] Because none of the more recent theoretical studies are directly comparable with the current experiments, we present some conjectures that derive from a very simplistic analysis. New theoretical work, however, will be necessary for a detailed understanding of these results.

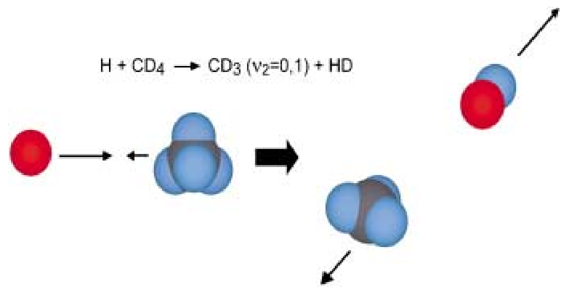

Figure 3. Illustration of the main reaction channel: The CD_3 products are formed in their ground state and with one quantum of umbrella bending motion. They are sideways/backward scattered with respect to the incident H-atom direction.

In 1965 Wolfgang[16] offered a pictorial model in which abstraction occurred by one of two mechanisms: 1) axial—in which the incoming atom is directed along a C–D bond and the HD product rebounds backward while the methyl radical goes forward; 2) stripping—in which the velocity of the H atom is perpendicular to the C–D bond and the HD product is carried into the forward hemisphere while the methyl goes backward. Our results indicate that reaction at 2 eV is in closer accord with the stripping mechanism than the axial mechanism. But we do observe a significant amount of sideways scattering that most likely comes from trajectories intermediate between these limiting cases. Trajectory studies, as well as conventional wisdom,[24] support the notion that at the lowest energies the axial mechanism dominates because the stripping mechanism has a larger angular-momentum barrier. At higher energies the stripping mechanism is expected to become more important. It is likely that our collision energy is intermediate between these two limits.

As another aid, we use the simple hard-sphere model of reactive scattering,[24,25] in which a one-to-one correspondence exists between scattering angle θ and impact parameter b. Recall that the impact parameter b is the distance of closest approach (Figure 4) if the reagents are to follow straight-line paths. By using this model the experimental DCS can be converted to an opacity function $P(b)$, which gives the probability that reaction occurs for collisions at a distance b to $b + db$. If CD_4 were correctly pictured as a "ball of deuterium atoms," then the resulting opacity function $P(b)$ would be constant for $b < d$, where d is the hard-sphere collision radius. Instead, Figure 5 shows a derived $P(b)$ with a markedly different behavior. We find that the abstraction channel has a strong preference for large impact parameters, which is opposite to what is expected for the exchange channel. The latter, having a large barrier (1.65 eV) and small cross section, should favor small impact parameter collisions. It is possible that abstraction and exchange channels compete at small impact parameters, depending on how the H-atom velocity lines up with the C–D bond. This competition would result in a depletion of the forward-scattered CD_3 products.

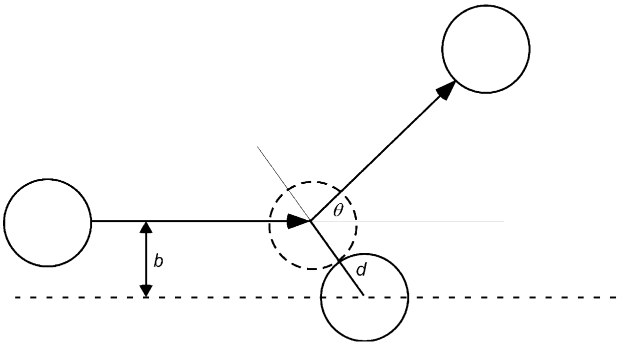

Figure 4. Hard-sphere model: θ is the scattering angle in the center of mass frame, b is the impact parameter, and d is the hard-sphere collision radius. There is a one-to-one correspondence between b and θ in this model.

In conclusion, we have measured the product-state distributions and DCSs of the CD_3 fragment produced by the reaction H + CD_4 at 1.95 eV. The main product channels are ground state and umbrella-bending mode excited methyl radicals. The presence of a significant amount of CD_3 ($\nu_2 = 1$) shows that the simple picture of CD_4 as a pseudo-diatomic species is not strictly correct. The CD_3 products are scattered sideways and backwards. While the exact origin of this behavior is unknown, we speculate it comes from a stripping mechanism at large impact parameter collisions, or a competition between abstraction and exchange at small impact parameter collisions, or the action of both. Clearly, the polyatomic nature of this reaction goes beyond the atom–diatom pictures that have been so frequently used to describe reaction dynamics.

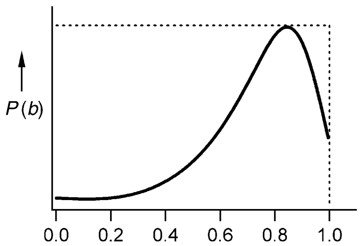

Figure 5. The solid line displays the opacity function $P(b)$ for the CD_3 reaction products obtained from conversion of the measured DCS. The dashed line represents the $P(b)$ function expected where methane acts as a "ball of deuterium atoms."

Experimental Section

The experimental setup used and the method of determining the DCS is described in detail elsewhere.[12] A 1:2:8 mixture of hydrogen bromide (Matheson, 99.8%), perdeuteromethane (Cambridge Isotopes, 99% [D_4]), and helium (liquid carbonic, 99.995%) is expanded from a pulsed (General Valve, Series-9) nozzle into the extraction region of a linear Wiley-McLaren time-of-flight (TOF) spectrometer. Photolysis of HBr with linearly polarized light at 212.8 nm (fifth harmonic of the Nd:YAG laser) produces fast H atoms to initiate the reaction. At this wavelength approximately 85% of the H atoms are produced coincident with ground-state Br atoms and a kinetic energy of 2.04 eV. The remaining fraction comes with spin–orbit excited Br* atoms (KE = 1.59 eV).[26] This photolysis wavelength gives a collision energy in the center-of-mass frame of 1.95 and 1.52 eV respectively. After a time delay of approximately 30 ns the methyl radical reaction products are probed with 2+1 REMPI through the $3p_z$ Rydberg state[27] around 333 nm. The ions, after drifting down the flight tube, are detected by Chevron-type microchannel plates.

Received: August 13, 2003 [Z52642]
Published Online: October 14, 2003

Keywords: gas-phase chemistry · hot-atom chemistry · methane · reaction dynamics

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