

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

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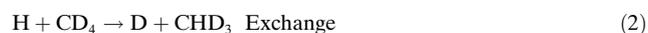
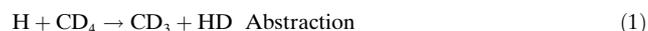
Reactions occurring at a carbon center are one of the most important and useful classes of reactions in chemistry. The simplest reaction at a carbon atom with a tetrahedral environment is that of an H atom with methane, and understanding this prototypical reaction has implications for a number of fields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

Herein we report the first study of the nascent CD<sub>3</sub> products from the H + CD<sub>4</sub> reaction. This isotope combination was chosen for experimental reasons because this arrangement allows for the detection of all possible reaction products: CD<sub>3</sub>, HD and D. We also examined the CH<sub>3</sub> products from the H + CH<sub>4</sub> reaction and find that it shows very similar behavior<sup>[11]</sup> to that reported herein for the H + CD<sub>4</sub> reaction. By using the well-established photoloc technique,<sup>[12]</sup> we find that at a collision energy of 1.95 ± 0.05 eV the CD<sub>3</sub> products are produced in their ground vibrational state or have one quantum of excitation in the low-frequency umbrella-bending mode ( $\nu_2$ ). In addition, the CD<sub>3</sub> 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<sub>2</sub> → 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.<sup>[13]</sup> The H + D<sub>2</sub> reaction is a logical choice for comparison with the H + CD<sub>4</sub> abstraction reaction because they are both nearly thermoneutral and have similar classical barriers.<sup>[14,15]</sup> We propose two possible explanations for the unusual angular distribution of the CD<sub>3</sub> 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<sup>[16]</sup> and photolytic sources.<sup>[17]</sup>

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



but have very different classical barrier heights (0.65 and 1.65 eV respectively).<sup>[14]</sup> Since the early hot-atom studies, experimental probes of the dynamics have been rather sparse. Valentini and coworkers<sup>[18]</sup> examined the abstraction channel by measuring the rovibrational state distributions of the HD product from H + CD<sub>4</sub> 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<sup>2</sup>, 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  $\nu = 0,1$ ; 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<sup>[19]</sup> examined the exchange channel by detecting the D-atom products from the H + CD<sub>4</sub> → D + CHD<sub>3</sub> reaction at a collision energy of ~2 eV. The absolute cross section for exchange was measured to be 0.084 ± 0.014 Å<sup>2</sup>, and the average D-atom kinetic energy was 86 ± 7% of the collision energy. They concluded that the exchange channel proceeds through an S<sub>N</sub>2-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<sub>3</sub> products in the region of the 0<sub>0</sub><sup>0</sup>, 1<sub>1</sub><sup>1</sup> and 2<sub>1</sub><sup>1</sup> bands, corresponding to ground state, symmetric stretch ( $\nu_1$ ), and umbrella-bending ( $\nu_2$ ) excited methyl radical fragments, respectively. This spectrum is dominated by the large Q-branch members of the 0<sub>0</sub><sup>0</sup> band; however, some members of the S and O branches (N ≤ 9) of the 0<sub>0</sub><sup>0</sup> band are also apparent. The position of the Q branch

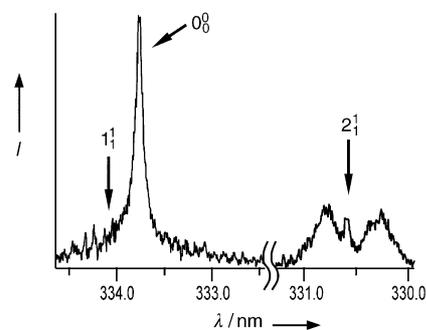


Figure 1. (2+1) REMPI spectrum of CD<sub>3</sub> products from the H + CD<sub>4</sub> reaction. Arrows indicate the positions of the 0<sub>0</sub><sup>0</sup>, 1<sub>1</sub><sup>1</sup> and 2<sub>1</sub><sup>1</sup> bands of the CD<sub>3</sub> (3p<sub>z</sub>–X) transition.

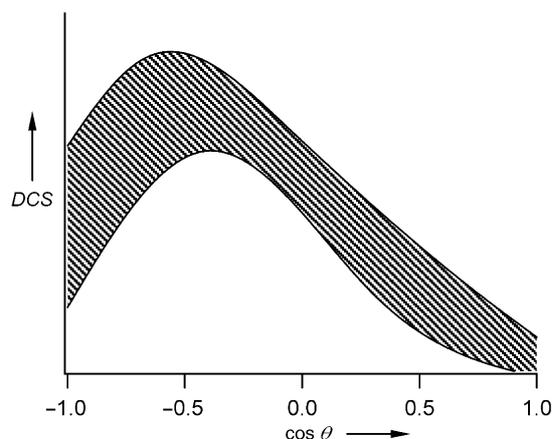
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for the  $\text{CD}_3$   $1_1^1$  band is indicated by the arrow in Figure 1. No products were observed on this transition within the signal-to-noise ratio of our experiment. In contrast, the  $2_1^1$  band is observable and has roughly the same integrated 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  $\text{CD}_3$  ( $\nu_1 = 1$ ), 2) the major product channels are the ground state and umbrella-bending mode  $\text{CD}_3$  ( $\nu_2 = 0,1$ ), 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.<sup>[4]</sup> 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  $\text{CD}_4$  (1.091 Å), the  $\text{C}_{3v}$  saddle point (1.080 Å) and the product  $\text{CD}_3$  (1.079 Å), thus suggesting no excitation of the stretching mode ( $\nu_1$ ) is to be expected in the methyl radical product, in agreement with the REMPI spectrum. The relaxation of the  $\text{sp}^3$ -hybridized C of methane to the  $\text{sp}^2$ -hybridized C of the methyl radical predicts the presence of  $\text{CD}_3$  ( $\nu_2 = 1$ ), 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  $\text{CD}_3$  ( $\nu_2 = 1$ ) observed in these experiments suggests that a simple pseudo-diatomic picture of methane as  $(\text{CD}_3)\text{-D}$ , in which the methyl radical acts as a spectator, is insufficient to understand fully the dynamics.

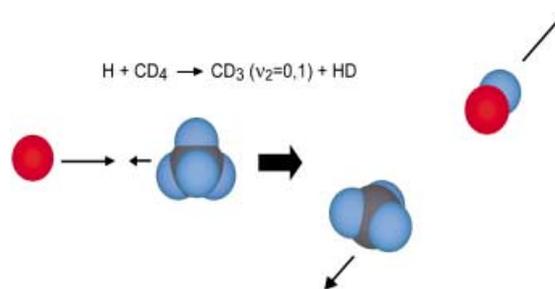
Figure 2 shows the  $\text{CD}_3$  differential cross section (DCS), which is a measure of the angular distribution of the products in the center-of-mass frame, averaged over all HD quantum states; the DCSs for  $\text{CD}_3$  ( $\nu = 0$ ) and for  $\text{CD}_3$  ( $\nu_2 = 1$ ) are the same within the experimental resolution. The reaction has an obvious preference for sideways/backward scattering of  $\text{CD}_3$ ,



**Figure 2.** Differential cross section of the  $\text{CD}_3$  products as a function of the cosine of the center-of-mass scattering angle  $\theta$ . The uncertainty in the experimental measurements is indicated by the shaded region.

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.

This result is unexpected in light of previous trajectory calculations. Polanyi and co-workers<sup>[20]</sup> 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 =  $\text{CD}_3$ ). In all cases, the reaction was direct and concerted. At the energy of the current experiment, the  $\text{CD}_3$  product was forward-scattered and had an average scattering angle of  $\langle \cos \theta \rangle = +0.5$ , thus indicating a rebound mechanism. Raff,<sup>[21]</sup> and Valencich and Bunker<sup>[22]</sup> 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



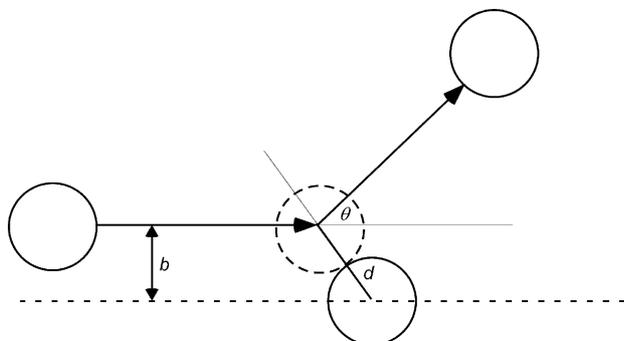
**Figure 3.** Illustration of the main reaction channel: The  $\text{CD}_3$  products are formed in their ground state and with one quantum of umbrella bending motion. They are sideways/backward scattered with respect to the incident H-atom direction.

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.<sup>[23]</sup> 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.

In 1965 Wolfgang<sup>[16]</sup> 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,<sup>[24]</sup> 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.

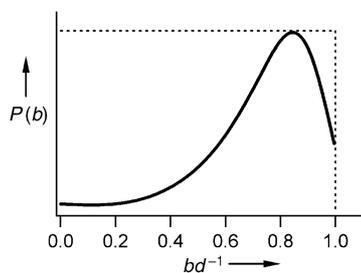
As another aid, we use the simple hard-sphere model of reactive scattering,<sup>[24,25]</sup> in which a one-to-one correspondence exists between scattering angle  $\theta$  and impact parameter  $b$ . Recall that the impact parameter  $b$  is the distance of closest approach (Figure 4) if the reagents are to follow straight-line



**Figure 4.** Hard-sphere model:  $\theta$  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  $\theta$  in this model.

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  $\text{CD}_4$  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  $\text{CD}_3$  products.

In conclusion, we have measured the product-state distributions and DCSs of the  $\text{CD}_3$  fragment produced by the reaction  $\text{H} + \text{CD}_4$  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  $\text{CD}_3$  ( $\nu_2 = 1$ )



**Figure 5.** The solid line displays the opacity function  $P(b)$  for the  $\text{CD}_3$  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.”

shows that the simple picture of  $\text{CD}_4$  as a pseudo-diatom species is not strictly correct. The  $\text{CD}_3$  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.

### Experimental Section

The experimental setup used and the method of determining the DCS is described in detail elsewhere.<sup>[12]</sup> A 1:2:8 mixture of hydrogen bromide (Matheson, 99.8%), perdeuteromethane (Cambridge Isotopes, 99%  $[\text{D}_4]$ ), 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  $\text{Br}^*$  atoms ( $\text{KE} = 1.59$  eV).<sup>[26]</sup> 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<sup>[27]</sup> around 333 nm. The ions, after drifting down the flight tube, are detected by Chevron-type microchannel plates.

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