Corrections

CHEMISTRY

The authors note that author name Zeng Xie should have appeared as Zhen Xie. The online version has been corrected.

Weiqing Zhanga,1, Yong Zhoua,1, Guorong Wua, Yunpeng Lub, Huilin Panb, Bina Fua, Quan Shuaib, Lan Liub, Shu Liub, Lilian Zhangb, Bo Jianga, Dongxu Daid, Soo-Ying Leeb, Zhen Xiec, Bastiaan J. Braamsm, Joel M. Bowmans, Michael A. Collinsm, Dong H. Zhangn, and Xueming Yangn,o,

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MICROBIOLOGY

The authors note that, due to a printer’s error, the sequence deposition number was not published with the manuscript. The data have been deposited in the GenBank database (accession no. CP001666).

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PROFILE

The editors note that Philip Downey should have been listed as the author of the Profile. This information has been updated online.

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NEUROSCIENCE
Correction for “SH3TC2/KIAA1985 protein is required for proper myelination and the integrity of the node of Ranvier in the peripheral nervous system,” by Estelle Arnaud, Jennifer Zenker, Anne-Sophie de Preux Charles, Claudia Stendel, Andreas Roos, Jean-Jacques Médard, Nicolas Tricaud, Joachim Weis, Ueli Suter, Jan Senderek, and Roman Chrast, which appeared in issue 41, October 13, 2009, of Proc Natl Acad Sci USA (106:17528–17533; first published September 29, 2009; 10.1073/pnas.0905523106).

The authors note that Henning Kleine and Bernhard Luscher should be added to the author list between Nicolas Tricaud and Joachim Weis. Henning Kleine should be credited with performing research. Bernhard Luscher should be credited with analyzing data. The online version has been corrected. The corrected author and affiliation lines, and author contributions appear below.

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Depression of reactivity by the collision energy in the single barrier \( \text{H} + \text{CD}_4 \rightarrow \text{HD} + \text{CD}_3 \) reaction

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Edited* by Richard N. Zare, Stanford University, Stanford, CA, and approved June 8, 2010 (received for review May 18, 2010)

Crossed molecular beam experiments and accurate quantum scattering calculations have been carried out for the polyatomic \( \text{H} + \text{CD}_4 \rightarrow \text{HD} + \text{CD}_3 \) reaction. Unprecedented agreement has been achieved between theory and experiments on the energy dependence of the integral cross section in a wide collision energy region that first rises and then falls considerably as the collision energy increases far over the reaction barrier for this simple hydrogen abstraction reaction. Detailed theoretical analysis shows that at collision energies far above the barrier the incoming H-atom moves so quickly that the heavier D-atom on CD\(_4\) cannot concertedly follow it to form the HD product, resulting in the decline of reactivity with the increase of collision energy. We propose that this is also the very mechanism, operating in many abstraction reactions, which causes the differential cross section in the backward direction to decrease substantially or even vanish at collision energies far above the barrier height.

For chemical reactions with energetic barriers, raising the temperature can enhance reaction rates as described by the well-known Arrehnious equation. This naturally leads us to assume that the reactivity always increases or at least remains constant with an increase of the collision energy, as used in deriving the Arrehnious equation and transition state theory. Indeed, extensive dynamical studies have revealed that for most direct reactions with an energetic barrier the integral cross section first increases very quickly with collision energy (from a threshold), and then saturates at high collision energy, as predicted by the well-known line-of-center model (1, 2). On the other hand, collinear model calculations for triatomic reactions with energetic barriers often show that the reaction probability first increases with collision energy and then begins to decrease with the further increase of collision energy. However, this strange behavior has not drawn much attention because it seldom manifests in integral cross sections for this kind of reaction in the energy region normally considered in experimental or 3D theoretical studies.

A major aim of both theoretical and experimental reaction dynamics study is to elucidate the mechanisms and rates of important elementary bimolecular chemical reactions and, in the process, test the validity of simple models like transition state theory and the Arrehnious equation (3, 4). For different reasons, precise measurements and accurate calculations of truly polyatomic reactions are difficult. Polyatomic molecules have high densities of quantum states, and state-to-state resolution is demanding (5). Accurate quantum dynamics requires accurate molecular potential energy surfaces and scattering wave functions that depend on many degrees of freedom. Only in the last decade have accurate calculations and dynamics experiments achieved consensus for reactions involving as many as four atoms (6, 7).

In this article, we report a combined experimental and theoretical study of the \( \text{H} + \text{CD}_4 \rightarrow \text{HD} + \text{CD}_3 \) reaction that shows that the collision energy can depress reactivity when it is far above the barrier height. This H-atom abstraction reaction plays a central role in CH\(_4\)/O\(_2\) combustion and has been studied in both bulk kinetic and molecular beam experiments (8–15). Because five of the six atoms involved are light, it is amenable for high-level ab initio and quantum dynamics calculations. As a result, it (and isotopic variants) has assumed the role of a benchmark or test case in the development of theoretical chemical dynamics for polyatomics (16–26). Zare, Schatz, and coworkers have recently performed combined experimental and theoretical studies on this reaction system using the Photoloc and direct dynamics methods (13–15). However, up to now, there has been no successful comparison of accurate dynamics theory with detailed crossed-beams experiment for this benchmark polyatomic reaction. Here we present accurate quantum dynamical calculations and crossed-beams scattering experiments for the title reaction in an extended collision energy range, which are in excellent agreement.

Experimentally, we performed a crossed-beam scattering study on the title reaction by using a time-sliced velocity map ion-imaging technique (27). Theoretically, we constructed an accurate full dimensional potential energy surface (PES) for the system using the modified Shepard interpolation method (28) and carried out quantum reactive scattering calculations for this six-atom reaction by restricting the nonreacting CD\(_3\) group to C\(_{\text{sym}}\) symmetry (16, 20). Fig. 1 compares experimental integral cross sections (ICS) for the title reaction that were obtained by measuring the total image signals (Fig. S1), with the quantum mechanical (QM) ICS obtained on the PES reported here and that of ref. 24. These two PESs were constructed using two totally different approaches, yet the ICS obtained are essentially identical, indicating that both PESs are well converged to a quantitative level of accuracy. The beam experiments only report relative cross sections, so the present results and those of Camden et al. (14) have been scaled to the calculated values at \( E_c = 1.66 \) eV and 2.06 eV, respectively. Clearly, the energy dependence of the cross sections on the two independently derived PESs are in excellent agreement with the two sets of experimental data. The ICS has a threshold


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energy of 0.52 eV, slightly lower than the barrier height of 0.64 eV, indicating some quantum tunneling effects for this D atom transfer. Above the threshold, the ICS first increases quickly with \( E_c \) to a maximum value of 0.17 a.u. at about \( E_c = 1.2 \) eV, then declines with the further increase of collision energy. The very small ICS makes it extremely difficult to study this reaction in a cross-beam experiment. The accuracy of the PES and dynamics is also verified by the excellent agreement between theory and experiment on the thermal rate constants for the \( H + CH_2 \) reaction (see Fig. S2).

For a direct reaction with a barrier, one expects that higher and higher collision energies above the barrier would mean that more and more of the collisions can surmount the energy barrier to reaction. The ICS should simply rise with increasing energy. However, the ICS falls as the energy increases beyond about 1.25 eV as shown in Fig. 1. Ab initio quantum chemistry calculations show that the minimum energy pathway for reaction involves a collinear approach of the H atom along a CD bond direction (there are four equivalent paths), with a substantial classical energy barrier of about 0.64 eV. If \( E_c \) is high enough, the H atom can approach at an angle to the CD bond and still surmount (or tunnel through) any energy barriers encountered. We define this angle, \( \theta \), as the angle between the vector connecting the incoming H atom and the center of mass of CD group and the vector connecting the reacting D atom and the nonreacting CD group. At a given energy, there is a “cone of acceptance” enclosing angles at which reaction occurs. As the energy rises, the angle of this cone increases as the accessible region of the walls of the reactant valley widen so the H atom can approach the CD bond more obliquely and still react.

Fig. 2 shows the ICS distribution as a function of \( E_c \) and \( \theta \), calculated on a surface passing through the saddle point that divides product from reactant. At low collision energy, the ICS density behaves precisely as expected, increasing with increasing energy and with a maximum at \( \theta = 0 \) (collinear \( H + D \cdot C \) collisions). However, as \( E_c \) increases further, the ICS density eventually falls at any angle, resulting in the decline of the ICS above a collision energy of 1.25 eV, despite the fact that the cone of acceptance angle actually widens.

Collinear quasiclassical trajectory calculations (see SI Text) reveal that the incoming H atom, with a collision energy well above the barrier, is always reflected in a collision by the repulsive wall at the “interaction” end of the reactant valley, because the mass of the nonreacting CD group is considerably larger than that of the incoming H atom. Only when the D atom happens to depart from the CD group sufficiently quickly, at the time the H atom is reflected, does the reflection lead to a reaction. At even higher collision energy, the H atom moves too fast after the reflection for the D atom to catch up. As a result, the reaction probability declines with increasing collision energy, as found by Connor (29) and Lepetit (30) in their collinear studies. Raising \( E_c \) even higher merely exaggerates this effect. In other words, for this abstract reaction, all the reactive events occur through a tug-of-war between the incoming H atom and nonreacting CD group, similar to that discovered recently by Zare and coworkers in the inelastic scattering process in the \( H + D_2 \) reaction (31). Too much excess collision energy can only increase the chance for the H atom to lose in the tug-of-war. Obviously, this conclusion drawn from collinear studies is valid in the full 3D case as seen from Fig. 2. Because the barrier height increases as the angle increases, the ICS density peak position shifts to higher energy as the angle increases.

The fact that the acceptance angle with the maximum contribution to the ICS gradually shifts from zero to a larger value as \( E_c \) increases indicates that the H atom prefers to abstract the D atom more obliquely at higher collision energy. For collisions with zero acceptance angle (head on), the product scattering angle distribution is mainly backward. Once a more oblique approach can succeed, substantial sideways scattering is observed, due to the mutual repulsion of the CD and HD fragments pushing the products apart in a direction “sideways” to the initial approach. Fig. 3 compares the experimental product angle distributions (Fig. 3A) for the four collision energies with the corresponding calculated ICS distributions as a function of the acceptance angle (Fig. 3B). Clearly, the ICS distributions resemble the experimental product angle distributions very well. Both show a substantial decrease of product signal in the backward direction together with a shift of the product angle distributions from backward to sideways when the collision energy increases from 1.06 eV to 1.99 eV, in accord with the observations of Zare and coworkers (13). They also measured significant sideways scattering at \( E_c = 1.21 \) eV and ascribed this feature to a “stripping” mechanism. The increase of sideways scattering product can be explained by the participation of larger impact parameters. However, the fast decrease of product signal in the backward direction with an increase of collision energy is a consequence of the depression of reactivity by collision energy; otherwise, at high collision energies, the low impact collisions would produce backward scattering product. We expect that the backward scattering eventually vanishes with further increase of collision energy.

Accurate quantum reactive scattering calculations for some triatomic abstraction reactions have shown substantial decrease of differential cross sections (DCS) in the backward direction.
DCS in the backward direction vanishes completely. In strong the abstraction channel shifts to the forward direction, and the channel (32). As the collision energy increases, the DCS for 12784 Fig. 3.

The abstraction H


contrast, the DCS for the exchange reaction peaks in the backward direction, although the amplitude for sideways scattering increases. We believe that the DCS behavior for the abstraction reaction is caused by the very mechanism discussed above, and this kind of behavior is very general in abstraction reactions, although the integral cross sections may not decline substantially with increasing collision energy.

Materials and Methods

The H + CD₃ → HD + CD₄ reaction was studied experimentally by using the crossed-beams scattering method with a newly developed time-sliced velocity map ion-imaging apparatus (27). Briefly, the H-atom beam was produced by photodissociating the HI molecule in a molecular beam using photolysis lasers at the two spin-orbit iodine channels for the HI photodissociation. The CD₄ beam was made by expanding a pure CD₄ sample directly through a pulsed nozzle. Each beam passes through a skimmer before entering the interaction chamber. The two beams then cross at an angle of 120° in a region located at the center of an ion-optics set for time-sliced velocity ion-imaging detection. The reaction product CD₄(000) was then ionized by 2 + 1 REMPI and imaged through the ion-optics set to the imaging MCP detector that can be time-sliced. No CD₄ products at vibrationally excited levels were detected. Relative integral cross sections (ICS) for the title reaction can be measured by calibrating the intensity of the H-atom beams generated at different photolysis energies. Because the cross section of this reaction is very small, it is essential to eliminate all possible backgrounds. The experiment was made possible by taking extreme care to ensure that the photolysis laser pass is sealed off so that no background can be generated due to the photolysis lasers.

To study this reaction theoretically, we have constructed a full dimensional potential energy surface (PES) by interpolation (28) of high-level ab initio quantum chemistry calculations of the molecular energy. These calculations have accounted for electron correlation using the coupled cluster method with account of single and double excitations, and perturbative treatment of triple excitations (CCSD(T)), using the Dunning aug-cc-pVTZ basis set. We have also employed a PES, based on the same high quality ab initio level, constructed using symmetry invariant polynomials (23, 24). Using both PES, we have carried out quantum scattering calculations using the time-dependent wave packet method to obtain the ICS (20). In the quantum dynamics, the nonreacting CD₄ group is constrained to be rigid (in Cᵥ symmetry) except for the umbrella mode as originally proposed by Palma and Clary (16). Thus, the twelve dimensional internal degrees of freedom of the H + CD₄ system are reduced to seven (16, 20). Experimental results revealed that no vibrational modes were excited in the CD₄ product, suggesting that the nonreacting CD₄ group well maintains Cᵥ symmetry during the reaction process. Hence, the model employed in the quantum dynamics calculation is expected to be of quantitative accuracy.

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