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Direct Dynamics Trajectory Study of Vibrational Effects: Can Polanyi Rules Be Generalized to a Polyatomic System?

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Polanyi et al.[1] developed successful rules to predict the importance of reactant vibration and collision energy (E_{col}) in driving reactions over barriers for triatomic A + BC systems; i.e., vibration should be relatively ineffective compared to E_{col} for barriers early along the reaction coordinate, and the reverse is true for systems with late barriers. Reactions of polyatomic species are complicated, with many degrees of freedom and multiple reaction pathways, raising the question of whether some sort of analogous rules are possible.

We recently reported an experimental study of a hydrogen abstraction (HA) reaction:[2] $H_2CO^+ + CD_4 \rightarrow H_2COD^+ + CD_3$. The reaction is exoergic by 0.18 eV with no activation barriers in excess of reactant energy. Nonetheless, the reaction efficiency is quite low (~10%), unusual for ion−molecule reactions involving simple atom transfer. Reactivity is strongly enhanced by excitation of methane distortion vibrations (ν_4 and ν_2) but mode-specifically inhibited by different H_2CO^+ vibrations, even at high E_{col}. Observation of mode-specific effects is consistent with ab initio results, indicating that the transition state (TS) on the minimum energy path is reactant-like,[2] such that the system still remembers its initial state at the TS. From a Polanyi rule perspective, however, a reactant-like TS would be regarded as "early", and thus substantial enhancement from CD_4 vibrations would not be anticipated.

Here we report a direct dynamics trajectory study of the effects of CD_4 distortion vibrations on this reaction that, for the first time, shows how vibrational effects originate in the reaction of small polyatomic species and how they relate to barrier location. Trajectories were calculated using VENUS99[3] and GAUSSIAN01.[4] The MP2/6-31G* level of theory was used because of methods fast enough for use in trajectories, it best fits benchmark calculations at the QCISD(T)/cc-pVDZ level. Figure 1 shows a representative reactive trajectory, where rCD is the separation of the abstracted D atom from the methane carbon atom, etc.. At the E_{col} studied (1.5 eV), trajectories are direct with a single turning point in the relative motion of the center-of-masses of reactants and products. As shown in the Supporting Information, the trajectories accurately reproduce both integral and differential cross sections for the reaction.

To explore the origins of the vibrational effects, we focus on correlations between reactivity and various trajectory parameters, sampled at the turning point of the inter-reactant separation (Figure 1). The turning point occurs within a few femtoseconds of the point of maximum potential energy. Another point of interest is the "HA point", defined here as the point from which rCD of the CD_4 bond is being broken, increases monotonically (labeled "HA" in Figure 1). The HA point occurs ~15 fs after the turning point; i.e., the actual CD bond breaking event occurs as the reactants rebound. In this sense, the HA point is "late" from the perspective of Polanyi rules.

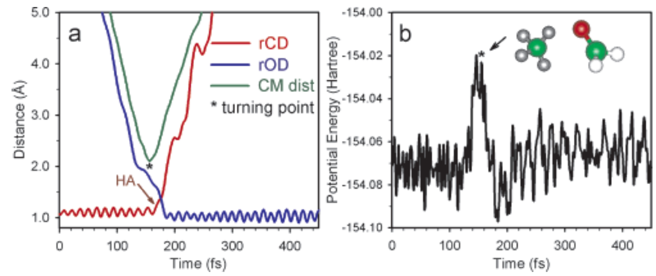

Figure 1. A representative plot of hydrogen abstraction trajectories. (a) The variation of rCD, rOD, and center-of-mass reactant distance during trajectory and (b) the variation of potential energy during trajectory.

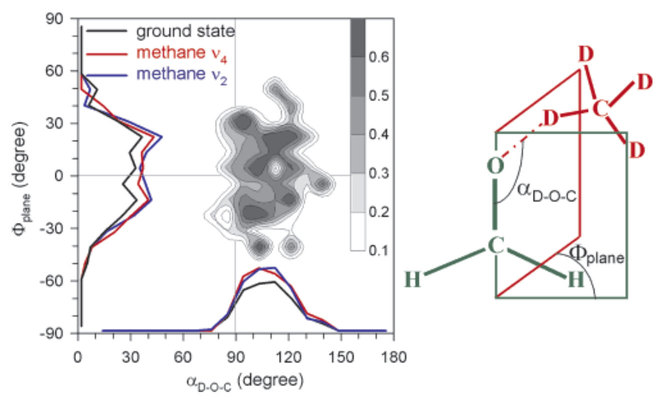

Figure 2. Dependence of reaction probability on angles α_{D-O-C} and Φ_{plane}. The contour map is plotted for the ground state only.

Low reaction efficiency suggests a dynamical bottleneck along the reaction path, and the vibrational effects presumably reflect behavior at the bottleneck. In Figure 2, the dependence of the bottleneck on reactant orientation is shown as a map of reaction probability for ground-state CD_4, versus orientation at the turning point. Reaction probability is calculated as the fraction of trajectories leading to reaction for each range of two orientation parameters found to be critical. The two parameters are the angle between the CO bond and the abstracted D atom (α_{D-O-C}) and the dihedral angle that the D atom makes with respect to the H_2CO^+ equilibrium plane (Φ_{plane}). Positive and negative Φ_{plane} correspond to approach to the convex and concave faces of the vibrating H_2CO^+, respectively. Note that maximum reaction probability (~0.6) is for the CD_4 approach with the D atom in the H_2CO^+ plane, with α_{D-O-C} near 110°. The Φ_{plane} asymmetry implies that approach to the convex face of H_2CO^+ is slightly favored, presumably because of less steric interference. Because E_{col} is too high for significant orientation steering during reactant approach, the narrow range of

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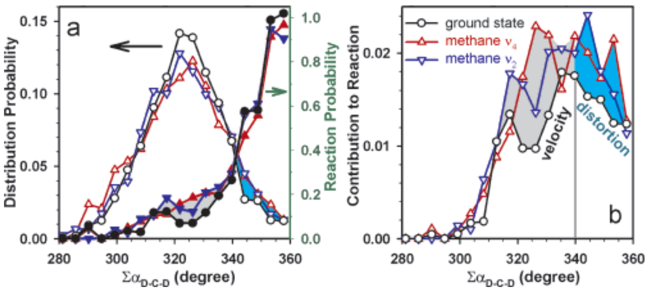

Figure 3. (a) (Left) Probability of colliding with $\Sigma\alpha_{D-C-D}$ in different ranges; (Right) Reaction probability versus $\Sigma\alpha_{D-C-D}$ for all collisions. (b) Contribution of each $\Sigma\alpha_{D-C-D}$ range to reaction (reactive collisions only).

reactive orientations can account for the low reaction efficiency. Figure 2 also gives curves showing reaction probability vs α_{D-O-C} and Φ_{plane} for ground state and for CD_4 with ν_4 and ν_2 excitation. Vibrational excitation does not expand the reactive range of either orientation parameter but instead increases the reactivity in favorable orientations. Clearly, orientation controls overall reactivity, but CD_4 vibration enhances reactivity for favorable orientations.

The CD_3 product of the HA reaction is planar; thus it is interesting to examine correlations between reactivity and the extent to which the CD_3 moiety in CD_4 approaches planarity during the reaction. We quantify the approach to planarity by calculating the sum of the three D−C−D angles ($\Sigma\alpha_{D-C-D}$) for the three D atoms which *are not* being abstracted (the three furthest from H_2CO in nonreactive collisions). The methane equilibrium geometry corresponds to $\Sigma\alpha_{D-C-D} = 328°$. A planar CD_3 moiety corresponds to 360°. Figure 3a (left axis) shows the $\Sigma\alpha_{D-C-D}$ distribution for different states recorded at the turning point, including reactive and nonreactive trajectories. The distributions for vibrationally excited CD_4 are somewhat broader than that for the ground state; however, the probability of colliding when the CD_3 moiety is planar is small for all states. Figure 3a (right axis) shows reaction probability vs $\Sigma\alpha_{D-C-D}$. Note that reaction probability approaches 100% as the CD_3 moiety approaches planarity, for all three states. Reactivity that is 100% results from a synergistic combination of CD_3 distortion and orientation; i.e., such large distortions occur only for collisions in near-optimal orientation, hence, the high reactivity. On the other hand, collisions in the optimal orientation react with an average probability of only ~60% (Figure 2), because other collision parameters (e.g., CD_4 vibrational phase) may be unfavorable.

Figure 3b gives the contribution of each angular range to the reactivity, i.e., the product of the reaction probability and the $\Sigma\alpha_{D-C-D}$ distributions in Figure 3a. Two effects contribute to the vibrational enhancement. Vibrationally excited CD_4 has a significantly higher probability of distorting into the highly reactive, planar-CD_3 geometry during collisions (shaded area labeled "distortion" in Figure 3b). Most collisions occur with $\Sigma\alpha_{D-C-D}$ nearer its equilibrium value, but vibration still enhances reaction probability. In such collisions, the enhancement results from the D atoms having vibration-induced velocities along the reaction coordinate (area labeled "velocity", Figure 3b). The division between "velocity" and "distortion" effects is arbitrary, but both are clearly important. The roughly equal contributions from the two effects probably reflect the fact that the ν_4 and ν_2 vibrational periods (33 and 31 fs) are comparable to the time scale when inter-reactant interaction is strong (30−40 fs, Figure 1).

As noted, the true TS (i.e., the saddle point along the minimum energy path) is reactant-like, and from a simple Polanyi-rule perspective, vibrational enhancement would not be predicted. On the other hand, the "HA point" does occur late in the collision, where vibrational enhancement would be expected. The question

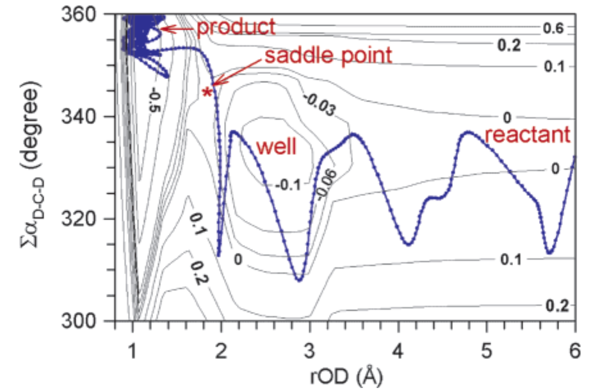

Figure 4. Potential energy contour map for $H_2CO^+ + CH_4 \rightarrow H_2COH^+ + CH_3$ calculated at MP2/6-31G*. The numbers are the potential energy (eV) relative to the reactant. The blue line is a reaction trajectory.

is whether there are ways to look at the potential energy surface (PES) that would allow one to predict the vibrational effect, without having to run trajectories. In Figure 4, we show a 2D cut through the 21-dimensional PES for this reaction, fit to 1050 points calculated at the MP2/6-31G* level of theory. For a reactive collision, rOD is the reactant approach coordinate, and $\Sigma\alpha_{D-C-D}$ serves as a coordinate, correlated with CD_4 vibration, describing the transition from reactants to products. To reduce dimensionality, we fixed α_{D-O-C} at 110° and Φ_{plane} at 0°, i.e., in the optimal orientation, and forced the CD_3 moiety to stay in C_{3v} symmetry. All other coordinates were optimized at each point.

On this cut, there is a deep well corresponding to products (rOD ~1.15 Å, $\Sigma\alpha_{D-C-D}$ ~360°) separated from reactants by a ridge running along rOD ≈ 1.6−1.7 Å. The saddle point is productlike, in the sense that there is significant CD_3 distortion toward the planar product geometry. In Polanyi rules parlance, it is a late barrier with respect to the CD_3 distortion, *even though it is still reactant-like with respect to bond lengths* (i.e., rCD = 1.1 Å, rOD = 1.8 Å). The figure also shows a typical reactive trajectory projected onto the 2D PES. As expected, the trajectory does not follow the minimum energy path due to the kinetic energy in vibration and E_{col}.[5] Instead, the methane vibrational motion gives the system substantial momentum transverse to the entrance valley, and this momentum carries the system across the barrier. The behavior is quite reminiscent of trajectories used to illustrate the Polanyi rules in late barrier A + BC reactions,[1] suggesting that by considering appropriate cuts through a multidimensional PES, with a few trajectories for guidance, it may be possible to devise Polanyi-type rules for complex polyatomic reactants.

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Supporting Information Available: Methods of trajectory calculations and other trajectory results. This material is available free of charge via the Internet at http://pubs.acs.org.

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