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Nonstatistical Dynamics in Deep Potential Wells: A Quasiclassical Trajectory Study of Methyl Loss from the Acetone Radical Cation

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It has been well established that methyl loss from the acetone radical cation, **3**, when generated in a mass spectrometer by 1,3 H migration of its enol isomer, is inconsistent with RRKM theory.[1−3] Although the two methyl groups are related by symmetry in **3**, the methyl newly formed by the hydrogen transfer is lost preferentially (Figure 1). This asymmetry in product ratio was first ascribed to nonspecific chemical activation, involving deposition of excess vibrational energy in the newly formed methyl by the migrating hydrogen.[1] Dissociation of this methyl was proposed to occur competitively with intramolecular vibrational energy distribution (IVR). Subsequent infrared multiphoton dissociation studies by Osterheld and Brauman led to the proposal of a more detailed mechanism.[4] In particular, they deduced an important role for CCO angle bending.

This system is of particular interest because the branching occurs from a deeper potential well than is typical of systems exhibiting nonstatistical dynamics.[6] The quasiclassical trajectory study reported here sought to examine the mechanism of nonstatistical methyl loss in greater detail.

Direct-dynamics trajectories were run on an AM1-SRP[7] surface parametrized to fit energies and geometries of key stationary points, as determined at the B3LYP/cc-pVTZ level of theory; 1807 trajectories were run from the transition state for keto/enol isomerization **2**, and 1816 were run from the acetone radical cation minimum **3**. Initial states were generated by quasiclassical normal mode sampling.[8,9] Rotations were treated classically. A microcanonical ensemble of initial states was selected so that each trajectory had a total energy of 10 kcal/mol in excess of the zero-point energy of the transition state. DFT calculations were performed using the Gaussian 98[10] program. AM1-SRP trajectories were run using a modification of MOPAC 93[11] in which MOPAC was used to calculate single-point energies and gradients that were forwarded to a fourth-order Beeman routine[12] for integration of the equations of motion.

The branching ratio[13] observed for methyl loss in trajectories originating from **2** is 1.13 ± 0.01, which is in qualitative agreement with the experimental values of 1−1.4.[4] Quantitative comparison of the simulation with the outcome of any particular experiment is difficult due to uncertainty in the exact experimental conditions and sensitivity of the calculations to the AM1-SRP parameters. However, most qualitative features of the simulation results were found to be reproducible with different parameter sets and appeared to be physically meaningful. The discussion will therefore focus on those aspects of the calculations.

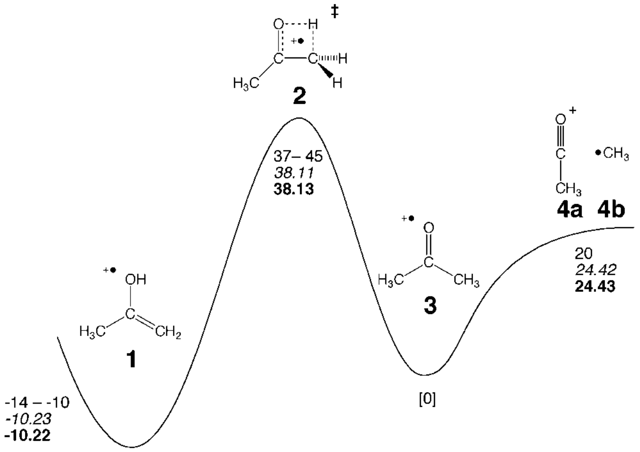

Figure 1. Important structures and energy profile for formation of and subsequent methyl loss from the acetone radical cation. Energies are in kcal/mol. Experimental,[4,5] B3LYP/cc-pVTZ (in italics), and AM1-SRP (bold) are given. B3LYP and AM1 energies do not include zero-point corrections and are therefore not directly comparable to experimental energies.

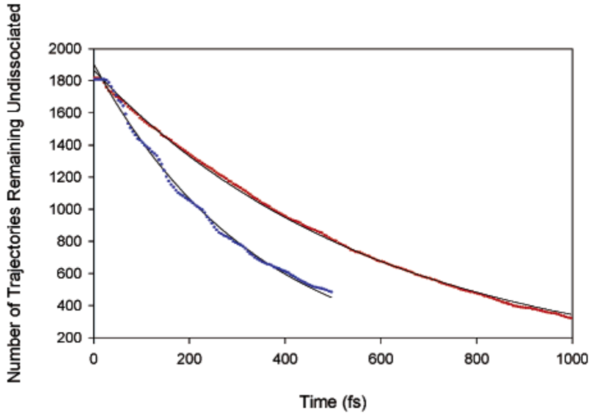

Figure 2. Number of trajectories remaining undissociated vs time with best fit exponential decays. Data for trajectories initiated from **2** are in blue; data for trajectories initiated from **3** are in red.

As expected, trajectories initiated from the vicinity of **3** showed essentially equal loss of either methyl (branching ratio 1.01 ± 0.01). An exponential fit to a plot of the number of radical ions having yet to dissociate versus time (Figure 2) indicated a half-life of 409 fs. Trajectories initiated from **2** exhibited more complicated methyl loss versus time behavior. Although not accurately described as a single population with a characteristic half-life, an exponential fit to a plot of undissociated ions versus time yielded a half-life of 238 fs. These lifetimes are in reasonable agreement with an experimental estimate of 500 fs.[14]

The higher rate for the reaction initiated from **2** is significant because the trajectories beginning at **2** and **3** had identical total energies. Insight into the origins of this phenomenon could be gained by investigating the time dependence of the branching ratio. The trajectories were divided, with a resolution of 5 fs, into sets

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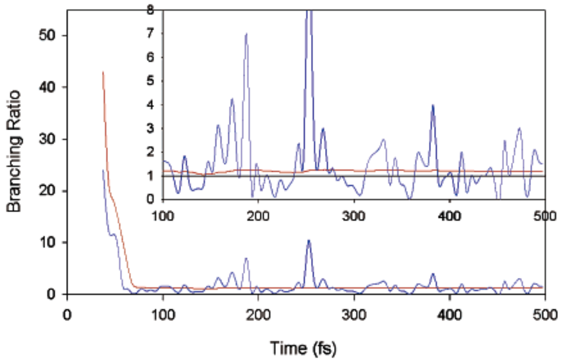

Figure 3. In blue, the branching ratio[13] for methyl loss in each 5-fs interval for the simulation. In red, the cumulative braching ratio as the simulation progresses. Note that since a ratio is plotted points with a branching ratio of less than one are more significant than they appear.

defined by the time at which one of the methyl C−C bonds passes through a length of 2 Å for the final time in a trajectory. For each set the branching ratio was calculated and plotted against its characteristic time. The result is the blue line in Figure 3. A cumulative branching ratio was also calculated and is plotted in red on the same graph.

Two features of Figure 3 stand out immediately. First, there seems to be a unique phenomenon that strongly favors loss of the newly created methyl at very short reaction times. Second, the branching ratio oscillates above and below 1 for at least 400 fs, indicating that loss of *both* the newly formed and existing methyl groups is enhanced when the trajectories are initiated at TS **2**. Examination of the trajectories that lose the newly formed methyl at very short times reveals that they never really enter the PES minimum for **3**. The geometry of TS **2**, with one CCO angle near 90° and one >120°, is quite close to that required for dissociation of the newly created methyl. The shortest duration trajectories simply take this exit without ever attaining the equilibrium geometry of **3**.

Those trajectories that do enter the PES minimum for **3** are apparently formed with selective excitation of the in-plane methyl rocking vibration that brings first one CCO angle and then the other near to 90°. As each methyl in turn reaches this geometry, it is approaching an exit for its dissociation. On each excursion of the vibration, some methyls do dissociate, leading to the periodicity shown in Figure 3. That explanation is supported by Figure 4, which shows the time dependence of the average CCO angle for all of the trajectories in which a methyl was lost in 300 fs or less. It reveals a coherent motion with a period, roughly 100 fs, matching that of the dissociation peaks in Figure 3.

The results of this study agree well with experiment. Despite uncertainties about the appropriate initial conditions or parameter set to use, some trends seem clear. A branching ratio greater than 1 is consistently reproduced. Enhanced reaction rates are observed for trajectories originating at **2** compared to **3**. This phenomenon appears to be due to nonstatistical coupling of the kinetic energy acquired during the **2** → **3** transformation into modes of importance for the subsequent dissociation of **3**. In particular CCO angle bending motions are implicated, as had been proposed by Osterheld and Brauman. Of potential relevance to the dynamics of other polyatomic systems is the observation of chemically significant nonstatistical dynamics for an intermediate that sits in a potential energy well some 20 kcal/mol deep.

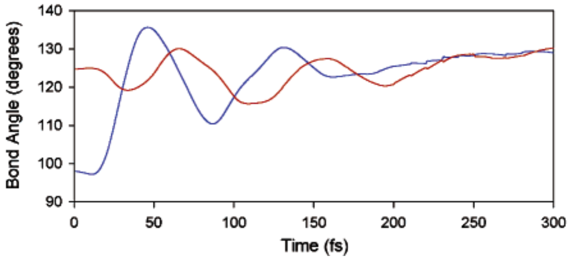

Figure 4. Average CCO bond angles, for all trajectories dissociating within 300 fs, at each fs. The angle for the newly formed methyl is shown in red, and the angle for the preexisting methyl is shown in blue.

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