Femtosecond Dynamics of Transition States and the Concept of Concertedness: Nitrogen Extrusion of Azomethane Reactions

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In this communication, we report femtosecond, real-time studies of the nature of the transition states and the concept of concertedness in the nitrogen extrusion reaction of azomethane. Many thermal and photochemical reactions involve the breaking or making of several chemical bonds. Important to the mechanism are the following questions: How do the two (or more) bonds break? What is the time scale for the elementary steps? What is the true nature of the transition states (TS)? The literature is very rich with discussions on the relationship between the nature of the transition state or structural intermediate and the two extreme descriptions of the reaction, concerted or consecutive, i.e., stepwise (see, e.g., refs 1 and 2). These descriptions are critical to the understanding of the reaction path, the stereochemistry, and the structure of the TS, but in many studies their definition is operational depending on the experimental approach and time scales. With femtosecond resolution, nuclear motions can be studied, allowing for a true description of concertedness and a clear distinction between TS(s) and intermediate(s).

The thermal and photochemistry of azomethane typifies this case. The reaction represents one of the most known to extrude nitrogen and produce methyl radicals, which have been used in a variety of radical chemistry and other applications. But, the mechanism has been questioned, both experimentally and theoretically, for 70 years since the early work of Ramsperger in 1927. For these azoalkanes, the elementary steps are classified according to concertedness:

\[ \text{R} - \text{N} \rightarrow \text{N} = \text{N} \rightarrow \text{R} \rightarrow \text{R} + \text{N}_2 \quad \text{concerted(TS)} \]

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(1)

For reaction path (1), the two C–N bonds are broken concertedly, while for path (2), the reaction must first produce the intermediate R–N2 which then liberates the nitrogen molecule. Besides the importance to the reaction mechanism, the presence of the intermediate describes the state of final products (e.g., hot or cold N2), the stereochemistry, which depends on the lifetime of the intermediate, and the branching to other reaction channels.

Recently, experimental studies of the asymptotic product fragments (N2 and CH3) have addressed the dissociation mechanism. With Coherent Anti-Stokes Raman spectroscopy (CARS), Weisman and co-workers have measured product-state distributions of both CH3 and N2, following excitation at 355 nm. They concluded a stepwise mechanism, with the first step occurring in less than 1 ns and the second in 5.3 ns. In contrast, using molecular beam translational spectroscopy, Lee’s group concluded less than 1 ns and the second in 5.3 ns. In contrast, using molecular beam translational spectroscopy, Lee’s group concluded a stepwise mechanism, with the first step occurring in less than 1 ns and the second in 5.3 ns.

The amplified pulses were typically 80 fs, and the energy was ~200 μJ, attenuated to be in the linear regime (Figure 1). We observed the parent (mass /amu = 58), the intermediate (CH3N2 radical, mass /amu = 43), and the products. By gating at mass 58 and 43 amu, respectively, we observed the transient signals for the parent and the intermediate, Figure 1. A least-squares-fit with proper convolution gives τ = 70 ± 10 fs for the parent decay. For the intermediate, we obtained a comparable rise time (70 fs) and a decay time of 100 ± 20 fs.

These results indicate several points. First, the observation of the intermediate CH3N2 provides evidence of the nonconcerted trajectory of the reaction. Second, the first C–N bond breaks in time, order of magnitude faster than the estimated time scale of the molecular rotation. The measured time is also inconsistent with the isotropic distribution of the fragments (β = 0), which was attributed to the many rotations of the parent molecule prior to bond breakage. Third, the fs time scale for the second C–N bond breakage indicates that the TS involved is that of a very low-energy barrier.

Figure 2 depicts the PES we obtained by ab initio molecular orbital (MO) theory using the G2M(CC1) approach. The structures of the stationary points, Figure 2, were optimized using the Density Functional Theory (DFT) at the B3LYP/6-311G(d,p) level; normal vibrational frequencies and zero-point energies of all species were also calculated. For the concerted ~1 ps. They also deduced that the parent excited azomethane molecule persists for many rotational periods, i.e., many picoseconds, suggesting that the second C–N cleavage is not feasible to clock in real time. Weitz’s group obtained the energy content of the CH3 radicals and concluded a stepwise process. At higher energy (193 nm), where it is known that the products are 99% CH3 and N2, Huber’s group measured the angular and kinetic energy distributions of the fragments and concluded that the mechanism is consistent with a concerted process. Theoretical ab initio studies have been reported, and recent work from Morokuma’s group gives a theoretical description of the mechanism on a multidimensional potential energy surface.

Here, we report our first study of the femtosecond (fs) dynamics of the reaction. Using fs-time-resolved mass spectrometry, the two elementary steps were studied. The intermediate CH3N2, hitherto unobserved, was detected and isolated in time. The reaction is found to be not concerted, and both the first and second C–N bond breakage occur on the fs time scale. Thus, true concertedness must describe the motion in reference to the frequency of the reaction coordinate (the C–N vibrational period is ~30 fs) and not to the rotational time of the entire molecule (ps). To compare with theory, we have performed ab initio calculations of the potential energy surface (PES) of the ground state and calculated the microcanonical reaction rates after locating the transition states.

The experimental details can be found in ref 11. Briefly, a fs laser system was integrated to a molecular beam apparatus with the capability of measuring the time-of-flight (TOF) mass spectra. Figure 1 shows the TOF mass spectrum obtained with fs pulses. The amplified pulses were typically 80 fs, and the energy was ~200 μJ, attenuated to be in the linear regime (Figure 1). We observed the parent (mass /amu = 58), the intermediate (CH3N2 radical, mass /amu = 43), and the products. By gating at mass 58 and 43 amu, respectively, we observed the transient signals for the parent and the intermediate, Figure 1. A least-squares-fit with proper convolution gives τ = 70 ± 10 fs for the parent decay. For the intermediate, we obtained a comparable rise time (70 fs) and a decay time of 100 ± 20 fs.

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behaves statistically. As discussed elsewhere,\textsuperscript{15} the theory is not into consideration. It is not suggested that the intermediate intersection at which the S\textsubscript{0} and S\textsubscript{1} surfaces cross each other when together. Morokuma and co-workers have found a conical products.\textsuperscript{4} Upon excitation of the molecule, the LUMO electron fact that thermal and photochemical reactions give the same The following mechanism accounts for our observations and the stepwise path, the latter has a much looser TS than the former. (Figure 2), the calculation gives a lifetime of 6 ps. Though the concerted reaction path, our value of the energy barrier is in good agreement with that calculated using a multireference configuration interaction (MRCI) scheme.\textsuperscript{10c} However, the MRCI method was unable to handle the stepwise reaction path due to the dramatic increase in the number of configurations in the low-symmetry system; details will be published later.

The experimental rates were compared with those predicted via statistical Rice–Ramsperger-Kassel-Marcus (RRKM) theory,\textsuperscript{13} or the variational version,\textsuperscript{14} after locating the TS. At the total available energy (Figure 2), the lifetime is calculated to be 700 fs, an order of magnitude longer than the measured value. A much shorter lifetime (<100 fs) was obtained for the second bond breakage, due to the small energy barrier involved (2.9 kcal/mol); the translational energy distributions of the fragments\textsuperscript{6} were taken into consideration. It is not suggested that the intermediate behaves statistically. As discussed elsewhere,\textsuperscript{15} the theory is not applicable on this fs time scale. For the concerted reaction path (Figure 2), the calculation gives a lifetime of 6 ps. Though the concerted path has an energy barrier lower by 2.6 kcal/mol than the stepwise path, the latter has a much looser TS than the former. This looseness makes the number of states much higher (entropic), leading to the nonconcerted path with higher rates.

The reaction dynamics is described by two elementary steps. The following mechanism accounts for our observations and the fact that thermal and photochemical reactions give the same products.\textsuperscript{5} Upon excitation of the molecule, the LUMO electron \( \pi^* \) on nitrogen significantly weakens the N=\( \pi \) bond and thus makes the rotation around the NN axis (CNNC torsion) comparably easy. However, this torsional motion increases the energy on the S\textsubscript{0} surface (corresponding to the barrier for cis–trans isomerization) so that it brings the S\textsubscript{0} and S\textsubscript{1} surfaces close together. Morokuma and co-workers have found a conical intersection at which the S\textsubscript{0} and S\textsubscript{1} surfaces cross each other when

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