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A Direct Observation of a Concerted Two-Bond Breaking Reaction

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The concept that a chemical reaction involving breaking (or making) of two or more chemical bonds might be concerted has intrigued chemists for decades.[1] The two extreme descriptions of the mechanism, *concerted versus stepwise*, are central to our understanding of reactivity and stereochemistry of a wide range of reactions, such as the Diels−Alder reaction and its reverse.[2,3] As pointed out elsewhere,[4] the true concertedness must address the nuclear motion in reference to the time scales of the reaction coordinate. Direct observations satisfying this criterion have been very scarce.[3,5] In this communication, we report an affirmative observation of concerted breaking of two chemical bonds in the photodissociation of dimethyl sulfoxide (DMSO).

Photodissociation of DMSO has been studied by several groups.[6−9] It was concluded that, upon excitation near 200 nm, DMSO decomposes into SO + 2CH$_3$ with a quantum yield of ~1.5 for the methyl products.[7,8] One group[6] has reported results that are suggestive of a concerted dissociation mechanism, while others have detected the CH$_3$SO intermediate and concluded that the reaction mainly proceeds via the stepwise mechanism.[7−9] In this study, DMSO was excited in the gas phase with femtosecond (fs) laser pulses at 200 nm to initiate the reaction. The temporal behaviors of the products were then monitored in two different experiments. In one experiment, SO (X, $v'' = 0{-}3$) products were probed by laser-induced fluorescence (LIF) detection through the SO X → B transition. In the other experiment, fs mass-selected resonance-enhanced multiphoton ionization (REMPI) and fs time-resolved photofragment translational spectroscopy (TR-PTS) were employed to measure the temporal evolution and translational energy distributions of free CH$_3$ ($\tilde{X}$, $v'' = 0$) product. Details of these experiments have been described elsewhere[10] and are given in the Supporting Information.

Figure 1 shows the results of the fs pump−LIF−probe experiments. These SO transients are characterized by a small but very rapid initial rise followed by a much larger but slower one. Nonlinear least-square fits gave $\tau_1 = 50 \pm 10$ fs for the initial rapid rise (green dashed line) and $\tau_2 = 20{-}80$ ps (blue dashed line) for the much slower ones depending on the vibrational levels of SO(X) probed. The amplitude ratios of the fast to slow rises are about 0.1−0.2. Because of the resonance LIF detection, free SO can be observed only when the two C−S bonds break completely. Thus, the transients shown here immediately suggest that there are at least two pathways leading to three-body dissociation. The small instantaneous rise observed in the SO transients indicates that a small fraction of SO is produced in about 50 fs! Because this time scale is similar to the C−S vibrational period (~50 fs) and to the time needed to break a single C−S bond on a repulsive surface,[11] we concluded that *the nearly instantaneous appearance of SO must be due to a simultaneous breaking of the two equivalent C−S bonds, or a concerted three-body dissociation*. The much slower rise component (20−80 ps) is probably due to the decomposition of CH$_3$SO intermediate in a stepwise pathway that competes with the concerted channel. The vibrational-level dependence of the slow component suggests that the decomposition of the CH$_3$SO intermediate is nonstatistical.

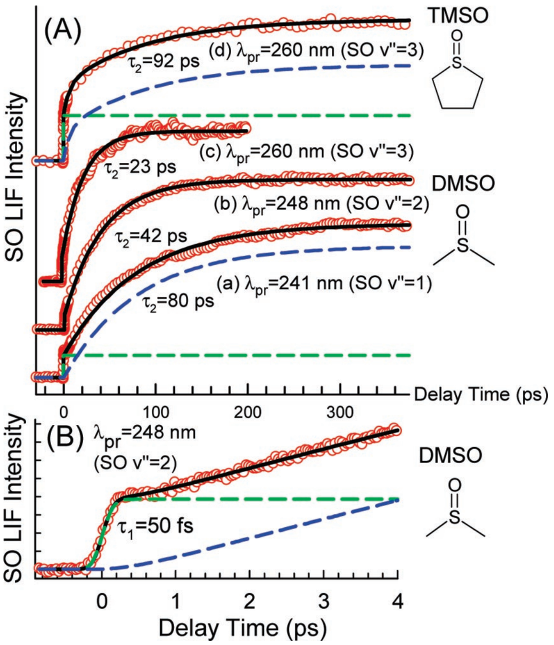

Figure 1. (A) Long time scale fs pump−LIF−probe transient of SO(X) produced in the photodissociation of DMSO (a−c) and TMSO (d). The black solid lines are the best fits to the data, and the colored dashed lines are the decomposed components. The data have been normalized and shifted vertically for clarity. (B) Short time scale view of trace (b) in (A).

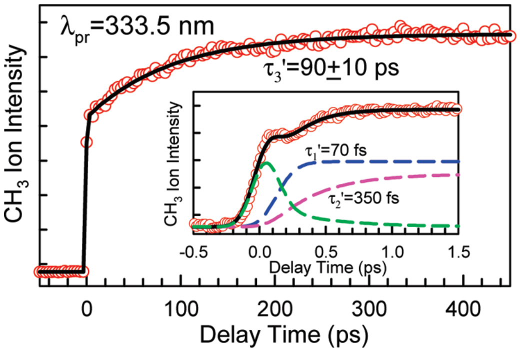

Figure 2. Femtosecond pump−REMPI−probe transient of CH$_3$ ($v = 0$) products produced in the photodissociation of DMSO.

Figure 2 shows the results of the fs pump−REMPI−probe experiments. At the first glance, the transient seems to be composed of a very rapid rise and a much slower rise of about 90 ps. However, the short time scale transient shown in the inset reveals that the fast rise actually consists of at least two components: one rises in 70 ± 20 fs (blue dashed line) and the other in 350 ± 50 fs (pink dashed line). A fast decay component (green dashed line) arising from dissociative ionization was also identified on the bases of laser-irradiance dependence and fs TR-PTS results. The 70 fs component

10.1021/ja0684747 CCC: $37.00

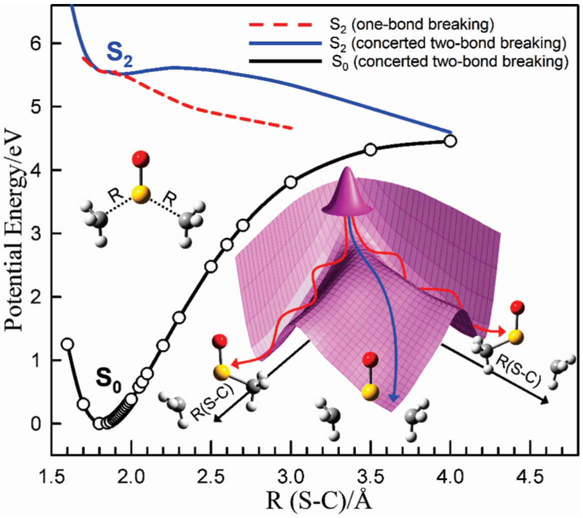

Figure 3. Calculated potential-energy curves along reaction coordinates for the concerted breaking of two C−S bonds (solid line) and for the breaking of one C−S bond (dashed line) in DMSO. The inset is a schematic S_2 state potential-energy surface based on the calculated results.

is consistent with the concerted dissociation channel identified in the SO transients, although its large amplitude suggests the existence of other dissociation pathways on the same time scale, such as the fast channel reported by Blank et al.[7] The 350 fs component can be assigned to the primary C−S dissociation in a lower state, presumably the S_1 state, after a rapid internal conversion. The much slower rise of about 90 ps is due to the decomposition of the hot CH_3SO intermediate and can be correlated with the slow rises observed in the SO transients.

We have also carried out ab initio calculations to support our observations and aid in the elucidation of the dissociation mechanism. Briefly, we calculated the potential-energy curves of several excited states along the ground-state minimum-energy path (MEP) for the concerted breaking of two C−S bonds and for the breaking of a single C−S bond. The details of the calculations are given in the Supporting Information, and the results are summarized in Figure 3. According to the calculated vertical excitation energies, the photoexcitation of DMSO at 200 nm reaches the severely overlapped S_2, S_3, and possibly S_4 states region. The S_2 state, which carries a major oscillator strength in this spectral region, can be approximately described as the $(\pi^*_{SO}/\sigma_{SC}) \rightarrow \sigma^*_{SC}$ excitation. Along the ground-state concerted two-bond dissociation MEP, the S_2 state exhibits a generally repulsive profile (blue line) with a very low barrier. Note that this curve is simply a cross section of the global potential-energy surface (PES) along the ground-state MEP. It is likely that a purely repulsive pathway toward concerted dissociation may exist on the S_2 surface. The S_2 state PES along the ground-state single C−S bond dissociation MEP is also repulsive (red dashed line) with an even steeper slope and leads to a CH_3SO electronically excited state. Therefore, the S_2 PES is generally repulsive for the breakage of the two equivalent C−S bonds. A schematic PES of the S_2 state is shown in the Figure 3 inset. The initial wave packet is launched on the S_2 surface at the ground-state equilibrium geometry (pyramidal) along the diagonal direction. The topology of the S_2 surface suggests that, although the majority of the trajectories will go asymmetrically and result in breaking of a single C−S bond, a significant fraction of trajectories may slide into the diagonal region and lead to a concerted, but not necessarily synchronous, breaking of the two C−S bonds. Thus, both the concerted and stepwise trajectories are present on the global S_2 PES, and the branching is determined by the initial motion and symmetry of the wave packet. This description is consistent with the small amplitude of the 50 fs rise observed in the SO LIF transients, and the 70 fs rise resolved in the methyl transient probably includes contributions from both the concerted two-bond and one-bond breaking on the S_2 surface. Combination of the theoretical and experimental results also suggests that some other trajectories undergo a rapid internal conversion to the S_1 state and then dissociate to produce CH_3 and CH_3SO in about 350 fs. Decomposition of the latter is responsible for the observed slow rise (20−90 ps) in the SO and CH_3 transients.

Additional support for the competing concerted and stepwise dissociation comes from the photodissociation of tetramethylene sulfoxide (TMSO) shown in Figure 1A (trace d). Upon photodissociation at 200 nm, TMSO gives a much larger instantaneous (50 fs) SO rise. In TMSO, the two C−S bonds are linked together with an alkyl chain, and therefore, the dissociation of a single C−S bond is somewhat hindered by the chain constraint and becomes less repulsive. This constraint does not exist in the concerted pathway, making it more competitive and resulting in a larger branching ratio as observed.

Acknowledgment. This work was supported by the National Science Council of Taiwan, R.O.C. (NSC 94-2113-M-007-037).

Supporting Information Available: Detailed experimental and calculation procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) On the basis of photofragment translational energy measurements and the available energy for the three-body dissociation into $2CH_3 + SO$ at 200 nm, we estimated that the terminal relative speed of C−S separation is no greater than 5000 m/s. Therefore, it takes at least 50 fs to extend the C−S bond by 2.5 Å to become about 4.5 Å at which the bond can be considered as broken.

JA0684747