It is therefore possible that the products of reaction 1 are HI$^-$ and Qn$^+$. This is unlikely, since the charge-transfer reaction is more endothermic than the proton-transfer reaction ($\Delta H = 7.2$ eV compared to 3.53 eV[5,6]). With the *tert*-butyl iodide source, we get no signal unless the pyrolysis cell is turned on, so that the signal cannot be due to unpyrolyzed *tert*-butyl iodide. The bulb source precludes this possibility as well. Quinuclidine does not start absorbing light until 256 nm,[7] well outside the window provided by the crown glass lens. The peak of the first absorption band of HI is at 208 nm, but the band extends up to 364 nm.[8] The absorption is entirely dissociative. I atoms can react by the charge-transfer reaction, I + Qn → I$^-$ + Qn$^+$, but this reaction is more endothermic than reaction 1 (4.3 eV as compared to 3.53 eV).[5] Although the photodissociation of HI produces translational energy in the products, almost all of this goes into the H. Thus, the photodissociation of HI produces a less reactive species than HI. I atoms do not absorb light in the region of interest. The first UV absorption is at 183 nm, and the spin–orbit transition at 1.3 μm gives too little energy to make a difference. We have added I$_2$ to the *tert*-butyl iodide, but this did not produce any extra signal. Dimers of HI or Qn have twice the energy of monomers and can react in the absence of light. Furthermore, the amount of dimers depends strongly on nozzle temperature, and we see no such temperature variation in our results. Complexes with carrier gases will react in much the same way as the uncomplexed species. There is a possibility that the ions are photodissociated from the surfaces in the reaction region. The only surface not at the extraction voltage is a fine cage made of nickel mesh coated with graphite (Aquadag). The surface would rapidly remove all the initial translational energy plus the energy of adsorption so that the photon would have to supply all of the 3.53 eV (351 nm) necessary for the reaction. It is highly unlikely that both positive and negative ions sitting on that surface would be photodissociated cleanly without reacting with the junk adsorbed on the surface.

Because of the unusual nature of the reaction, it is useful to give a plausible model for it. We believe that the reaction takes place on two potential-energy surfaces, one covalent, dissociating to the reactants, and one ionic, dissociating to the products. On the reactant side the covalent surface is lower in energy but becomes repulsive at small distances, since the neutral products I + HQn are not bound. The ionic surface is strongly attractive due to the Coulombic force and intersects the covalent surface. An electron then jumps from Qn to HI, and the reaction continues on the ionic surface. This is the "harpoon" mechanism used by Herschbach to explain the large cross sections in alkali reactions.[9] The products must then overcome their Coulombic attraction to form separated ions. The formation of separated product ions is endothermic by 3.53 eV,[5] but the formation of a bound ion pair is probably exothermic. Below the threshold for reaction, it is still possible to form the ion pair complex, but the complex does not have enough energy to dissociate. Because of the large number of vibrational modes in the system, the complex should have a long lifetime (microseconds) before dissociating to the reactants. Absorption of a photon promotes the complex to the repulsive covalent surface. Since the transition results in a large change in dipole moment, it should have a large oscillator strength. As it dissociates, it again crosses the ionic surface and can then form separated ions. The advantage of this type of system over those studied earlier is in the very long lifetime of the complex, comparable to the transit time in the reaction region.

There are roughly 5×10^{17} photons/s going into the reaction zone of 0.2 cm^3. With an extinction coefficient of 10^4 mol^{-1} dm^3 cm^{-1} we can then excite ~0.02% of the complexes formed. Since the photoinduced signal is very roughly 1% of the dark signal at higher energies, the excited complex has about 50 times the reaction probability of the dark reaction.

We are now looking at the wavelength dependence of the effect as well as looking for other, similar reactions. Our reactions differ from previously studied photon-induced reactions[1] in the arrangement of surfaces and in the large number of vibrational modes.

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Relaxed Triplet Energies of Phenylnorbornenes. The Role of Phenyl–Vinyl Torsions. On the Origin of Nonvertical Triplet Excitation Transfer

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In mechanistic organic photochemistry, the concept of "nonvertical" triplet excitation transfer (NVT)[3-9] refers to any process for which (a) triplet excitation transfer occurs from donors D with triplet energy $E_T(D)$ insufficient to provide isothermal or exothermic formation of the spectroscopically observed acceptor (A) triplet, and (b) the rate of the process is enhanced relative to the rate expected on the basis of making up the energy deficit $E_T(A) - E_T(D)$ by thermal activation. Such processes are encountered when the ground and excited triplet states have significantly different equilibrium geometries. The original evidence for NVT derived from experiments with *cis*-stilbene (**1**) as the acceptor,[3-7] and the origin of NVT to **1** was ascribed to torsion of the C═C double bond concomitant with NVT. However, Gorman et al.[9] showed that 2,3-diphenylnorbornene (**2**) as an acceptor exhibited rate enhancements nearly identical to those for **1**. The chromophores of **2** and **1** are identical but for the severe restriction of double-bond twisting in **2**. They concluded that the role of double-bond torsion in NVT to **1** was minimal and proposed that NVT to flexible and nonplanar acceptors (cf. **1** and **2**) was a consequence of single-bond torsion in the ground-state acceptor.

The relative importance of single-bond vs double-bond torsion in the relaxation of T_1 remained to be explored. We have now used time-resolved photoacoustic calorimetry (PAC)[10-13] to

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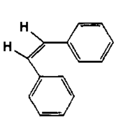
measure the relaxed triplet energies of **2** and 2-phenylnorbornene **3**. The relaxed triplet of **2**, though higher in energy than that for **1**, is substantially lower than its previously reported spectroscopic triplet, but the relaxed and spectroscopic triplet energies of **3** are nearly identical. Phenyl–vinyl torsion is dominant in the relaxation of ^{3}**2**.



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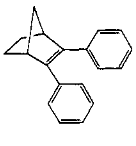

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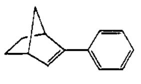

3

Our PAC measurements[14] for compounds **2**[15] and **3**[16] in acetonitrile employed benzophenone (B) as sensitizer (ca. 0.06 M).[13] Flash photolysis[17] afforded excellent linear plots of k_{obsd} vs [alkene], giving a rate constant for ^{3}B + **2** of $k_{ET}(2) = 6.8 \times 10^9$ M^{-1} s^{-1}, and for ^{3}B + **3**, $k_{ET}(3) = 6.0 \times 10^9$ M^{-1} s^{-1}. Of the six parameters[18] required by the mechanism (Φ_1, τ_1 corresponding to the formation of ^{3}B, Φ_2, τ_2 for triplet excitation transfer, and Φ_3, τ_3 for decay of the alkene triplet), $\Phi_1 = 0.15$, $\tau_1 = 0.1$ ns, and $\tau_2 = 1/k_{ET}(2)[\mathbf{2}]$ or $1/k_{ET}(3)[\mathbf{3}]$ were constrained. E_T(A) is then $E_{h\nu}(1 - \Phi_1 - \Phi_2)$ kcal/mol. Variations in E_T(A) with concentration and pulse energy were not significant. E_T values and 90% confidence limits of the means of N determinations were 46.9 ± 0.8 kcal/mol for **2** ($N = 21$) and 56.0 ± 0.5 kcal/mol for **3** ($N = 34$), robust to ±0.3 kcal/mol for 20% variation in τ_2. A value for **3** previously reported[13] is slightly low, most probably due to excessive laser power.

The total relaxation available is ca. 15 kcal/mol for **1** (based on its relaxed triplet energy of 42.0 ± 1.5 kcal/mol[13]), ca. 10 kcal/mol for **2**, and ca. 1.2 kcal/mol for **3**. These values derive from the most reliable spectroscopic energies: for **1**, ca. 57 kcal/mol;[19-21] for **2**, identity[9] with **1**; and for **3**, 57.2 kcal/mol.[13] The relaxation in **2** is strikingly large in view of its inability to twist around the double bond. The minimal relaxation of **3** contrasts with the 7–10 kcal/mol for acyclic styrenes[13] and shows that the norbornene skeleton substantially inhibits double-bond twisting.

What, if not double-bond twisting, is the origin of the relaxation of **2**? We have obtained ground-state phenyl–vinyl torsional angles of 37.7° and 36.0° for **1**, 42.4° and 32.8° for **2**, and 18.3° for **3** using PC Model 2.0 (Serena Software, Bloomington, IN). The rather large torsional angles for **1** and **2** are strikingly similar and are in good agreement with X-ray data.[9,22] Since HOMO–LUMO excitation is expected to increase the π bond orders of the essential single bonds, reduction of large torsional angles will lower the energy of the triplet, as observed for **2**. **3** is less crowded as expected, much nearer planarity, which explains the low relaxation observed. Indeed, Hückel calculations for stilbene and styrene HOMO–LUMO states, with β for the bonds in question proportional to the cosine of the dihedral angle, show that the stabilizations achievable by twisting to planarity are -0.56β for **2** and -0.07β for **3** or 9 and 1 kcal/mol, respectively, for $\beta = -16$ kcal/mol.[23] No modes of relaxation seem appropriate to **2** but not to **3** except for the two phenyl–vinyl torsions in **2**, and we assign the energy of relaxation of **2** accordingly. Using **2** to model **1**, *some two-thirds of the relaxation energy of* ^{3}***1*** *is due to phenyl–vinyl torsion and about one-third to double-bond torsion.* Clearly, however, the approach of ^{3}**2** to small phenyl–vinyl dihedral angles requires some other geometric relaxation for obvious steric reasons (cf. either small torsional distortions or slight pyramidalization at the triplet norbornene double bond).

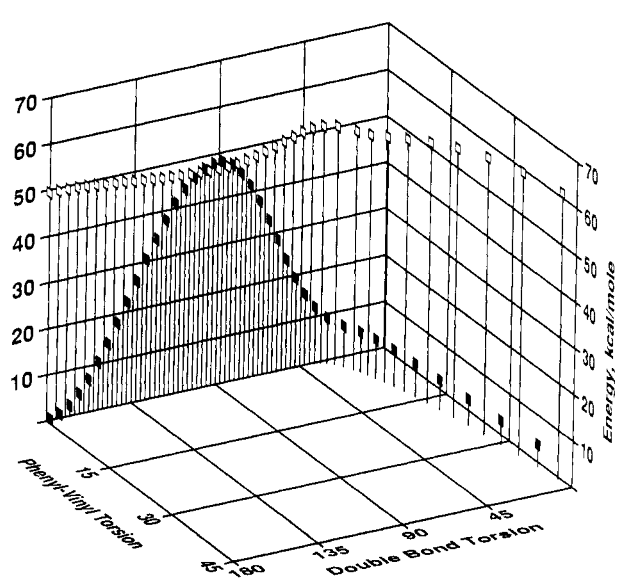

Figure 1. Schematic section of energy surface of stilbene triplet showing the trajectory we suggest as most probable for isomerization of *cis*-**1** by nonvertical triplet excitation transfer, beginning on the right with phenyl–vinyl torsional angles assumed as 40° and double-bond torsion as 0°. Open diamonds represent the triplet state and solid diamonds represent the ground state, each relative to the planar trans ground state as 0 kcal/mol. See text for explanation of energies of critical points.

This result is clearly consonant with the proposal that NVT to **1** and **2** proceeds with ground-state distortion in the same sense. *There is thus no necessity to invoke double-bond torsion to any energetically significant extent to explain NVT to **1**.* Single-bond aryl–vinyl torsion appears to be more important than double-bond torsion in the relaxation of excited states of other arylakenes as well, most notably tetraarylethylene singlets.[24-26] and single-bond aryl–aryl torsion is the source of NVT to biphenyl derivatives.[27] Triplet excitation to *trans*-β-methylstyrene (presumably essentially planar) from low-energy sensitizers is vertical[28] although double-bond torsion leads to >7 kcal/mol relaxation.[13]

We summarize our present picture of geometric change upon sensitized isomerization of **1** schematically in Figure 1. The zero of energy is taken as that of *trans*-stilbene. The spectroscopic energy of **1** is 57 kcal/mol,[19] leading to an energy of 61.6 kcal/mol given the enthalpy of ground-state isomerization ($\Delta H° = 4.6$ kcal/mol[7]). Relaxation largely by the two phenyl–vinyl torsions leads to the plateau at 51.5 kcal/mol (modeled as 46.9, E_T for **2**, +4.6 kcal/mol). Figure 1 assumes slight geometric involvement of double-bond torsion to accommodate phenyl–vinyl coplanarity. Further relaxation leads to the perpendicular triplet at 46.5 kcal/mol,[13] the global minimum. The spectroscopic trans triplet at 49.0–49.3 kcal/mol[29-31] is also shown.

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(14) PAC experiments used the Q-switched Nd-YAG third harmonic, a dielectric mirror (355 nm/normal incidence) as the cell back, and a Tektronix DSA602 digitizer. A 45° 1064-nm reflecting dielectric mirror in front of the cell rejected the YAG fundamental. Experiments for **2** were at (1.4–5.9) × 10^{-3} M with pulse energies of 0.15–0.7 mJ, and experiments for **3** were at (6–24) × 10^{-3} M with pulse energies of 0.2–1.0 mJ. The known energy of ^{3}B was always obtained in the absence of quenchers.

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In this view, NVT is driven by conformational changes in the ground state; Figure 1 depicts the triplet energy along the ground-state trajectory and is not intended to show a mandatory path for relaxation in the isolated triplet. That it recognizes the necessity for considering modes of relaxation other than double-bond torsion is in our view an improvement over most previous energy profiles for arylalkene triplets.

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L-Edge X-ray Absorption Spectroscopy of *Pyrococcus furiosus* Rubredoxin

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In this communication we present new experiments and theoretical simulations, using iron L-edge X-ray absorption spectroscopy, to study the metalloprotein *Pyrococcus furiosus* rubredoxin. The 3d transition metal L-edges are found between 400 and 1100 eV, in the soft X-ray region. Synchrotron radiation beam lines producing the high photon flux and high-energy resolution necessary to observe and resolve 3d transition metal L-edge spectra have only become available in the last few years.[1] L-edge spectra are interesting not only because of the 3-4-fold-higher energy resolution (vs K-edges) but also for the sensitivity to spin state, oxidation state, and ligand field offered by p → d transitions.[2-6] In addition, the X-ray magnetic circular dichroism (XMCD) of transition metal L-edges is predicted to be strong,[7-10] and experiments have confirmed these predictions.[11]

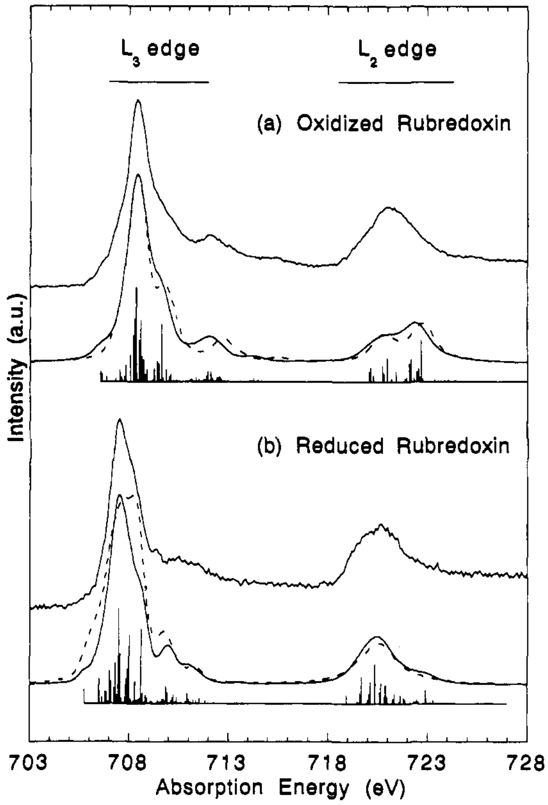

Figure 1. Experimental spectra (upper), calculated spectra (center) with (—) and without (- - -) crystal field and Slater integral reduction, and stick diagrams (lower) for the $L_{2,3}$ edges of *Pyrococcus furiosus* rubredoxin: (a) oxidized Fe^{3+} protein; (b) reduced Fe^{2+} protein. The stick diagrams show the strengths of individual transitions before line-width broadening. Indicated are the L_3 and L_2 regions of the spectrum.

Rubredoxins are small proteins which contain single iron atoms coordinated by a distorted tetrahedron of cysteinyl sulfur ligands.[12] This being the simplest iron-sulfur protein, an understanding of the rubredoxin electronic structure and redox mechanism is necessary for progress on biological electron transfer and more complex iron-sulfur proteins. Comparison of our experimental data with theoretical simulations reveals, as expected, an approximately tetrahedral symmetry for the Fe site. The analysis also finds similar covalency for the oxidized and reduced rubredoxin sites. Transition metal L-edge spectroscopy thus seems to be a promising new technique for bioinorganic systems.

In order to obtain the spectra, several difficulties in measuring soft X-ray absorption of metalloproteins were overcome. Because absorption cross sections in the soft X-ray region are very high,[13] work in this region requires ultrathin windows or vacuum conditions. By using partially dehydrated thin film samples,[14] 10 K

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(14) *Pyrococcus furiosus* rubredoxin was purified using published procedures.[15] For L-edge spectroscopy, the protein samples were partially dehydrated thin films. These were made by placing about 0.1 mL of 5.00 mM protein in 10 mM Tris·HCl buffer pH 8.0 on a silicon plate at 4 °C and evaporating under partial vacuum. The reduced rubredoxin samples contained 20 mM sodium dithionite. UV-visible absorption and EPR spectroscopy of the oxidized rubredoxin films gave spectra that were essentially identical to those of solution samples. Redissolving the films in buffer gave spectra indistinguishable from the originals by absorption and EPR spectroscopies.