

Photoinduced C–C Bond Cleavage in Dithiane–Carbonyl Adducts: A Laser Flash Photolysis Study

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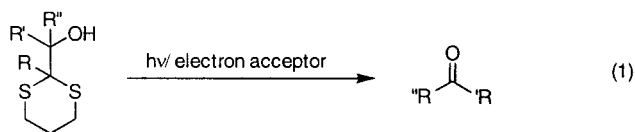
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Introduction

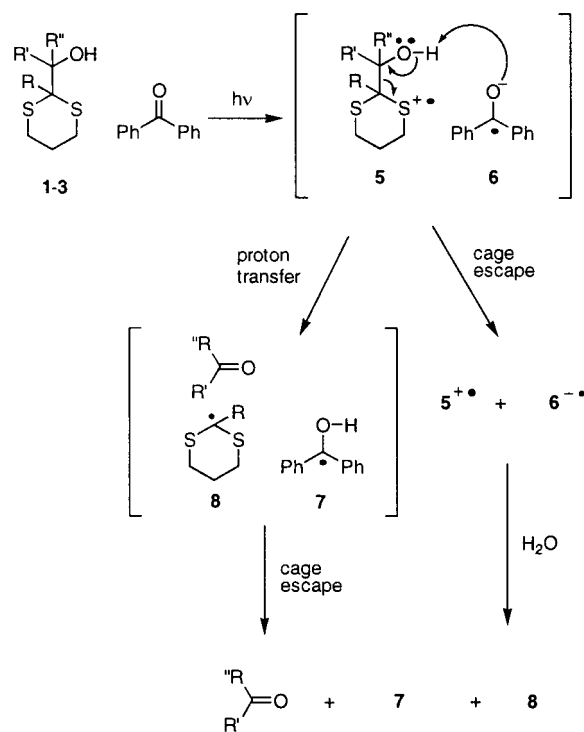
Molecular fragmentations induced by oxidative electron transfer present a fascinating theoretical challenge and generate a great deal of interest due to their potential applications. It is well-known, for example, that in vicinal diols, amino alcohols, and amino ethers, C–C bonds weakened by photoinduced electron transfer cleave efficiently and selectively. Mechanistic aspects of this cleavage have been studied extensively by several research groups.¹ In contrast, such C–C fragmentations in analogous organosulfur systems have not been studied in depth, and we attribute the lack of experimental data to the propensity of organosulfur systems to cleave the C–S bond rather than the C–C bond.

Recently we reported a photosensitized fragmentation of dithiane–carbonyl adducts, eq 1.² This process repre-



sents a novel method for photochemically uncaging protected aldehydes and ketones.³ It is also interesting

Scheme 1



from a mechanistic point of view as it represents a rare example of C–C bond scission in an organosulfur system. Earlier, we proposed that this process was initiated by a photoinduced electron-transfer mechanism involving (i) photoinduced electron transfer from the dithiane moiety to an excited benzophenone and (ii) benzophenone radical anion assisted O-deprotonation coupled with C–C bond scission. The benzophenone radical anion assistance in acetonitrile was deduced on the basis of the kinetic isotope effect and Hammett plot mechanistic studies, although an unassisted cleavage in more polar solvents was not ruled out.

In this paper, we report laser flash photolysis (LFP) studies on the photosensitized C–C bond cleavage of dithiane–carbonyl adducts. LFP experiments were carried out on benzophenone (the photosensitizer) and the 1,3-dithiane–carbonyl adducts (**1–3**). The results of these experiments are consistent with the proposed electron-transfer mechanism shown in Scheme 1.

Results and Discussion

The LFP experiments were carried out using 355 nm as the excitation wavelength. This light is absorbed by the sensitizer but not the dithianes. As expected, LFP of benzophenone alone gives its well-characterized triplet state ($\lambda_{\text{max}} = 520$ nm). Addition of the dithianes **1–3** quenches the triplet state of benzophenone with second-order rate constants, k_{ET} , listed in Table 1. Under these conditions, k_{ET} varies with the steric bulk near the

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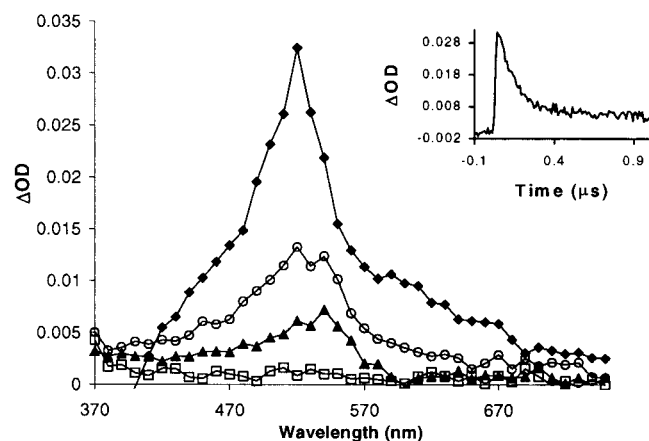


Figure 1. Transient absorption spectra from LFP (355 nm) of benzophenone and 10 mM **1** in acetonitrile: (◆) 50 ns, (□) 200 ns, (▲) 400 ns, (○) 5 μs. Inset: LFP waveform at 540 nm.

Table 1. Electron Transfer Rate Constants for Dithiane–Carbonyl Adducts in MeCN and 10% H₂O/MeCN

Dithiane Compound	$k_{\text{ET}} (\text{M}^{-1} \text{s}^{-1})$ MeCN	$k_{\text{ET}} (\text{M}^{-1} \text{s}^{-1})$ 10% H ₂ O/MeCN	$k_{\text{H}} (\text{s}^{-1})$
(3)	$4.3 \pm 0.3 \times 10^8$	$14.6 \pm 0.5 \times 10^8$	1.6×10^5
(1)	$8.4 \pm 0.7 \times 10^8$	$13.1 \pm 0.6 \times 10^8$	1.5×10^5
(2)	$11.6 \pm 0.8 \times 10^8$	$13.4 \pm 2.2 \times 10^8$	2.7×10^5
(4)	$15.2 \pm 1.1 \times 10^8$	$30.0 \pm 2.0 \times 10^8$	

dithiane ring, with the relatively unencumbered **2** reacting faster than the more crowded substrates **1** and **3**. This quenching process results in formation of $\text{Ph}_2\text{C}^{\bullet}\text{OH}$ radical **7**, which was detected by its absorption at 540 nm. Figure 1 shows the transient absorption spectrum for a sample where benzophenone is excited in the presence of 10 mM **1**. In the presence of **1**, the triplet state is seen immediately following the laser pulse. Within 400 ns, this is converted to radical **7**. No absorption bands for the benzophenone radical anion or the 1,3-dithiane radical cation **5** were observed. The radical anion absorbs with a $\lambda_{\text{max}} = 630$ nm and the radical cation **5** absorbs around 625 nm.⁴ Compounds **2** and **3** give transient absorption spectra similar to that of **1** with peaks for the benzophenone triplet and radical **7** only.

The detection of **7** is consistent with the proposed mechanism. However, there remains the possibility that it could form via direct hydrogen atom abstraction from the dithiane ring. This was tested by carrying out LFP experiments with 2-methyl-1,3-dithiane (**4**), which lacks the OH group believed to be responsible for the proton transfer. As with the other dithianes, **4** efficiently quenches the triplet state of benzophenone, but in this case neither radical **7** nor any other intermediates are observed, even at the highest concentration of **4** (10 mM)

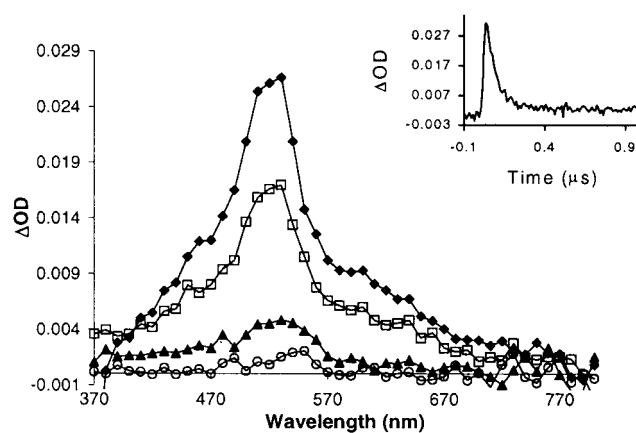


Figure 2. Transient absorption spectra from LFP (355 nm) of benzophenone and 10 mM **4** in MeCN: (◆) 50 ns, (○) 100 ns, (▲) 200 ns, (□) 5 μs. Inset: LFP waveform at 540 nm.

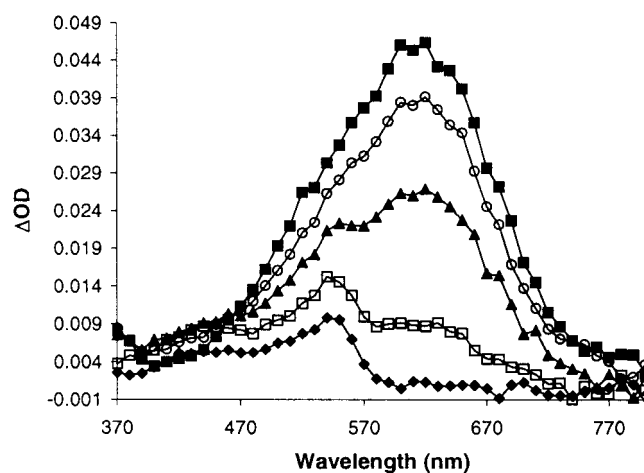
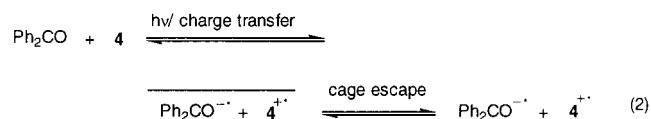


Figure 3. Transient absorption spectra from LFP (355 nm) of benzophenone and 10 mM **4** in 50% MeCN/H₂O: (■) 50 ns, (○) 500 ns, (▲) 1.5 μs, (□) 5 μs, (◆) 20 μs.

(Figure 2). We assume that the proposed electron transfer is followed by a rapid back-electron transfer within the geminate ion radical pair. This was confirmed by repeating the LFP experiment in 50% H₂O/MeCN solvent



mixture. This medium, being more polar, is expected to stabilize the ion radical pair allowing cage escape to compete with back-electron transfer. As shown in Figure 3, LFP of benzophenone/**4** mixtures in the more polar solvent produces a strong signal for **6** ($\lambda_{\text{max}} = 630$ nm) that is not present immediately following the laser pulse. After about 1 μs, this anion radical is protonated to give radical **7** ($\lambda_{\text{max}} = 535$ nm).

The experience with **4** suggested that we might also be able to observe ion radical intermediates from **1–3** in more polar solvent mixtures. It was expected that the more polar solvent mixture would increase the chance of the benzophenone radical anion **6** escaping from the solvent cage, allowing it to be observed in the LFP experiments. In the H₂O/MeCN solvent mixtures LFP of benzophenone again gives the triplet state, and addition

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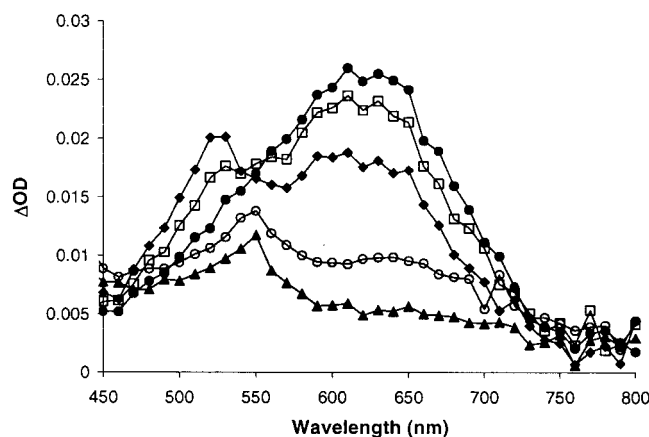


Figure 4. Transient absorption spectra from LFP (355 nm) of benzophenone and 10 mM **1** in 30% H₂O/MeCN: (◆) 50 ns, (□) 100 ns, (●) 300 ns, (○) 10 μs, (▲) 20 μs.

of **1–3** quenches it. Under these more polar conditions k_{ET} values are all near the diffusion limit (Table 1). In the aqueous mixtures the quenching process gives a new absorption band at 630 nm due to the benzophenone radical anion **6**, which over a longer period is converted to its conjugate acid **7** ($\lambda_{max} = 540$ nm). The band at 630 nm has been assigned to the benzophenone radical anion because it is quenched after purging the solution with oxygen.

Figure 4 shows the transient absorption spectrum of benzophenone excited in the presence of 10 mM **1** in 30% H₂O/MeCN. As with the LFP experiments in neat MeCN the benzophenone triplet state ($\lambda_{max} = 520$ nm) is seen immediately following the laser pulse. However, within 300 ns the triplet state is converted to the benzophenone radical anion **6** ($\lambda_{max} = 630$ nm). The latter is then converted to radical **7** after 20 μs. Dithianes **2** and **3** in 10% H₂O/MeCN also give transient absorption spectra with peaks for the benzophenone triplet, radical anion **6**, and radical **7**. The rate of decay for radical **6** was found to be about $2 \pm 1 \times 10^5$ s⁻¹ for all three of the dithiane compounds.

The 1,3-dithiane cation radical is known to absorb at 625 nm,³ and we assume that **5** would have a similar spectrum. However, this band would likely be obscured by the signal for radical anion **6**. In an attempt to detect **5**, we carried out the LFP experiment where O₂ was added to quench radical anion **6**. Under these conditions, the signals for the excited triplet state of benzophenone (520 nm) and radical anion **6** (630 nm) are quenched within 100 ns. At times greater than 100 ns there are very weak and long-lived ($t_{1/2} = 40$ μs) absorption bands at 430 and 660 nm which would be consistent with radical cation **5**. Unfortunately, the low signal-to-noise ratio for this signal precludes a more detailed analysis. Figure 5 shows the transient absorption spectrum for this experiment.

The observation of the benzophenone radical anion **6** in the more polar solvent mixtures leads to the conclusion that there is a competition between proton transfer and cage escape of the radical ion pair. In 100% acetonitrile, proton transfer predominates and only the ketyl radical **7** is seen. In the more polar mixtures the cage escape predominates and radical anion **6** is observed. Radical anion **6** is then protonated by the solvent rather than **5**,

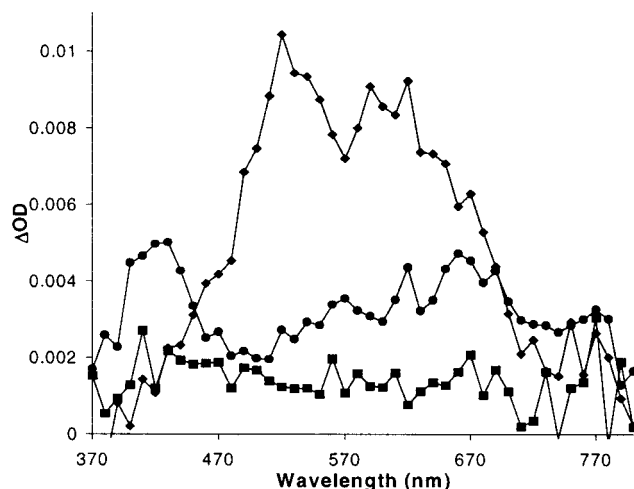


Figure 5. Transient absorption spectra from LFP (355 nm) of benzophenone and 10 mM **1** in 30% H₂O/MeCN purged with O₂: (◆) 50 ns, (●) 5 μs, (■) 50 μs.

to give the ketyl radical **7**. This mechanism is supported by the fact that the decay of radical anion **6** is first order and not second order as would be expected if it were protonated by **5** and the observation that the protonation rate is independent of **5** (Table 1). Mariano observed a similar solvent-dependent partitioning between proton transfer in contact ion pairs and cage escape to form free ion radicals.⁵ He obtained different product ratios for silylamine photoadditions to cyclohexanones depending on whether the solvent was acetonitrile, leading to proton transfer, or methanol, leading to cage escape.

It is also plausible that in dry acetonitrile the triplet benzophenone is hydrogen-bonded to the adduct. Following the electron transfer, this makes the cleavage in the radical ion pair, coupled with the proton transfer, extremely fast and efficient. Such hydrogen bonding certainly is not unprecedented in the literature. A recent observation of high regio- and diastereoselectivity of Paternò–Büchi photoaddition of benzophenone to chiral allylic alcohols led Adam's group to a conclusion that in aprotic solvents there is considerable hydrogen bonding between the allylic alcohol and the incoming triplet-excited benzophenone.⁶ Although our LFP results in dry acetonitrile do not provide a direct evidence for such hydrogen bonding between the hydroxy group of the adducts and excited benzophenone, it is conceivable that such pre-coordination precludes cage escape of the benzophenone radical anion, rendering its observation difficult or impossible. Instead, a fast proton transfer occurs producing ketyl radical.

Experimental Section

Laser flash photolysis experiments were performed using the third (355 nm) harmonic output from a Continuum II-10 Q-switched Nd:YAG laser as the excitation source. The probe beam was produced by a 350 W xenon lamp, which passed through the sample cell at a right angle to the excitation beam. The transient waveforms were recorded using a Lecroy 9420 digital oscilloscope. All samples were placed in a sealed quartz

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cuvette and purged with nitrogen or oxygen for 15 min prior to the LFP experiments. Electron-transfer rate constants were determined using a psuedo-first-order rate analysis. Solutions contained 10 mM benzophenone and concentrations ranging from 0 to 10 mM of **1–4**.

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