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Photolysis of Thymine Oxetanes Produces Triplet Excited Carbonyl Compounds with High Efficiency

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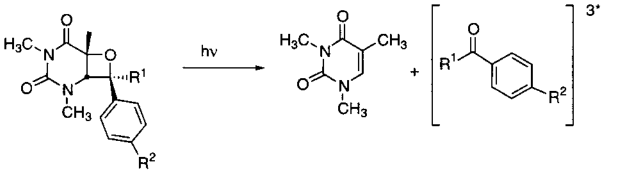
Most photochemical reactions produce ground-state products. This is generally attributed to efficient electronic state mixing at conical intersections (i.e., geometries where the excited-state potential energy surface approaches the energy of the ground-state surface).[1,2] Reactions where stable products are produced in their electronically excited state are termed "adiabatic photochemical reactions".[3−5] Aside from proton transfers[6] and formation of various open-shell species, adiabatic photochemical processes are extremely rare and limited to only a few structural classes. Photochemical ring-opening of cyclobutenes[7] (including dewar benzenes)[8,9] often yields electronically excited products. Photoinduced cycloreversion of [2+2][10] and [4+4][3,11] dimers of arenes can lead to the excited states of the final products. Photolysis of 1,1,2,2-tetramethyldioxetane (formally the [2+2] cycloadduct of acetone) produces one triplet-state acetone and one ground-state acetone.[4,12,13]

Pursuant to our longstanding interest in DNA photodamage and photoenzymatic repair, we have prepared several oxetane adducts of 1,3-dimethylthymine (DMT) with benzophenone (**1**), tolualdehyde (**2**), and anisaldehyde (**3**).[14,15] We studied their behavior under photoinduced electron transfer conditions designed to model the recently discovered photoenzymatic repair of the DNA (6-4) photoproduct. In the course of these investigations we had occasion to examine the direct photolysis of oxetanes **1**−**3**. As reported previously such photolyses effect cycloreversion, cleanly producing thymine and the carbonyl compound. Herein are described laser flash photolysis (LFP) experiments which show the photolysis of **1**−**3** results in a rare, adiabatic, photochemical reaction producing ground-state 1,3-dimethylthymine (DMT) and the excited triplet state of the carbonyl (eq 1).



(1)

1 : R^1 = Ph, R^2 = H
2: R^1= H, R^2= CH$_3$
3: R^1 = H, R^2= OCH$_3$

Synthesis of **1**−**3** is described elsewhere.[15] These oxetanes are thermally stable. For example, heating **1** at 100 °C for 8 h results in no noticeable decomposition. The UV−vis absorption spectra of these compounds show either a shoulder (**1** and **2**) or a peak (**3**) in the region of 220−230 nm and then an asymptotic decay to wavelengths >310 nm with no clear or distinct absorption onset. No fluorescence could be detected from the oxetanes (CH_3CN solutions, N_2-purged).

Photolysis of the oxetanes results in the clean and efficient formation of DMT and the corresponding carbonyl compound. Solutions of **1**−**3** in N_2-purged CH_3CN were irradiated with the unfocused 266 nm output from a pulsed Nd:YAG laser and the photolysis mixtures were analyzed by HPLC. Average yields of the photoproducts from triplicate determinations range from 78% to 96% (Table 1). No side products could be detected by HPLC.

The quantum yields for photolysis (Φ_K) were determined in a similar way. The amount of oxetane remaining following photolysis was determined by HPLC and the number of absorbed photons was determined by measuring the average laser power before and after photolysis with a pyroelectric joulemeter.[16] In all cases the conversion of the oxetane was kept below 10%. As with the chemical yields, the Φ_K values in Table 1 represent averages of three independent determinations where each measurement fell within 0.1 of the stated average.

Shown in Figure 1 is the transient spectrum resulting from LFP (266 nm, 6 ns, 2−5 mJ/pulse) of oxetane **1** in CH_3CN. This spectrum shows excellent agreement with the well-characterized triplet-state spectrum of benzophenone (λ_{max} = 525 nm).[17] The remaining oxetanes also give spectra of the corresponding aldehydes: **2** giving triplet tolualdehyde (λ_{max} 350 nm) and **3** giving triplet anisaldehyde (λ_{max} = 390 nm).[18] For comparison purposes we generated the same triplets through direct irradiation of the carbonyl compounds, again using our 266 nm excitation source, and again, excellent agreement was observed between the oxetane-derived spectra and those of the authentic triplet carbonyl compounds.

The excited triplet carbonyl compounds are formed very efficiently from photolysis of the oxetanes. This was ascertained by comparing the initial intensity of transient signal from the oxetanes with that from an optically matched solution of the carbonyl compound. (Benzophenone as well as the aromatic aldehydes all form their excited triplet states rapidly and with unit quantum efficiency.[17]) These ratios, which correspond to the quantum yields of adiabatic triplet formation from oxetane photolysis (Φ_T), range from 0.3 to 0.6 (Table 1).

Because adiabatic photochemical reactions are rare, it is necessary to consider several alternative ways in which LFP of the oxetanes could lead to formation of excited-state products. The most obvious concern would be that the observed signals originate from carbonyl impurities in the oxetane sample. HPLC analysis of the oxetane sample both prior to and following the LFP experiments showed that there was <1% of the carbonyl compound at any point in the experiment.

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(1) Förster, T. *Pure Appl. Chem.* **1973**, *34*, 225−234.
(2) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH: New York, 1995.
(3) Förster, T. *Pure Appl. Chem.* **1970**, *24*, 443−449.
(4) Turro, N. J.; Lechtken, P.; Lyons, A.; Huatala, R. P.; Carnahan, E.; Katz, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 2035−2037.
(5) Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechken, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 572−586.
(6) Solntsev, K. M.; Huppert, D.; Agmon, N.; Tolbert, L. *J. Phys. Chem. A* **2000**, *104*, 4658−4669.
(7) Leigh, W. J.; Postigo, J. A.; Zheng, K. C. *Can. J. Chem.* **1996**, *74*, 951−964.
(8) Yang, N. C.; Carr, R. V.; Li, E.; McVey, J. K.; Rice, S. A. *J. Am. Chem. Soc.* **1974**, *96*, 2297−2298.
(9) Carr, R. V.; Kim, B.; McVey, J. K.; Yang, N. C.; Gerhartz, W.; Michl, J. *Chem. Phys. Lett.* **1976**, *39*, 57−60.
(10) Noh, T.; Gan, H.; Halfon, S.; Hrnjez, B.; Yang, N.-c. C. *J. Am. Chem. Soc.* **1997**, *119*, 7470−7482.
(11) Mori, Y.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 869−875.
(12) Turro, N. J.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 3878−3860.
(13) Smith, K. K.; Koo, J.-Y.; Schuster, G. B.; Kaufmann, K. J. *Chem. Phys. Lett.* **1977**, *48*, 267−2270.
(14) Prakash, G.; Falvey, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 11375−11376.
(15) Joseph, A.; Prakash, G.; Falvey, D. E. *J. Am. Chem. Soc.* **2000**, *122*, 11219−11225.
(16) This procedure slightly underestimates the actual number of photons absorbed because there are some losses due to reflections from the walls of the cuvette. However, we estimate these to be <10%.
(17) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 420.
(18) Görner, H.; Kuhn, H. J. *J. Phys. Chem.* **1986**, *90*, 5946−5955.

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Table 1. Chemical Yields, Quantum Yields, and Enthalpy Changes for the Splitting of Oxetane Adducts **1**−**3**

	yield[a]	Φ_K	Φ_T	ΔH_{split}[b] (kcal/mol)	E_T[c] (kcal/mol)
1	78	0.5	0.4	−22	72
2	96	0.8	0.3	−16	72
3	92	0.7	0.6	−16	69

[a] Yield based on carbonyl compound. [b] From AM1 calculation for ground states. $\Delta H_{split} = \Delta H_f$(carbonyl compound) + ΔH_f(DMT) − ΔH_f(oxetane). [c] Triplet state energy of carbonyl compound, ref 17.

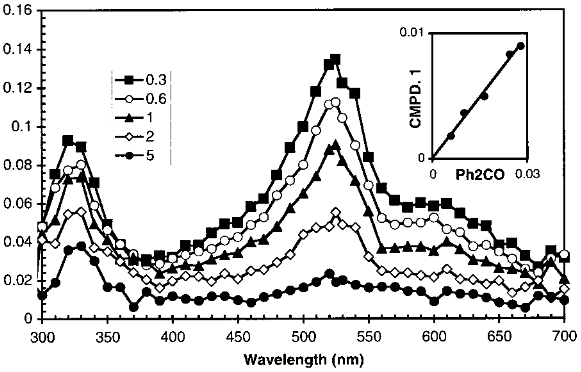

Figure 1. Transient absorption spectra from laser flash photolysis (355 nm. 2 mJ, 6 ns) of oxetane **1** in CH_3CN taken at 0.3, 0.6, 1.0, 2.0, and 5.0 μs following the laser pulse. The inset shows the dependence of the oxetane signal on the laser pulse energy, which was determined by the intensity of the signal from LFP excitation of benzophenone.

If the triplet carbonyl signals observed in the photolysis of **1**−**3** are due to photoproducts that accumulate from repetitive laser photolysis of the samples, then we would expect that their intensity will increase with the number of laser pulses applied to a given sample. Therefore, we examined the LFP signals for the carbonyl triplets on fresh solutions of **1**−**3** which were each subjected to a single laser pulse (typically data are accumulated by signal averaging ca. 20 shots). In no case did the intensity of these signals differ from those of signals obtained after 10 shots into the same solution. This provides further evidence against the signals being due to accumulated photoproducts.

Also considered was the possibility that the excited triplets result from a biphotonic process where the first photon effects a diabatic splitting of the oxetane ring and a second photon from the same laser pulse excites the carbonyl compound product. This situation would result in a quadratic dependence of the carbonyl triplet signal on the laser pulse energy. The intensity of the triplet signal from oxetanes **1**−**3** on the excitation pulse energy was examined and in each case found to be linear. This is illustrated for the case of **1** in the inset to Figure 1 and similar behavior was observed for **2** and **3**. Thus the biphotonic mechanism can be ruled out.

The adiabatic process is energetically feasible. The lowest singlet-state energy of oxetanes **1**−**3** can be estimated at 90 kcal/mol from their absorption onsets of ca. 310 nm. The triplet state energies for the carbonyl fragments range from 69 (**1**) to 71 kcal/mol. Semiempirical calculations (AM1) provide the enthalpy for the ground-state-to-ground-state splitting (ΔH_{split}) of −22 kcal/mol for **1** and −16 kcal/mol for both **2** and **3**.[19] Thus the estimated energy changes in going from the vibrationally equilibrated singlet states of the oxetanes to the observed triplet states of the carbonyls range from −40 to −34 kcal/mol. Because $\Phi_K < 1$ there must be some state along the reaction coordinate with a sufficient lifetime to allow for a fraction of the excited species to cross to the ground-state surface and from there partition between ground-state products and reactants.

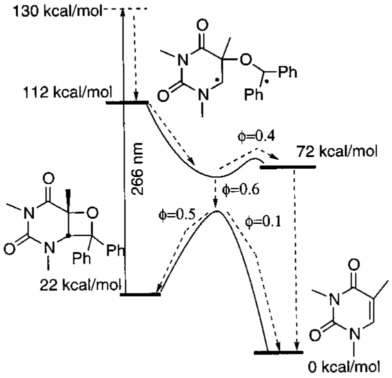

Figure 2. Potential energy diagram for the adiabatic photochemical cycloreversion of thymine oxetane adduct **1**.

A potential energy diagram for **1** based on these considerations, provided as Figure 2, is consistent with our observations. However, there are still several aspects of the mechanism that remain unclear. For example, it is not known whether intersystem crossing to the triplet surface occurs before bond scission, after the products are formed, or at some intermediate geometry. Also the nature of the intermediate state responsible for reversion to the ground state is unclear. We suggest that this is a 1,4 diradical derived from C6−C bond scission as indicated in Figure 2. However, a diradical derived from C5−O bond scission or some sort of exciplex cannot be excluded. Tetramethyldioxetane photolysis is thought to occur through a dissociative excited state that does not vibrationally equilibrate prior to bond dissociation.[4] If this holds for **1**−**3**, then the 266 nm excitation would provide a larger than estimated driving force for adiabatic dissociation.

We are unaware of previous reports of adiabatic cycloreversion of oxetanes (or indeed any previous investigations of oxetane photolysis). Numerous [2+2] cycloadducts of pyrimidine bases in DNA are found in nature. For example, pyrimidine−cyclobutane dimers are formed through the direct photolysis of DNA.[20] Likewise photolysis of psoralen derivatives in the presence of DNA leads to [2+2] adducts between psoralen and the pyrimidine bases.[21] There is also evidence that urocanic acid forms [2+2] cycloadducts with DNA bases.[22,23] The possibility that these biologically important base cycloadducts might photocleave in a similar adiabatic fashion will be the subject of future investigations.

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Supporting Information Available: Transient absorption spectra from photolysis of oxetanes **2** and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(20) Cadet, J.; Vigny, P. In *Bioorganic Photochemistry*; Morrison, H., Ed.; Wiley: New York, 1990; pp 1−272.

(21) Shi, Y.-B.; Lipson, S. E.; Chi, D. Y.; Spielmann, H. P.; Montforte, J. A.; Hearst, J. E. In *Bioorganic Photochemisty: Volume 1: Photochemistry and the Nucleic Acids*; Morrison, H., Ed.; Wiley: New York, 1990; pp 341−425.

(22) Morrison, H.; Bernasconi, C.; Pandey, G. *Photochem. Photobiol.* **1983**, *38*, 23−27.

(23) Mohammad, T.; Morrison, H.; HogenEsch, H. *Photochem. Photobiol.* **1999**, *69*, 115−135.