Photochemistry of Diketones: Observation of a Triplet State−Oxygen Adduct

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An early report by Saltiel et al. reports on the photooxidation of benzil by oxygen. This process was proposed to be mediated by a biradical intermediate in the form of an excited α-diketone−oxygen adduct.[1] The sensitized photoepoxidation of olefins in the presence of benzil or diacetyl and oxygen was also established to occur through this biradical intermediate,[2] within the general framework of the photosensitized oxygen-transfer mechanism originally suggested by Schenck.[3,4]

Later reports (see Scheme 1), based on the 1:2 stoichiometry of α-diketone (**1**) consumed to epoxide (**7**) formed, have established that the sensitizer-oxygen adduct (**3**) is only a precursor of the epoxidating agent and does not play an active role in the olefin (**6**) epoxidation. The active species was proposed to be an acylperoxyl radical (**5**),[5−8] formed from the cleavage of the biradical (**3**). The acyl radical (**4**) that results from this cleavage is trapped by oxygen producing a second epoxidizing agent.[6]

Several results support the mechanism of Scheme 1: (1) the reduced singlet oxygen lifetime sensitized by diketones following laser excitation, explained by quenching of singlet oxygen by acylperoxyl radicals,[10] (2) the enhanced photodecomposition of α-diketones under O_2 vs N_2,[1,6] and (3) the reduced reactivity of benzil in the presence of *trans*-stilbene, an efficient benzyl triplet quencher.[1,6] The observed epoxidation stoichiometry also supports the proposed mechanism.[8,9] However the triplet oxygen−adduct intermediate (species **3** in Scheme 1) has never been observed.

With the aim of understanding better the photochemistry of diketones in the presence of O_2, we performed laser flash photolysis (LFP) studies with 2,2′-thenil (TL) (see Scheme 2).

Following irradiation of TL under nitrogen a transient absorption spectrum is observed with maxima at 730 and 430 nm and a shoulder at 530 nm, as well as bleaching with a minimum at 310 nm (data not shown). The reactivity of the transient was examined in the presence of various quenchers; TL has a triplet energy (E_T) of 228 and 233 kJ/mol (from phosphorescence) in methylcyclohexane and 4:1 methanol/ethanol, respectively. Thus, O_2, 1,3-cyclohexadiene (E_T 219 kJ/mol[11]), and *trans*-stilbene (E_T 208 kJ/mol[11]) show quenching rate constants in excess of 10^9 M^{-1} s^{-1}, while naphthalene (E_T 253 kJ/mol,[11] i.e., above the TL triplet) shows no quenching. The quenching rate constants for trolox and for 1,4-cyclohexadiene, both good hydrogen donors, are fast, supporting an n,π* triplet. These results (see Table 1) establish the main transient as the TL triplet state.

The short lifetime of the TL triplet under oxygen also supports this assignment. In this case, not only the triplet−triplet absorption is observed following excitation, but also a new band, with maximum at 340 nm appears concurrently with TL triplet decay in acetonitrile, as shown in Figure 1. Similar transient spectra are obtained in toluene (see Supporting Information). The fitting of these traces shows that the growth rate constant at 340 nm (1.5 × 10^7 s^{-1}) has the same value as the triplet decay rate constant monitored at 420 nm (ca. 1.3 × 10^7 s^{-1}) (see Supporting Information). Similar observations were made in toluene, where

Scheme 1. Photooxidation of Diketones in the Presence of O_2 and Olefins[1,6,9]
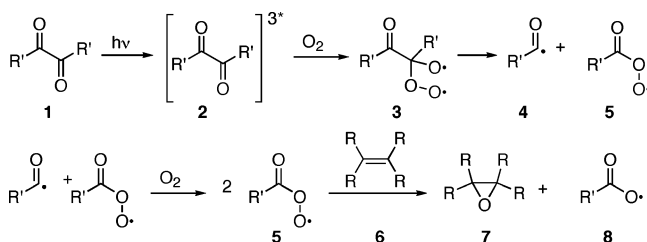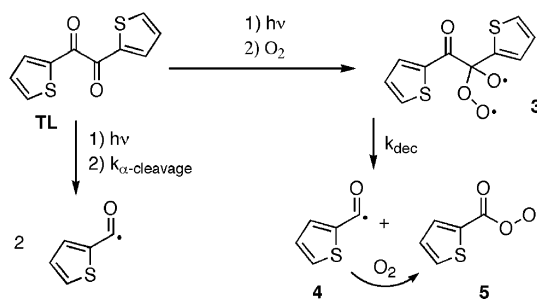
Scheme 2. α-Cleavage vs Triplet−Oxygen Adduct Formation

Table 1. Reactivity of 2,2′-Thenil with Various Substrates in Acetonitrile[a]

quencher	$k_q/M^{-1} s^{-1}$ [d]
O_2 [b]	1.8 × 10^9
tert-stilbene [c]	1.0 × 10^{10}
1,3-cyclohexadiene [c]	1.0 × 10^{10}
trolox [b]	8.2 × 10^9
1,4-cyclohexadiene [b]	4.6 × 10^8
naphthalene [b]	no quenching (≪10^6)

[a] All the values obtained in acetonitrile; TL concentration in the range of 9−30 × 10^{-5} M, laser 355 nm. [b] Monitored at 720 nm. [c] Monitored at at 650 nm. [d] Estimated error ≤ 10%.

the growth at 360 nm (rate constant of 8.2 × 10^6 s^{-1}), matches the triplet decay at 540 nm (rate constant of 7.5 × 10^6 s^{-1}). The new transient decays with rate constants of 3.3 × 10^6 s^{-1} and 1.0 × 10^6 s^{-1} in acetonitrile and toluene, respectively.

In Figure 2-A and 2-B we present the transient absorption time evolution, monitored at 340 nm, following excitation of TL under oxygen and air-equilibrated acetonitrile solutions, respectively. In the air-equilibrated sample, the growth rate constant (3.2 × 10^6 s^{-1}) is ca. 5-fold smaller than that under oxygen (vide supra); the decay rate constant (3.3 × 10^6 s^{-1}) is, however, the same under both conditions.

The quenching of TL triplet by oxygen in acetonitrile (resulting in a singlet oxygen quantum yield of 0.47) is not purely photophysical; the appearance of the new band centered at 340 nm (vide supra) indicates the occurrence of a photoreaction. The rate constant of decay for this newly formed transient (3.3 × 10^6 s^{-1}) is independent of the oxygen concentration. This supports assignment
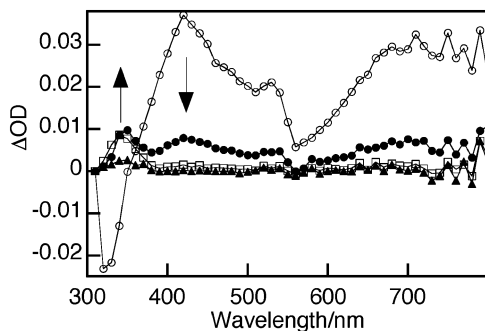
Figure 1. Transient absorption spectra obtained following 355 nm excitation of TL 1.21×10^{-4} M in acetonitrile, under O_2, recorded (○) 28 ns (triplet state contribution), (●) 140 ns, (□) 275 ns, (▲) 590 ns after the laser pulse.
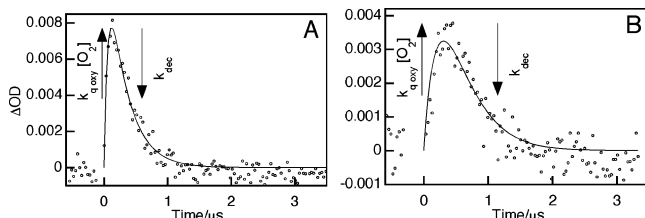

Figure 2. Transient absorption time evolution monitored at 340 nm, following 355 nm laser irradiation of TL 9.9×10^{-5} M in acetonitrile, (A) under O_2 atmosphere, and (B) in an air-equilibrated solution.

of structure **3** in Schemes 1 and 2 to the observed transient as proposed by Saltiel and later adopted by Bartlett and others.[1−4]

To gain knowledge on the dynamics of the triplet−oxygen adduct, we performed temperature-dependence studies on the decay rate constant of this transient to determine its characteristic Arrhenius parameters. From this we obtain activation energy values of 28.2 and 34.3 kJ/mol in acetonitrile and toluene, respectively. The respective preexponential values obtained are 3.2×10^{11} s^{-1} and 1.4×10^{12} s^{-1} for acetonitrile and toluene. This difference is within the experimental error of the ordinate. These values are reasonable for a unimolecular rearrangement, most probably the cleavage of the triplet−oxygen adduct (**3**) into products (**4**) and (**5**), according to Scheme 1.

We also considered two alternative intermediates that could account for the observed transient spectroscopy: (1) formation of an acyl radical produced from α-cleavage of the triplet diketone and (2) formation of an acylperoxyl radical produced following the reaction of the acyl radical and oxygen. Given the high reactivity of the acyl radical toward oxygen,[12] we can rule out the first possibility since the decay of the signal assigned to the triplet−oxygen adduct does not depend on oxygen concentration. The second possibility is not so easily eliminated. Acyl radicals are trapped by oxygen with a rate constant of 1.8×10^9 M^{-1} s^{-1},[12] about the same value we measured for oxygen quenching of TL triplets. To rule out the acyl−peroxyl radical as responsible for the observed growth band, experiments were recorded with di-*tert*-butyl peroxide and 2-thiophenecarboxaldehyde, as well as with 2,2′-thenoin. These substrates are convenient sources for acyl and the acyl−peroxyl radicals under N_2 and O_2 atmosphere, respectively.[13−16]

The results show that although the absorption spectra due to both radicals are similar to that assigned to the triplet−oxygen adduct, their time evolution differs significantly from that of the latter intermediate (see Supporting Information). These radicals show half-lives of at least 4 μs.

Product studies reveal the presence of 2-thiophenecarboxaldehyde formed following irradiation under nitrogen with Luzchem UVA lamps. Under oxygen the species formed is 2-thiophenecarboxylic acid. From these studies we can propose Scheme 2 as the operative one under the conditions employed, i.e. TL excitation under oxygen atmosphere. The formation of radicals would mostly be due to the cleavage of the triplet−oxygen adduct under these conditions.

We also attempted to observe the triplet−oxygen adduct for benzil and diacetyl, where its involvement has been inferred from product studies.[1,2,6,9,10] Transient absorption spectra were acquired for both species in acetonitrile under oxygen. There was no spectroscopic evidence for a transient with characteristics resembling those for the triplet−oxygen adduct observed in the TL system (see Supporting Information). Failure to detect **3** in these cases may be due either to weak absorbances or to short lifetimes. TL may be particular in that its triplet energy is almost the same as that for biacetyl (little triplet stabilization), but it bears an electron-donating moiety.

In summary, our LFP studies have produced compelling evidence consistent with the formation of a triplet α-diketone−oxygen adduct. The possibility of monitoring this new transient has enabled us to establish some of its decay parameters, such as activation energy and preexponential factor. Its lifetime (particularly at low temperature) is long enough to make additional reactivity studies possible.

Supporting Information Available: Experimental details and kinetic and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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