tions,[18a] additions of thiyl radicals to styrenes ($\rho \sim -0.4$ vs. σ^+),[22] and additions of $Cl_3C\cdot$ to styrenes ($\rho = -0.42$ vs. σ^+)[23] and aliphatic olefins ($\rho^* = -0.2$ to -0.4 vs. σ^0 or σ^*).[24] As shown in Table III, the substituent effects for additions of $PhCO_2\cdot$, $MeOO\cdot$, and t-$BuOO\cdot$ to styrenes also resulted in small negative ρ values ($\rho = -0.1$ to -0.3 vs. σ^+) with poor correlations. That is, these oxy radicals add to styrenes as a weak electrophile. In contrast, acylperoxy radicals afford large negative ρ values ($\rho = -1$ vs. σ^+), indicating the importance of polar effects in the radical additions to olefins.[25] The coincidence of ρ values between the reactions of $RCO_3\cdot$, RCO_3H, and $^1O_2$ is interesting. It is also interesting to recall that similar polar effects (i.e., $\rho = -0.3$ to -1.1 vs. σ^+) are known in benzylic hydrogen abstractions[27] where benzyl radicals are being formed.

In conclusion, α-diketones are photooxidized to 2 equiv of acylperoxy radical, which add to olefins 10^5-fold faster than alkylperoxy radicals and lead to effective epoxidations. Selective epoxidation of double bonds is possible since $RCO_3\cdot$ is not reactive to sulfides, sulfoxides, and pyridine. The photoepoxidation proceeds at low temperature or in the presence of pyridine; then is application to acid-sensitive or unstable epoxides may be possible.[26] The accompanying C–C cleavage of olefins proceeds via the addition of $RCO_2\cdot$ or $ROO\cdot$.

Experimental Section

GLC analyses were performed with a Yanagimoto G180 gas chromatograph using two different columns: PEG 20M, 20% on Chromosorb WAW; Silicon OV-17, 5% on Shimalite W. ^1H NMR spectra were recorded with a Hitachi R24B spectrometer.

Materials. Ring-substituted styrenes,[28] β,β-dimethylstyrene,[29] α,β,β-trimethylstyrene,[28] and 1,2-dimethylcyclohexene[30] were described previously. Other olefins were of commercial sources. Authentic epoxides were obtained by the epoxidations of olefins with perbenzoic acid.

Typical Photoepoxidation. General procedures were noted previously.[4] A 4 mL benzene solution of 2 mM benzil and 0.1 M α-methylstyrene in a Pyrex tube was irradiated under oxygen at over 320 nm with a 300-W medium-pressure Hg lamp for 1 h at 20 °C (water bath). As a filter solution, 5% aqueous sodium nitrate was used. GLC analysis showed 192% α-methylstyrene oxide, 138% acetophenone, 33% phenyl benzoate, 4% biphenyl, and 42% benzoic acid. % yields are mole % per mole of α-diketone consumed and benzoic acid was determined after the methylation with diazo methane. Acetophenone was also identified by $NaBH_4$ reduction to α-phenylethyl alcohol.

Relative rates of the olefin photoepoxidation were determined competitively by using 2 mM α-diketone and 0.02–1 M olefins. The relative yields of epoxides were determined by GLC analyses, affording the relative reactivities as listed in Tables III and IV.

Formaldehyde and methanol were detected for the photooxidation of biacetyl, but the reliable determination of their yields could not be attained by GLC analysis.

Registry No. $PhCH{=}CH_2$, 100-42-5; $PhMeC{=}CH_2$, 98-83-9; *trans*-$PhCH{=}CHMe$, 873-66-5; $PhCH{=}CMe_2$, 768-49-0; $PhMeC{=}CMe_2$, 769-57-3; *trans*-$PhCH{=}CHPh$, 103-30-0; *trans*-$PhCH{=}CHCOMe$, 1896-62-4; $CH_2{=}CHCN$, 107-13-1; $CH_2{=}CHCO_2Et$, 140-88-5; $CH_2{=}CHOCOMe$, 108-05-4; Ph_2S, 139-66-2; Ph_2SO, 945-51-7; Me_2SO, 67-68-5; $Ph_2C{=}CMe_2$, 781-33-9; $PhCO_3\cdot$, 35683-46-6; $PhCO_2\cdot$, 766-76-7; $MeCO_3\cdot$, 36709-10-1; $MeOO\cdot$, 2143-58-0; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1,2-dimethylcyclohexene, 1674-10-8; pyridine, 110-86-1; *p*-methoxystyrene, 637-69-4; *p*-methylstyrene, 622-97-9; *p*-chlorostyrene, 1073-67-2; *m*-chlorostyrene, 2039-85-2; benzil, 134-81-6; biacetyl, 431-03-8; benzoin, 119-53-9.

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(22) (a) Cadogan, J. I. G.; Sadler, I. H. *J. Chem. Soc. B* **1966**, 1191. (b) Church, D. F.; Gleicher, G. J. *J. Org. Chem.* **1975**, *40*, 536. (c) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 1701.

(23) Sakurai, H.; Hayashi, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945.

(24) Martin, M. M.; Gleicher, G. J. *J. Am. Chem. Soc.* **1964**, *86*, 233, 238, 242.

(25) (a) The observed preference of the addition of $RCO_3\cdot$ to C=C over H abstraction for cyclohexene has been explained by its highly electrophilic character.[13c,25b] (b) Zaikov, G. E.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3017.

(26) Such applications have been reported. (a) Malacria, M.; Goré, *J. Org. Chem.* **1979**, *44*, 885. (b) Büchi, G.; Fowler, K. W.; Nadzan, A. M. *J. Am. Chem. Soc.* **1982**, *104*, 544.

(27) Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 293.

(28) Ogata, Y.; Sawaki, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 194.

(29) Ogata, Y.; Sawaki, Y.; Shimizu, H. *J. Org. Chem.* **1978**, *43*, 1760.

(30) Sawaki, Y.; Ogata, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 793.

Photoreduction of Triplet Thioxanthone by Amines: Charge Transfer Generates Radicals That Initiate Polymerization of Olefins

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Thioxanthone triplet is photoreduced by amines via a charge-transfer or exciplex intermediate to thioxanthyl ketyl radical. This ion pair can be observed by nanosecond laser spectroscopy in polar solvents with easily oxidized dimethylaniline as reductant. The intermediacy of this species in benzene was indicated by the correlation of triplet quenching rates with amine ionization potential and by the absence of a significant isotope effect in triplet quenching by *tert*-butylamine-d_2. In contrast, tri-*n*-butylstannane reacts more rapidly than its ionization potential would dictate and exhibits a larger isotope effect. Addition of methyl methacrylate does not significantly alter the rates of decay for the ion pair of ketyl radical. Product studies show that the aminomethyl radical $PhN(CH_3)CH_2\cdot$ is the principal initiator of olefin polymerization.

Introduction

Mixtures of aromatic ketones with amines have acquired importance as photoinitiators of olefin polymerization.[1,2] It has normally been assumed that reduction of the excited state of the ketone by amine results in radicals which

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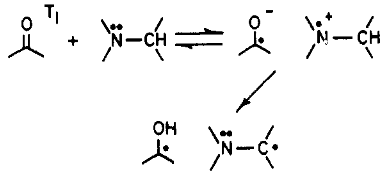
(1) Amirzadeh, G.; Schnabel, W. *Makromol. Chem.* **1981**, *182*, 2821.

(2) Davidson, R. S.; Goodin, J. W. *Eur. Polym. J.* **1982**, *18*, 597; Sandner, M. R.; Osborn, C. L.; Trecker, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *108* 3173.

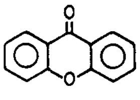
0022-3263/84/1949-3349$01.50/0

initiate the polymer chain. The identity of these radicals has not, however, been established.

The photoreduction of benzophenone by amines has been the focus of extensive work by Cohen[3-5] and Peters.[6] In contrast to the better-known photoreduction by alcohols, these authors have shown that this reduction occurs via an exciplex or ion pair intermediate which, in a subsequent step, transfers a proton to produce the expected radical pair. Evidence in support of this mechanism includes the direct observation of ion pairs in the picosecond domain,[6] the correlation of triplet quenching rate constants with the ionization potential of the quencher,[4] and the insensitivity of the quantum yield for ketyl formation to amine structure.[3] The only discordant note was truck by Cohen's observation[3] of significant deuterium kinetic isotope effects on the triplet quenching rate constant. He attributed these effects to a reversible electron-transfer step, followed by rate-determining proton transfer.



The electronic configuration of the lowest triplet state is known to have a major effect on the photoreduction of ketones.[7] Only ketones with lowest nπ^* triplet state are reduced by alcohols, while amines will reduce either nπ^* or $\pi\pi^*$ triplets. Surprisingly little work has been devoted to exploring the effect of substituting a ketone with a $\pi\pi^*$ triplet state for benzophenone, which has an nπ^* triplet. Studies involving xanthone[8] **1** and fluorenone[9] **2** have supported in broad outline the operation of a mechanism similar to that of benzophenone.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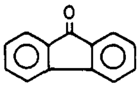
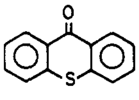

2


TX

In this work, the photoreduction of thioxanthone (TX), which has a lowest $\pi\pi^*$ triplet state at 65.5 kcal/mol,[10] has been investigated. We have sought to explore the consequences of the change of electronic configuration on the mechanism by nanosecond flash photolysis, kinetics, isotope effects, and product isolation. In addition, we investigated the effect of adding a polymerizable monomer on the various intermediates we identified.

Results

A. Nanosecond Spectroscopy, Assignment of Transient Products. The transient UV absorption spectrum of thioxanthone triplet has been reported by Yip and co-workers,[11] who observe a maximum at 630 nm in acetonitrile, and by Amirzadeh and Schnabel,[1] who report maxima at 630 nm in acetonitrile and between 650 nm and 670 nm in benzene. Pulsed irradiation of a deoxygenated benzene solution of thioxanthone with the 337.1 nm light of a nitrogen laser, set up as described previously,[12] provides a transient UV spectrum with a peak at 650 nm in benzene (Figure 1), or 620 nm in acetonitrile. Thioxanthone triplet is known to undergo a self-quenching reaction and rate constants in benzene of 1.8×10^6 M^{-1} s^{-1} [11] and 6×10^{10} M^{-1} s^{-1} [13] have been reported. Our apparent first-order rate constant at an initial thioxanthone concentration of 8.5×10^{-5} M is $2.21 \pm 0.04 \times 10^5$ s^{-1}, in reasonable agreement with the latter estimate of the bimolecular rate constant.

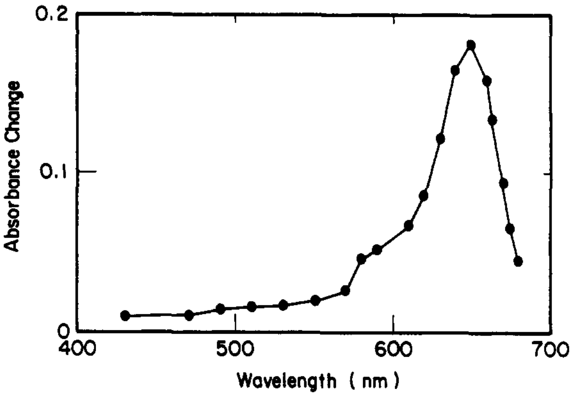


Figure 1. Transient absorption spectrum obtained 1.2 μs after pulse irradiation of 8.5×10^{-5} M thioxanthone in benzene.

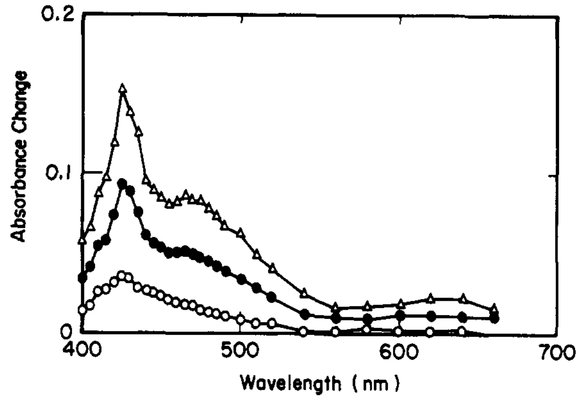


Figure 2. Transient absorption spectra of 1.1×10^{-3} M thioxanthone in 0.13 M DMA/benzene, obtained 2.8 μs (△), 15.4 μs (●), and 163 μs (○) after pulse irradiation.

The absorption at 650 nm is quenched when dimethylaniline (DMA) is added to a deoxygenated benzene solution of thioxanthone. A new absorption is noted with a maximum at 425 nm and a shoulder at 470 nm (Figure 2). This absorption, which grows in on the same time scale as the disappearance of the triplet absorption and then decays more slowly, is assigned to the thioxanthyl ketyl radical. In support of this assignment, the observed spectrum resembles those of Marteel et al.,[14] who irradiated thioxanthone in cyclohexane, and Schnabel and Amirzadeh,[1] who quenched 2-methylthioxanthone triplet with bis(2-hydroxyethyl)methylamine. Also, this absorption is

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(3) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419; *Ibid.* **1981**, *103*, 1048.

(4) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.

(5) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

(6) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403; *Ibid.* **1982**, *104*, 6542. Shaefer, C. G.; Peters, K. S. *Ibid.* **1980**, *102*, 7567. Peters, K. S.; Pang, E.; Rudzki, J. *Ibid.* **1982**, *104*, 5535.

(7) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(8) Wilkinson, F.; Garner, A. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 222.

(9) Guttenplan, J. B.; Cohen, S. G. *Tetrahedron Lett.* **1969**, 2125; *Ibid.* **1972**, 2163. Davidson, R. S.; Santhanam, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2355.

(10) Dalton, J. C.; Montgomery, F. C. *J. Am. Chem. Soc.* **1974**, *96*, 6230. Herkstroeter, W. G.; Lamula, A. A.; Hammond, G. S. *Ibid.* **1964**, *86*, 4537.

(11) Yip, R. W.; Szabo, A. G.; Tolg, P. K. *J. Am. Chem. Soc.* **1973**, *95*, 4471.

(12) Horn, K. A.; Schuster, G. B. *Tetrahedron* **1982**, *38*, 1095.

(13) DeBeer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 655.

(14) Marteel, J. P.; Decock, P.; Goudmand, P.; Derolder, P. *Bull. Soc. Chim. Fr.* **1975**, 1767.

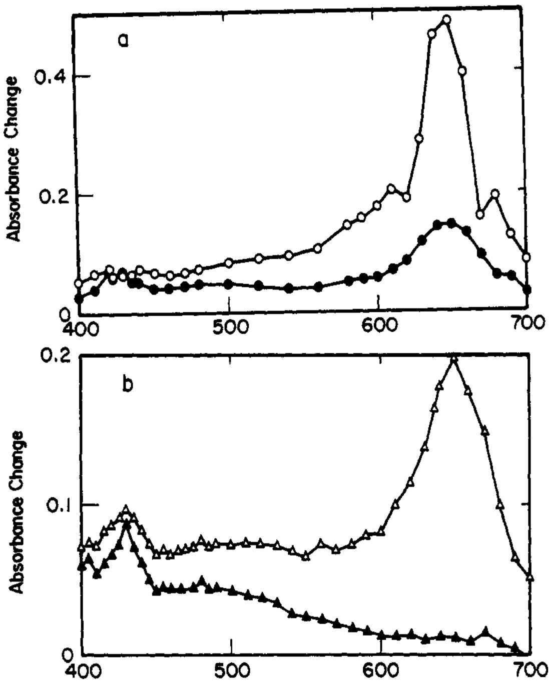

Figure 3. Transient absorption spectra of 1.0×10^{-3} M thioxanthone (a) in 0.2 M *tert*-butylamine obtained 80 ns (○) and 1400 ns (●) after pulse irradiation and (b) in 0.03 M tri-*n*-butylstannane obtained 345 ns (△) and 1505 ns (▲) after pulse irradiation.

rapidly quenched if oxygen-saturated solutions are used.

In these experiments the hydrogen atom donor apparently contributes little to the observed transient spectrum, allowing the hypothesis that the aminomethyl radical $PhN(CH_3)CH_2\cdot$ is present neither to be confirmed or denied. Scaiano[15] has recently shown this radical to be almost transparent in the region of interest.

Similar experiments showed that *tert*-butylamine (Figure 3a) or tri-*n*-butylstannane (Figure 3b) quench thioxanthone triplet in benzene and provide the same transient absorption at 425 nm. The peak shape was less completely resolved in these experiments since triplet quenching is slower, and the triplet absorption overlaps with the putative radical. The similarity of the spectra obtained by using the different quenchers lends additional confidence to our assignment of this transient product.

Spectra obtained by using DMA in acetonitrile are strikingly different from those in benzene solution. At 25 ns after the laser pulse (Figure 4), the transient UV spectrum shows two maxima at 460 and 620 nm. After 136 ns, the 620 nm peak has disappeared and is replaced by a new broad absorption at 650 nm, while the 460 nm peak grows somewhat and acquires a shoulder at 420 nm. Subsequent spectra show the decay of all three of these peaks. The 620 and 420 nm peaks have already been identified as corresponding to the thioxanthone triplet and ketyl radical, respectively. We assign the 460 and 650 nm peaks to the DMA radical cation and the thioxanthone radical anion.

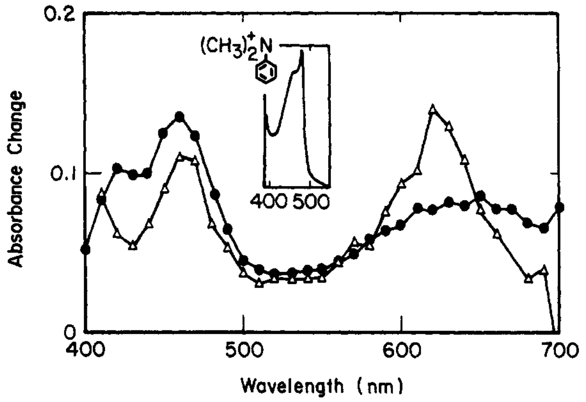

Figure 4. Transient absorption spectra of 6.8×10^{-4} M thioxanthone in 9.9×10^{-3} M DMA/CH_3CN obtained 25 ns (△) and 136 ns (●) after pulse irradiation. The inset shows the spectrum of $DMA^{+}\cdot$ obtained by radiolysis.[16]

Table I. Quenching of Triplet Thioxanthone

quencher	rate constant, $M^{-1}\,s^{-1}$ benzene	 acetonitrile	ionization potential, eV
dimethylaniline	$9.1 \pm 0.1 \times 10^9$	$5.3 \pm 0.8 \times 10^9$	7.14^a
triethylamine	$1.30 \pm 0.02 \times 10^9$		7.5[illegible]
dibutylamine	$2.7 \pm 0.1 \times 10^9$		7.[illegible]
tert-butylamine	$4.6 \pm 0.3 \times 10^6$	$8.7 \pm 0.5 \times 10^6$	8.[illegible]^b
tri-*n*-butylstannane	$5.1 \pm 0.3 \times 10^7$		8.80^c

^{a}Reference 4. ^{b}Watanabe, K.; Nakayama, T.; Mettl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369. ^{c}Beltram, G.; Fehlner, T. P.; Michida, K.; Kochi, J. K. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 153.

Spectra of varying provenance attributed to the DMA radical cation have been reported in the literature[16] and all have reported a peak in the 460–470 nm region. The optical spectrum of thioxanthone radical anion has not been previously reported, but the xanthone radical anion has been reported[8,17] to have a broad absorbance at 610 nm.

Two quenching experiments lend support to the assignment of the thioxanthone radical anion. In the first, a solution of thioxanthone and DMA containing 1.1×10^{-3} M acetic acid is compared to one containing no acid. The acid-containing solution shows enhanced absorption at 420 nm and reduced absorption at 650 nm. Such a result is consistent with protonation of the radical anion, leading to increased yields of ketyl radical.

In the second experiment oxygen-saturated acetonitrile solutions are used. This accelerates the decay of the 650 nm peak but does not affect the rate of decay of the peak at 460 nm. The 420 nm peak is not observed, consistent with the hypothesis that radical anion is reoxidized to thioxanthone before it can be protonated.

Spectra were also obtained by using *tert*-butylamine as quencher in acetonitrile. In contrast to the results with DMA, no ions are observed. Instead, the spectra strongly resemble those previously obtained in benzene; quenching of the triplet absorbance at 620 nm produced a new long-lived absorption at 420 nm, assigned to the ketyl radical.

B. Kinetics and Isotope Effects. Bimolecular rate constants for triplet quenching were determined for several quenchers, including those described above. The triplet decay was assumed to follow a rate law as in eq 1, and k_q

$$\frac{-d(T_1)}{dt} = k_d(T_1) + k_q(T_1)(Q) \tag{1}$$

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(15) Scaiano, J. C. *J. Phys. Chem.* **1981**, *85*, 7851.

(16) Shida, T.; Hammill, W. H. *J. Chem. Phys.* **1966**, *44*, 2369; Arimitsa, S.; Kimura, K.; Tsabomura, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1858; Shida, T.; Nosaka, Y.; Kato, T. *J. Phys. Chem.* **1978**, *82*, 695. Frolov, A. N.; El'tsov, A. V.; Kul'bitskaya, O. V.; Pomyaer, A. I. *J. Org. Chem. USSR* **1981**, *16*, 2099.

(17) Hirota, N.; Weissman, S. I. *J. Am. Chem.* **1964**, *84*, 2538.

Scheme I

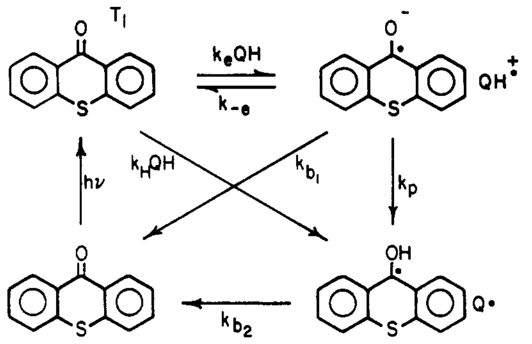


Table II. Isotope Effects on Triplet Thioxanthone Quenching

quencher	substrate	isotope effect (k_H/k_D) benzene	isotope effect (k_H/k_D) acetonitrile
t-BuNH$_2$	TX	1.3 ± 0.1	1.1 ± 0.1
t-BuNH$_2$	Ph$_2$CO	1.8[a]	
n-Bu$_3$SnH	TX	2.6 ± 0.2	

[a] Reference 3.

was determined by least-squares[18] fitting of the observed decay to a pseudo-first-order rate constant at each of several quencher concentrations. The slope of a plot of first-order rate constants vs. quencher concentration is k_q. These values are presented in Table I.

Note that the observed rate constants for the amines correlate well with the gas-phase ionization potentials of the quencher. Similar correlations have been noted for benzophenone[4] and fluorenone.[19] Note, however, that tri-*n*-butylstannane quenches thioxanthone triplet more rapidly than would be predicted from its ionization potential. Changing the solvent from benzene to acetonitrile has relatively little effect on reaction rates. This may indicate that, if an intermediate complex is present, it is relatively nonpolar.

Kinetic deuterium isotope effects ought to be a powerful tool in determining the relative importance of electron vs. hydrogen atom transfer in the quenching of thioxanthone triplet. As inspection of Scheme I shows, of the two rate-determining steps, k_e and k_H, only k_H ought to have a primary isotope effect. Isotope effects for *tert*-butylamine and tri-*n*-butylstannane were determined by the technique described above, with the appropriate deuterated substrates. The results are presented in Table II. Quite small isotope effects were obtained for *tert*-butylamine in both benzene and acetonitrile. Apparently, charge transfer or exciplex formation is more important than hydrogen atom transfer, even for a poor electron donor like *tert*-butylamine. Tri-*n*-butylstannane has an ionization potential very similar to that of *tert*-butylamine, but its isotope effect is much higher. This presumably reflects a change in mechanism, with rate-determining hydrogen atom transfer (k_H) becoming dominant.

C. Radical Yield Isotope Effect. Monitoring of the transient absorbance at 425 nm provides a useful measure of the relative yield of ketyl radical. Absolute yields cannot be obtained because the extinction coefficient of the radical is unknown. This technique could be used, however, to perform an interesting isotope effect experiment designed to probe the partitioning of the presumed exciplex intermediate between its various modes of decomposition. As was shown in Scheme I, this intermediate could transfer a proton to provide the ketyl radical (k_p), or undergo back electron transfer (k_{-e} or k_{b_1}) to either the triplet or the ground state. Since k_p ought to show a substantial isotope effect, use of a deuterated quencher should reduce the yield of ketyl radical so long as k_{-e} or k_{b_1} are of comparable magnitude to k_p. Equal concentrations of *tert*-butylamine, or *tert*-butylamine-d_2 were added to a thioxanthone solution in benzene. Several transient decays of each sample were obtained at 430 nm, extrapolated to zero time, and averaged. The ratio of the absorbances (A_H/A_D) is 1.02 ± 0.05. Thus, we can conclude that back electron transfer to either the triplet or ground state is not important, and the primary mode of decomposition of the exciplex is proton transfer.

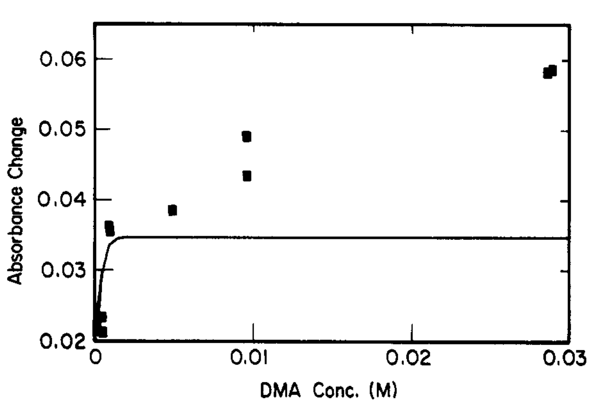
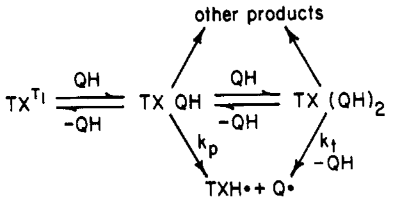


Figure 5. Plot of the theoretical and observed dependence of the ΔOD at 430 nm, observed 58 ns after pulse irradiation, on the concentration of DMA.

Scheme II



D. Intermediacy of Triplexes. Increasing numbers of photoreactions have been reported to involve triplexes.[20] We probed for the intermediacy of triplexes in our reaction by examining the effect of dimethylaniline concentration on the radical yield. We reasoned that if a triplex is an intermediate in the pathway to ketyl radical, that exciplex and triplex ought to generate the radical with different efficiencies, since k_p could only equal k_t by coincidence. The efficiency of production of radical from exciplex would thus be dependent on the amine concentration. If no triplex is formed, or if the triplex had no mode of decay other than return to the exciplex, this efficiency would be invariant, and the yield of radical would be proportional to the yield of exciplex. This, of course, varies with amine concentration but in an easily predicted manner. Thus, if the latter hypothesis is correct, the absorbance of the ketyl radical ought to follow the curve described by eq 2,

$$A = \frac{A_c k_q \tau Q}{1 + k_q \tau Q}(1 - e^{-k_q Q t}) \qquad (2)$$

where k_q is the triplet quenching rate constant, τ is the triplet lifetime, Q is the amine concentration, t is the time after the laser flash at which the analysis is performed, and A_c is a proportionality constant. As can be seen in Figure

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[18] Computer program RLS, written by J. R. Hurst, University of Illinois, Urbana, IL, 1983.

[19] Guttenplan, J. B.; Cohen, S. G. *Tetrahedron Lett.* **1972**, 2163.

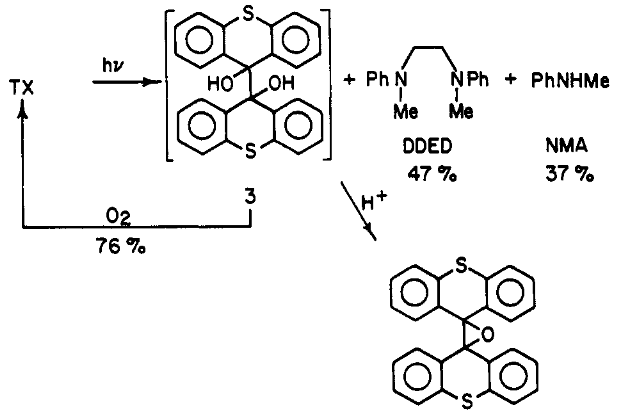
[20] Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *18*, 1.

5, this equation describes a curve which levels off at ca. 0.002 M in amine. At this concentration, all the triplet is quenched by amine, and the yield of exciplex (and thus radical) depends solely on light intensity.

As can be seen from Figure 5, the experimental points diverge from the calculated line. Thus, simple formation of an exciplex does not adequately explain the observed results. A triplex or other DMA concentration-dependent species is needed to explain the dependence of radical yield on amine concentration at higher amine concentration. The divergence of the experimental points is in the positive direction, implying increased efficiency as the equilibrium concentration of triplex increases.

E. Identification of Products. Preparative scale reactions were run with excess DMA as reductant in Vycor vessels in a Rayonet reactor equipped with 350 nm lamps. The UV absorption of thioxanthone at 380 nm ($\epsilon_{\text{PhH}} = 6.15 \times 10^3$ M^{-1} cm^{-1}) provides a useful way of estimating the extent of reaction, while amine concentrations were measured by GC using an internal standard. Simultaneous monitoring by UV and GC showed that, in deoxygenated benzene, 1 equiv of DMA consumes 1 equiv of thioxanthone. Two volatile primary products were observed by GC and were identified as *N*-methylaniline (NMA) (37%) and *N,N'*-dimethyl-*N,N'*-diphenylethylenediamine (DDED) (47%) by comparison to authentic samples.

Both of these photoproducts are logically derived from $PhN(CH_3)CH_2\cdot$, the amine radical partner of the thioxanthyl ketyl radical. NMA is a common product[5] in ketone photoreductions and is believed to be derived from hydrolysis of the iminium salt $PhN(CH_3){=}CH_2^+$. The latter photoproduct (DDED), formed by coupling of two amine radicals, has not to our knowledge been observed previously in a photoreduction, though it has been observed in other reactions in which the amine radical was implicated.[21] This product is itself a good photoreducing agent and in a control experiment is rapidly destroyed by thioxanthone with concomitant formation of 1 mol of NMA per mole of dimer consumed.



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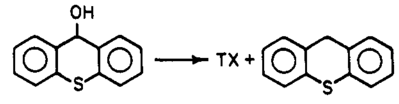
The identity of the thioxanthone reduction product was at first unclear. When a preparative photolysis sample is worked up in air by extraction with dilute hydrochloric acid, the sole product is thioxanthone, which is recovered in 76% isolated yield. Closer investigation showed that even in a cell closed by a Teflon stopcock, thioxanthone begins to return immediately after the photolysis. This process could be followed by UV at 380 nm. The thioxanthone return can be inhibited by storing the photolysate in a sealed ampule from which oxygen had been eliminated by repeated freeze/thaw degassing or by addition of 9.1×10^{-3} M 2,5-di-*tert*-butyl-4-methylphenol.

This return also occurs thermally. GC analysis of the photolysate indicated that thioxanthone was present far in excess of its real concentration, as determined by UV spectroscopy. This is apparently due to pyrolysis of the photoproduct in the injection part of the GC.

Literature precedent[5,6] from benzophenone and fluorenone chemistry suggested thioxanthol **5** or dithioxanthyl pinacol **3** as possible identities for this easily oxidized material. The former is reported to disproportionate[22,23] on heating to thioxanthene **6** and thioxanthone and to air oxidize.[24] We therefore prepared authentic samples of both thioxanthol[24] and thioxanthene[25] by literature procedures.



5 6

Like the photoproduct, thioxanthol pyrolyzes in the GC injection part. Two peaks of equal area are produced, which comparison to authentic materials shows to be thioxanthene and thioxanthone. Thioxanthene, however, is only a minor product in the photoproduct pyrolysis (1.3% yield). This result sets an upper limit on the thioxanthol yield of 2.6%. This conclusion could be confirmed by ^{1}H NMR spectroscopy. Photolysate solutions, freed of amines by rapid washing with dilute hydrochloric acid, exhibit ^{1}H NMR spectra with a large multiplet of aromatic hydrogens at δ 7.9–7.1, but no resonances between δ 7.0 and 1.7. Specifically, the δ 5.6 and 3.9 resonances of thioxanthol and thioxanthene, respectively, are absent.

Dithioxanthyl pinacol has not been prepared previously. Dixanthyl pinacol has been prepared, however, and has been shown[22,26] to decompose to xanthone both thermally and photochemically. Attempts to prepare dithioxanthyl pinacol by zinc/hydrochloric acid reduction of thioxanthone[27] instead produced dispiroepoxide **4**, a product which logically results from acid-catalyzed dehydration of the desired pinacol. This material was stable to oxidation under conditions which oxidize the photoproduct. Treatment of the photoproduct with acid also provides epoxide in 24% yield. We suggest, then, that the easily oxidized intermediate formed in the photoreduction of thioxanthone is the pinacol.

F. Effect of Olefin Addition. Mixtures of ketone and amine are commonly used as photoinitiators of olefin polymerization. Comparison of transient absorption spectra obtained in 1.0 M methyl methacrylate in benzene and acetonitrile to spectra obtained in the absence of methacrylate shows that the only significant qualitative change is the reduction in overall intensity. This is undoubtedly related to the competition of DMA and methyl methacrylate for thioxanthone triplet. Spectra obtained by using styrene and butyl vinyl ether as the added olefin also resulted in no important qualitative changes.

This absence of quenching is also reflected in the effect

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(21) Swan, G. A.; Fayadh, J. M. *U. S. C.F.S.T.I. AD Rep.* **1969**, AD-692106; *Chem. Abstr.* **1970**, *72*, 73130p.

(22) Schönberg, A.; Mustafa, A. *J. Chem. Soc.* **1944**, 305.

(23) Field, E. K.; Meyerson, J. *J. Org. Chem.* **1965**, *30*, 937. Shine, H. J.; Hughes, L. *Ibid.* **1966**, *31*, 3142. Seidl, H.; Biemann, K. *J. Heterocycl. Chem.* **1967**, *4*, 209.

(24) Oehlschager, E. F.; MacGregor, I. *J. Am. Chem. Soc.* **1950**, *72*, 5332.

(25) Mustafa, A.; Hilmy, M. K. *J. Chem. Soc.* **1952**, 1343.

(26) Schönberg, A.; Mustafa, A. *J. Chem. Soc.* **1944**, 67. Bergmann, E.; Schuchardt, W. *Liebigs Ann. Chem.* **1931**, *487*, 225.

(27) This is a variant of Mayer's synthesis[28] of dithioxanthylidene.

(28) Mayer, F. *Chem. Ber.* **1909**, *42*, 1132.

Table III. Effect on Decay Rates of 1.0 M Methyl Methacrylate

	apparent first-order rate constants, s^{-1}		
system	ketal radical	ketal anion	amine cation
benzene	4.28×10^4		
benzene/MMA	2.74×10^4		
acetonitrile	6.82×10^4	9.61×10^4	6.72×10^4
acetonitrile/MMA	4.25×10^4	1.41×10^5	4.66×10^4

of these olefins on the rate of decay of the various intermediates. In Table III, the apparent first-order rates of decay of all three species are tabulated both in the presence and absence of methyl methacrylate. Note that in no case is the difference in rate greater than a factor of two, and that in most cases, even the direction of the change is the opposite of that expected. Since these observed rate constants probably include some bimolecular components, this change in direction may reflect the lower concentrations of the species involved. Even so, it is difficult to reconcile these low quenching rates with olefin trapping of the species involved. These results suggest that the intermediate immediately responsible for olefin polymerization is the amine radical. To test this hypothesis, we examined the effect of olefin addition on product yields.

Addition of 1.0 M methyl methacrylate to the reaction mixture has a drastic effect on the yields of the amine photoproducts. The yield of NMA decreases from 37% to 14%, and the yield of DDED to less than 1%. This logically reflects the draining off of amine radical to initiate polymer chains; the greater sensitivity of the yield of DDED is presumably due to the bimolecular nature of its formation.

The effects of methyl methacrylate on the thioxanthyl moiety is more complex. Irradiation of deoxygenated benzene solutions containing thioxanthone, dimethylaniline, and 1.0 M methyl methacrylate produces a shoulder at 420 nm in the absorption spectrum of the mixture, which grows in as the 380 nm peak of thioxanthone diminishes, and gives the solution a bright yellow color. As soon as the light is turned off, this new absorption begins to decay and the regeneration of thioxanthone begins. The process is more rapid than that observed in the absence of olefin, is dramatically accelerated by the admission of oxygen, and returns 52% of the ketone originally present.

Discussion

Our results clearly point to the intermediacy of an exciplex or ion pair intermediate in ketyl radical generation in the thioxanthone/amine system. Thioxanthone triplet is thus similar to benzophenone triplet in its propensity to react with electron donors. We base this conclusion on (1) the dependence of triplet decay rate on amine ionization potential, (2) the observation of UV absorbances assigned to ions in acetonitrile, and (3) the low isotope effect for reaction of thioxanthone with *tert*-butylamine.

Our observation of the effect of amine ionization potential on the rate implies that electron transfer is rate determining. The energetic outcome of electron transfer from an excited state can be calculated by using the Rehm–Weller equation[29] (eq 3), relates it to the oxidation

$$\Delta G_{ET} + 23.06[E(D/D^+) - E(A^-/A) - (e_0^2/\epsilon a)] - \Delta E_{0,0} \qquad (3)$$

potential $E(D/D^+)$ of the donor, the reduction potential $E(A^-/A)$ of the acceptor, the energy $\Delta E_{0,0}$ of the excited state, and an electrostatic term involving the dielectric constant of the solvent. In acetonitrile this last term ought to be small, and substitution of the appropriate values[30] shows that electron transfer should be exergonic for any quencher with a lower oxidation potential than 1.18 V. Thus electron transfer is probably complete for DMA (0.71 V vs. SCE[32]) and triethylamine (1.00 V vs. SCE[33]). Our observation of free ions in the thioxanthone/DMA system is consistent with this conclusion.

These conclusions cannot readily be extended to benzene solution, since both the electrostatic term and the redox potentials are solvent dependent. We observe no ions in this solvent, so it is likely that electron transfer is endergonic for all the amines used. If so, it is more likely that the intermediate is an exciplex with only partial charge transfer and that no more than a low steady-state concentration of it is formed.

Our observation of a small isotope effect confirms the conclusion that electron transfer is rate determining in the thioxanthone/*tert*-butylamine system. Observation of a substantial isotope effect in the thioxanthone/tri-*n*-butylstannane system shows that electrostatic factors do not completely determine the course of reaction. As was noted in Table I, the ionization potentials, and thus presumably the oxidation potentials, of the amine and the stannane are comparable. Yet the latter reacts more than ten times more rapidly, a result which, along with the observed isotope effect, shows the operation of the direct hydrogen-transfer mechanism (k_H in Scheme I).

The principal factors affecting this direct hydrogen transfer route are the hydrogen donating ability of the quencher and the accepting ability of the triplet state. The former should follow the bond strength in the appropriate hydrogen heteroatom bonds. Using typical values,[34] one can estimate a 30 kcal/mol difference in the energy needed to break a Sn–H compared with a N–H bond. This added stabilization is presumably reflected in the transition state, and lowers it below that for electron transfer for the stannane.

Orbital symmetry[7] imposes a barrier to hydrogen abstraction on $\pi\pi^*$ triplet ketones like thioxanthone but not on $n\pi^*$ ketones like benzophenone. Thus is it interesting to compare our isotope effects with *tert*-butylamine with the comparable one using benzophenone. Cohen et al.[3] found a distinctly larger effect (Table II) under identical reaction conditions. These authors explain their results by invoking rate-determining proton transfer from an exciplex in rapid equilibrium with the triplet. This would correspond to making k_p in Scheme I rate determining. However, in the thioxanthone system, our yield isotope effect experiment shows that electron transfer is not rapidly reversible, while our small isotope effects are inconsistent with rate-determining proton transfer.

A second difference comes to light if the reaction rate constants are compared. *tert*-Butylamine quenches benzophenone with a rate constant[3] of $6.4 \times 10^7\ M^{-1}\ s^{-1}$, roughly ten times faster than it does thioxanthone. Yet the reduction potentials of the excited states (measured

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[29] Rehm, D.; Weller, A. *Ber. Bunseges. Phys. Chem.* **1969**, *73*, 834.

[30] For thioxanthone $E(A^-/A) = -1.66$ V vs. SCE[31] and $\Delta E_{0,0} = 65.5$ kcal/mol.[10]

[31] Measured by G. Slocum of this laboratory and corrected to SCE.

[32] Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker, Inc.: New York, 1970, 275.

[33] Reference 32, p 279.

[34] The bond energy of Me_3Sn–H is 74 kcal/mol,[35] and that of MeNH–H is 103 kcal/mol.[36]

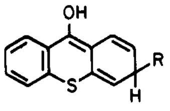
[35] Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17.

[36] Golden, D. M.; Solly, R. K.; Gae, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 363.

by 23.06 $E(A^-/A) + \Delta E_{0,0}$ from eq 3) of these two ketones are remarkably close,[30,37] and the previously noted correlation between ΔG_{ET} and reaction rate would lead one to predict that k_e for the two triplets would be similar. We suggest that, in light of our results, competition by a direct hydrogen-transfer route (k_H) may be important for $n\pi^*$ triplet ketones. Since the fraction of triplet participating in each route would depend on the exergonicity of electron transfer, this hypothesis would also explain the effect of solvent on the isotope effect we observed.

Our experiments in the presence of methyl methacrylate show that the amine radical is the most important initiator of polymerization in these systems. This conclusion is supported by (1) the absence of polymerization of olefins which quench the triplet too rapidly,[1] (2) the lack of detectable quenching of the radical ions or ketyl radical by olefin, (3) the change in amine product yields, and (4) the recovery of thioxanthone from the photolysis mixture.

The change in products signalled by the yellow intermediate is an unforseen result from this work. We identify this new intermediate as a "light-absorbing transient" (LAT) of the type previously reported by several authors.[39,40] Such products have normally been attributed to para coupling of the ketyl radical 7 with some other radical. In the present case, this second radical could be another ketyl radical or the polymeric radical formed during methacrylate polymerization. In either case, this assignment is in line with the thermal and oxidative instability of the product.



7

In contrast to many of these earlier observations, the yield of the LAT is quite high in this system. If it is assumed that the yield of thioxanthone from LAT can be no greater than 100%, then the yield of LAT must be at least 52%. This high yield does have one precedent in the work of Scaiano,[39] who observed enhanced formation of a LAT in aqueous micellar solution. Since both experiments involve restricting the motion of the ketyl radical, either by micelle formation or incipient polymerization, this may be important in dictating the partitioning of this radical between photoproducts.

Regardless of the identity of the new intermediate, it should be noted that these results confirm our earlier conclusion that the thioxanthyl ketyl radical is not the major initiator of olefin polymerization. The relatively high yield of recovered thioxanthone is in contrast to the sharp reduction noted in the yields of amine radical-derived products in the presence of the monomer.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian Associates HR-220 spectrometer equipped with a Nicolet computer. Mass spectra were obtained on either a Varian Associates MAT CH-5 or 731 mass spectrometer. Ultraviolet-visible spectra were recorded on a Perkin-Elmer Model 552 spectrometer. Gas chromatography was performed on a Varian Associates 3700 gas chromatograph equipped with a linear temperature programmer, flame ionization detector, and Hewlett-Packard 3390A integrator. Glass columns were packed with either 10% OV-101 or 10% QF-1 on silanized Chromosorb W. Melting points were obtained on a Büchi Schmelzpunktbestimmungsapparat and elemental analyses were performed by the Analysis Laboratory, University of Illinois.

Benzene (Burdick & Jackson, distilled in glass) and ether (J. T. Baker, anhydrous) were distilled from purple solutions of benzophenone ketyl. Acetonitrile was refluxed over calcium hydride under nitrogen and fractionally distilled with a 100-cm vacuum-jacketed column packed with glass helices. Thioxanthone was recrystallized from absolute ethanol. Dimethylaniline was distilled under reduced pressure. Butyl vinyl ether, methyl methacrylate, and styrene were distilled under nitrogen immediately before use. Thioxanthol,[24] thioxanthene,[25] and *tert*-butylamine-d_2[3] were prepared by literature procedures. DDED was prepared by reductive formylation[41] of 1,2-dianilinoethane.

Transient Spectra and Kinetics. Our nitrogen laser system has been described previously.[12] Solutions in dry benzene or acetonitrile were placed in 1-cm quartz fluorescence cells equipped with a stir bar and Teflon stopcock, and purged by bubbling nitrogen through them for 10 min. The solutions were continuously stirred during the photolysis. Triplet quenching rate constants were determined by using similarly prepared samples. The thioxanthone concentration was 1×10^{-4} M and transient decays showed first-order behavior.

Preparation of Dispiro[[9*H*]-thioxanthene-9,2′-oxirane-3′,9″-[9*H*]-thioxanthene] (4). A 50-mL three-neck round-bottom flask was equipped with a condenser, nitrogen line, pressure equalizing addition funnel, and stir bar. This was charged with 1.0 g (4.72 mmol) of thioxanthone and 40 mL of glacial acetic acid. This mixture was heated until the thioxanthone dissolved. Zinc dust (313.6 mg, 4.72 mmol) was added, followed by dropwise addition of 1.2 mL (14.2 mmol) of concentrated hydrochloric acid. Gas evolution was observed as the grey-green suspension turned orange-yellow. After 10 min, the mixture was allowed to cool. Suction filtration provided a white solid which was washed with 3 M hydrochloric acid.

The crude product (1.109 g, 110%) was triturated from 1,2-dichloroethane to remove 72.1 mg (7.2%) of white needles which were shown by comparison to authentic materials to be dithioxanthylidene. The residue was recrystallized from 1,2-dichloroethane to provide 302.1 mg (30.1%) of white crystals. The analytical sample was obtained by repeated chromatography on silica gel eluted with benzene (94.2 mg, 9.4%): mp 319–320 °C; IR ($CHCl_3$) no bands above 3100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.1 (16 H, m); mass spectrum, m/z (relative intensity) 408 (100.0), 392 (31.8), 379 (76.1), 347 (13.4); exact mass ($C_{26}H_{16}OS_2$) calcd 408.0643, obsd 408.0644.

Reisolation of Thioxanthone after Photolysis. A solution of 32.0 mg (0.15 mmol) thioxanthone in 30.0 mL of dry benzene was placed in a Vycor photolysis vessel closed with a Teflon stopcock. To this was added 0.4 mL (3.25 mmol) of DMA. The sample was purged by bubbling nitrogen through it for 5 min and then photolyzed in a Rayonet reactor equipped with 350 nm lamps for 13 min. The disappearance of thioxanthone was monitored by UV spectroscopy and at the completion of this period, the peak at 380 nm was no longer present.

The solution was transferred to a separatory funnel and washed 3 × 10 mL with 3 M hydrochloric acid. After the solution was dried with $MgSO_4$ and concentrated, 24.5 mg (76.2%) of a yellow powder was obtained. This was identical with authentic material by UV, ^1H NMR, MS, and melting point.

Conversion of Photolysis Product to Spiro Epoxide (4). A solution of 33.2 mg (0.156 mmol) of thioxanthone and 54 μL (0.423 mmol) of DMA in 30 mL of dry benzene was placed in a Vycor photolysis vessel and purged by bubbling nitrogen through the solution. This solution was irradiated in a Rayonet reactor for 15 min and then rapidly extracted 3 × 5 mL with 3 M hydrochloric acid. After drying with $MgSO_4$, the solution was concentrated.

The resulting white powder was placed in a 25-mL round-bottom flask equipped with a stir bar, condensor, and nitrogen inlet. After the flask was flushed with nitrogen, the solid was suspended in 1.2 mL of glacial acetic acid. The reaction mixture

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[37] For benzophenone $E(A^-/A) = -1.72$ V vs. SCE[38] and $\Delta E_{0,0} = 68.5$ kcal/mol.[10]

[38] Reference 32, p 184.

[39] Scaiano, J. C.; Abuin, E. B.; Steward, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.

[40] Lemire, A.; Mar, A.; Maharaj, U.; Dong, D. C.; Cheung, S. T.; Winnik, M. A. *J. Photochem.* **1980**, *14*, 265. Chilton, J.; Giering, L.; Steel, C. *J. Am. Chem. Soc.* **1976**, *98*, 1865.

[41] Lane, C. F. *Synthesis* **1975**, 135.

was heated to reflux and 36 μL (432 mmol) of concentrated hydrochloric acid was added. After 15 min at reflux, the suspension was cooled to room temperature and filtered. The resulting white powder (7.7 mg, 24.1% yield) was identical by ^{1}H NMR, MS, and mixed melting point to the spiroepoxide prepared above.

Acknowledgment. This work was supported by grants from Mead Corporation and from the National Science Foundation. We thank Dr. Paul Davis of Mead Corporation for telling us of some of his preliminary findings.

Registry No. 4, 91158-67-7; TX, 492-22-8; methyl methacrylate, 80-62-6; dimethylaniline, 121-69-7; triethylamine, 121-44-8; dibutylamine, 111-92-2; *tert*-butylamine, 75-64-9; tri-*n*-butylstannane, 688-73-3.

Olefin Oxidation Initiated by a Ground-State Electron Acceptor

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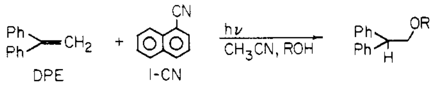
The reaction between 1,1-diphenylethylene (DPE) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF$_4$) in air-saturated acetic acid mimics the photochemical electron-transfer oxidation of this olefin. However, the mechanism of the photooxidation is apparently quite different from that observed for the TCNQF$_4$-mediated reaction. In the latter case a peroxide-initiated free-radical oxidation occurs.

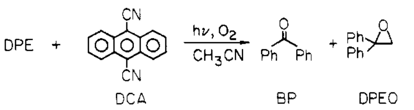
The reaction of olefins with powerful electronically excited electron acceptors frequently provides pathways for reactions which are not observed under other conditions. In this regard, Hixson[1] was the first to observe photochemical anti-Markovnikov addition of an alcohol initiated by excitation of a cyano-substituted aromatic chromophore. The potential of this process was developed more fully by Arnold and co-workers[2] who found, for example, that irradiation of an alcoholic solution of 1-cyanonaphthalene (1-CN) containing 1,1-diphenylethylene (DPE) gives good yields of ethers,[2b] eq 1.



(1)

The mechanism for this reaction is suggested to involve first the transfer of an electron from DPE to 1-CN*[1] giving DPE$^{+}\cdot$ and 1-CN$^{-}\cdot$. In subsequent steps the alcohol adds to DPE$^{+}\cdot$ to give the more stable benzylic radical, the radical is reduced by 1-CN$^{-}\cdot$ to give an anion, and, finally, the anion is protonated to give the observed ether. This general sequence has been invoked for other nucleophiles and other olefins as well.

When O$_2$ is present in solution DPE$^{+}\cdot$ can be diverted to other products. Oxidation of DPE by irradiation of its SbCl$_5$ complex in O$_2$-saturated CH$_2$Cl$_2$ gives a dimeric cyclic peroxide.[3] Foote[4] and later Schaap[5] have shown that electron-transfer photooxidation of DPE in acetonitrile solution gives benzophenone (BP) and diphenylethylene oxide (DPEO), eq 2. The mechanism for this reaction is thought to involve trapping of DPE$^{+}\cdot$ by O$_2^{-}\cdot$ generated from reduction of O$_2$ by DCA$^{-}\cdot$. Foote and Eriksen[4b] report that when this reaction is carried out in methanol there is a competition between addition and oxidation.



(2)

Similar mechanisms have been considered to explain the photooxidation of DPE initiated by irradiation of solid-state semiconductors.[6] In this case reduction of the semiconductor gives DPE$^{+}\cdot$ which may be bound to the surface while it reacts to become eventually BP and DPEO.

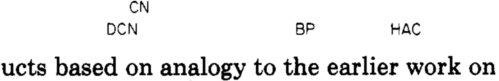
In the reactions described above it is reasonable that an exciplex, or an excited charge-transfer complex, is the precursor to the key radical ion intermediates. It is well-known that olefins such as DPE form ground-state "charge-transfer" complexes with suitable electron acceptors. We undertook this investigation to determine if these ground-state complexes can similarly serve to initiate reactions of olefin radical cations.

Results

Our investigation centers on the reactions of DPE in acetic acid. The electron-transfer photochemistry of DPE has not been reported previously in this solvent; we examined it briefly and compared it with the thermal reaction.

The fluorescence of 1,4-dicyanonaphthalene (DCN) in acetic acid is quenched by DPE. The Weller equation[7] predicts that electron transfer to form DCN$^{-}\cdot$ and DPE$^{+}\cdot$ during this process is favorable by ca. 10 kcal/mol.

Photolysis of an air-saturated solution of DCN and DPE at 350 nm gives benzophenone and the hydroxyacetate (HAC), in a ratio of ca. 3:1, eq 3. These are the expected



(3)

products based on analogy to the earlier work on related systems in methanol.[4b] In particular, we have shown that DPEO is converted rapidly to HAC in acetic acid.

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[1] (a) Hixson, S. S. *Tetrahedron Lett.* **1971**, 4211. (b) Hixson, S. S. *J. Am. Chem. Soc.* **1972**, *94*, 2505.

[2] (a) Neunteugel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (b) Arnold, D. R.; Maroulis, A. J. *Ibid.* **1976**, *98*, 5931. (c) Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407. (d) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535.

[3] Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737.

[4] (a) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391. (b) Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083.

[5] Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, L. W.-M. *J. Am. Chem. Soc.* **1980**, *102*, 389.

[6] (a) Fox, M. A.; Chen, C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 6757. (b) Fox, M. A.; Chen, C.-C. *Tetrahedron Lett.* **1983**, *24*, 547. (c) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Ibid.* **1980**, *21*, 467.

[7] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

0022-3263/84/1949-3356$01.50/0