J. Am. Chem. Soc. 1986, 108, 4214-4222

Photochemical Electron Transfer Involving 1,5-Dithiacyclooctane. A Recoverable Charge Relay in the Photosensitized Oxidation of Halide

Guilford Jones, II,* Vincent Malba, and William R. Bergmark[†]

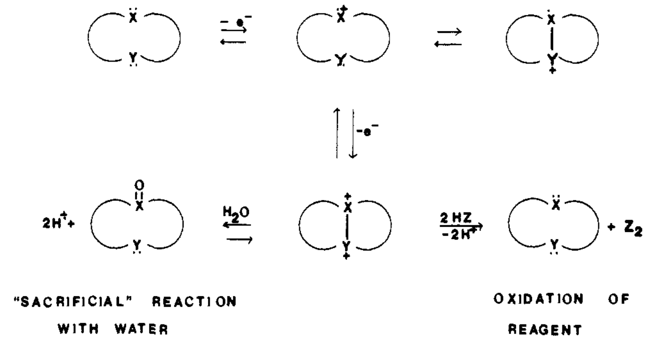
Contribution from the Department of Chemistry, Boston University, Boston, Massachusetts 02215. *Received August 22, 1985*

Abstract: The behavior of 1,5-dithiacyclooctane (DTCO) as an electron-transfer reagent in photochemical reactions has been investigated. The rate constants for quenching the excited states of benzophenone, biacetyl, and uranyl ion in aqueous acetonitrile are consistent with an electron-transfer mechanism. Quenching of benzophenone leads to ketone reduction to the pinacol and oxidation of DTCO to the sulfoxide derivative with moderate quantum efficiency (0.040). In the presence of oxygen, the ketone acts as a sensitizer for the oxidation of DTCO. Laser flash photolysis of benzophenone and DTCO was studied in detail with the identification of benzophenone ketyl radical or anion and DTCO$^{\bullet+}$ (λ_{max} = 400 nm). In the presence of both iodide ion and oxygen the photolysis of benzophenone and DTCO leads to the formation of iodine (I_3^-). In flash photolysis experiments, novel transients are identified which result from addition of the nucleophiles, hydroxide, and iodide to the photogenerated radical cation, DTCO$^{\bullet+}$. A mechanism with appropriate variations for sulfoxide formation and for iodide oxidation is proposed, involving one-electron oxidation of DTCO by the benzophenone triplet, superoxide formation through trapping of the benzophenone ketyl by oxygen, and disproportionation to peroxide. The oxidized species DTCO$^{\bullet+}$, trapped by iodide or by OH^-, reduces a second equivalent of oxygen, ultimately leading also to peroxide and to the sulfoxide derivative of DTCO. The oxidation of iodine is ultimately accomplished via a thermal reaction of an adduct of the dication, DTCO^{2+}, and iodide, or through reaction of iodide with peroxide. Also discussed is the design of molecules with linked donor moieties capable of two-electron oxidation leading reversibly to stable products. The tandem iodide oxidation, oxygen reduction provides an example of the deployment of latent oxidation equivalents (in the sulfoxide oxidation product of DTCO) in a sequential photochemical redox system.

The role of electron-transfer reactions in photochemical formation of a potential fuel[1] or in synthetic chemistry[2] is now well established. Much effort has been expended on the development of methods for diversion of high energy, primary redox photoproducts (radicals or radial ions) onto pathways to desired materials. A typical result is found in the photoformation of hydrogen from water,[3] for which "sacrificial" organic reagents provide reducing equivalents but are irreversibly decomposed to products of low value.[4] Another type of problem in electron-transfer photochemistry involves the desire to compartmentalize redox processes (to physically separate oxidation and reduction "half-reactions") so that intermediates or products are less prone to side or back reactions.[5,6] Of general interest also are systems which allow multiple electron transfer for each photoexcitation event.[10] These systems utilize agents in which two or more redox equivalents can be "stored" as the result of a sequence of photochemical and/or thermal steps.

Central to the present investigation is an evaluation of electron donors which display the sulfide (R–S–R) linkage. The quenching of excited states by sulfides has been reported in several studies.[11] A general result of these investigations is the correlation of quenching rate with the donor character of the sulfides along with the observation of low yields of photoreduction by sulfides (e.g., a moderate yield of ketyl radicals and net photoreduction for benzophenone).[11a,b] In the case of dehalogenation of haloaromatics by sulfides, electron transfer yielding radical ions is indicated.[11c] The use of sulfur compounds in photoredox processes related to water splitting is also known.[12] Cysteine, for example, has been shown to act as a two-electron sacrificial reducing agent in combination with several photosensitizers.[12,13]

Scheme I. Reversible Two-Electron Reducing Agents



Under certain circumstances, relatively simple sulfides are capable of facile electron transfer leading to radical ions or dications which can react with water to give stable sulfoxide (RR'S=O) products.[14] We have been attracted to this type of system since the sequence yields a product capable, in principle,

---

[†] On sabbatical leave from Ithaca College.

(1) (a) Grätzel, M.; Kalyanasundaram, K.; Kiwi, J. In *Structure and Bonding*; Springer Verlag: New York, 1982; Vol. 49, p 37. (b) Grätzel, M. *Energy Resources through Photochemistry and Catalysis*; Academic Press: New York, 1983. (c) Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 2730.

(2) (a) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (b) Mariano, P. S. *Tetrahedron* **1983**, *39*, 3845. (c) Albini, A. *Synthesis* **1981**, 249.

(3) *Photogeneration of Hydrogen*; Harriman, A., West, M. A., Eds.; Academic Press: London, 1982.

(4) See, for example: (a) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1978**, *62*, 1345. (b) Krasna, A. I. *Photochem. Photobiol.* **1980**, *31*, 75. (c) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. Helv. *Chim. Acta* **1978**, *61*, 2720. (d) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, *2*, 547.

(5) (a) Bolton, J. B. *Science* **1978**, *202*, 705. (b) Ebbesen, T. W.; Tembe, B. L.; Kozak, J. J. *J. Phys. Chem.* **1984**, *88*, 683.

(6) Separation of oxidation and reduction steps has been discussed in detail in the context of photoelectrochemical cells,[7] membranes,[8] vesicles,[9] and other organized media.

(7) Wrighton, M. S. *Acc. Chem. Res.* **1979**, *9*, 305.

(8) Clayton, R. K. *Photosynthesis*: *Physical Mechanisms and Chemical Patterns*; Cambridge University Press: London, 1980.

(9) Tunuli, M.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507.

(10) Schanze, K. S.; Gianotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 6326.

(11) (a) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1679. (b) Ronfard-Haret, J. C.; Bensasson, R. V.; Gramain, J. C. *Chem. Phys. Lett.* **1983**, *96*, 31. (c) Davidson, R. S.; Goodin, J. N.; Pratt, J. E. *Tetrahedron Lett.* **1982**, 2225.

(12) Jahansen, O.; Launikonis, A.; Loder, J. W.; Mau, A. W.-H.; Sasse, W. H. F.; Swift, J. d.; Wells, D. *Aust. J. Chem.* **1981**, *34*, 2347.

(13) Rougee, M.; Ebbesen, T.; Ghetti, F.; Bensasson, R. V. *J. Phys. Chem.* **1982**, *86*, 4404.

(14) Shine, H. J.. In *The Chemistry of* the *Sulfonium Group*; Sterling, J. M., Ed.; J. Wiley and Sons: New York, 1981; Part 2, c.

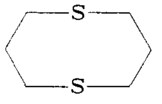
0002-7863/86/1508-4214$01.50/0

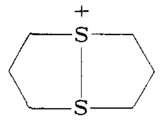
Table I. DTCO Quenching Data

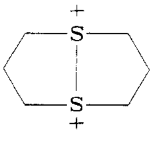
sensitizer[a]	K_{SV}, M^{-1}	k_q, M^{-1} s^{-1}	τ,[b] μs	E_{0-0}[c]	$E_{1/2}$[c]	ΔG_{et}[c,d]
biacetyl (S_1)	16	1.6×10^9	0.010[e]	2.8	−1.2[f]	−0.92
benzophenone		7.0×10^9	1.5	3.0	−1.5[h]	−0.87
UO_2^{2+}	4.8×10^4	1.3×10^{10}	6.6	2.5	−0.26	−1.6
$Ru(bpy)_3^{2+}$	<0.1	$<1.5 \times 10^5$	0.40	2.1	−1.5	+0.08

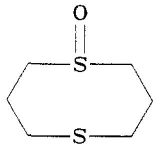
[a] In 80–95% acetonitrile. [b] Determined by laser flash photolysis, except as noted. In air, except for BP, which was degassed with Ar. [c] E_{0-0} and ΔG_{et} are in eV. $E_{1/2}$ values are given in volts vs. SCE. E_{0-0} were either estimated from the intersection of excitation and emission spectra or are from ref 24. $E_{1/2}$ values are from ref 23, except as noted. [d] E_p(DTCO) = 0.34 V vs. Ag/AgNO$_3$, 0.68 V vs. SCE. [e] From ref 22. [f] Cyclic voltammetry measurement for biacetyl in 80% CH_3CN gave an irreversible cathodic wave. $E_{pc/2}$ at 200 mV s^{-1} is reported. [g] The quenching of ^{3}BP was determined by monitoring the change in $k(^3BP)$ vs. [DTCO] with laser flash photolysis. See Experimental Section and Figure 2. [h] From ref 36.

of regeneration of oxidation equivalents on demand. The plan is elaborated in a general way in Scheme I. For a net two-electron oxidation (e.g., $R_2S \rightarrow R_2S{=}O$) two one-electron donor sites (X and Y) can be conveniently disposed for sequential reaction through covalent attachment. The first oxidation at X giving a radical cation may be facilitated through interaction with Y (a valence tautomeric or alternative resonance form may result). A second oxidation step is further facilitated by formation of a covalent bond between X and Y. The system has appeal on considering the possibilities for conducting the oxidation of linked XY at the site of photochemical reduction of a substrate with temporary "sacrifice" of the electron donor. This step is followed by transport of the latent oxidation equivalents via the oxide (X=O) intermediary to an alternate site for completion of the cycle via oxidation of species Z.


DTCO


DTCO^{+}•


DTCO^{2+}


DTCOS

For compounds with linked sulfur centers, the neighboring-group-facilitated two-electron oxidation has been carefully documented by several groups. Glass and his co-workers[15] have described the behavior of sulfide moieties with a variety of proximal functional groups under electrochemical oxidation conditions. Asmus[16] has characterized the bonding and spectroscopic behavior of linked sulfides (dithioethers) and their radical cations derived from pulse radiolysis. In addition, Musker and his co-workers[17] have provided an impressive variety of compounds with sulfur centers poised for neighboring group interaction (e.g., with -S, -CO_2H, -OH, and -N functions) and studied the oxidation chemistry for the series.

We chose for our photochemical study an important member of the linked sulffide series, 1,5-dithiacyclooctane (DTCO). The results of cyclic voltammetry for this dithioether are consistent with reversible two-electron oxidation in dry acetonitrile.[15] The dication, DTCO^{2+}, an isolable species (stable in air), is readily obtained on treatment with strong oxidants (e.g., NOBF$_4$).[18] On reaction with dilute bicarbonate DTCO^{2+} is converted in high yield to the sulfoxide (DTCS).[17] The radical cation DTCO$^{\bullet+}$ has been characterized in EPR[19] and pulse radiolysis[16a] studies. Stabilization of this species is apparent in the oxidation potential ($E_{1/2}$ = 0.68 V, compared to ca. 1.5 V vs. SCE for most sulfides)[15] and the photoelectron spectrum for DTCO. These effects have been ascribed to formation of an unusual three-electron S-S bond[15-17] (the DTCO$^{\bullet+}$ structure provided below represents one canonical form).

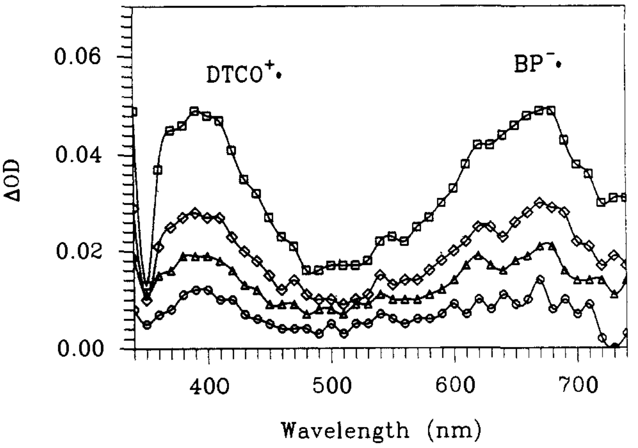


Figure 1. Transient absorption spectra recorded (□) 3, (◇) 9, (△) 15, and (○) 26 μs after laser excitation at 355 nm in an argon-purged solution containing 2 mM BP and 20 mM DTCO in CH_3CN (no added H_2O).

We wish to report in detail the photochemical oxidation of DTCO mediated principally by the triplet excited state of the well-known photosensitizer, benzophenone.[20] The direct observation by laser flash photolysis of transients resulting from electron transfer will be reported, including an identification of rare intermediates resulting from trapping of photogenerated sulfide radical cations by nucleophiles. In addition, the deployment of DTCO oxidation products as relays in the oxidation of iodide ion will be reported.

Results and Discussion

Excited-State Quenching by DTCO. The interception of excited species which potentially act as oxidizing agents for DTCO was monitored with use of various steady and flash irradiation techniques. The room temperature phosphorescence of benzophenone (BP) in Ar-purged aqueous acetonitrile (80% CH_3CN) which could be observed by laser flash photolysis (vide infra) was readily quenched by DTCO. A Stern–Volmer quenching constant, k_q, was obtained from the emission lifetime–[DTCO] profile. With use of the Stern–Volmer technique for treatment of emission intensity vs. [DTCO] in steady irradiation experiments, the quenching of three other potential sensitizers was examined. DTCO was active in reducing biacetyl fluorescence and the luminescence of uranyl ion but not that of $Ru(bpy)_3^{2+}$ as shown in Table I for aerated acetonitrile (AN) solutions.

The energetics of quenching were evaluated assuming a rate-determining electron transfer within a sensitizer/DTCO encounter complex by using the Weller equation

$$\Delta G_{et} = 23.1(E_{ox} - E_{red}) - E_{0-0}$$

where E_{ox} and E_{red} are half-wave potentials for oxidation of DTCO

---

(15) Ryan, M. D.; Swanson, D. D.; Glass, R. S.; Wilson, G. S. *J. Phys. Chem.* **1981**, *85*, 1069.

(16) (a) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436. (b) Göbl, M.; Bonifacic, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5984. (c) Göbl, M.; Bonifacic, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5988. (d) Glass, R. S.; Hojjatie, M.; Wilson, G. S.; Mahling, S.; Göbl, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5382.

(17) (a) Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200. (b) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1978**, *100*, 3533. (c) Doi, J. T.; Goodrow, M. H.; Musker, W. K. *J. Org. Chem.* **1986**, *51*, 1026.

(18) Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416.

(19) Brown, T. G.; Hirschon, A. S.; Musker, W. K. *J. Phys. Chem.* **1981**, *85*, 3767.

(20) For a preliminary account of this work, see: Jones, G., II; Malba, V. *Nouv. J. Chim.* **1985**, *9*, 5.

Table II. Transient Decay Resulting from DTCO Quenching of BP

λ_{mon}[a] (nm)	gas	solvent[b]	additive[c]	$\tau_{1/2}$ (μs)	τ (μs)	k (10^{10} M^{-1} s^{-1})	order
400	Ar	AN		5.5		1.2	2nd
400	Ar	4:1		8.0			mixed
400	Ar	4:1	H^+	21			mixed
400	Ar	4:1	OH^-	5.0			mixed
365	Ar	4:1	I^-	80			
400	O_2	AN		23			mixed
400	O_2	4:1		7.5	18		1st
400	O_2	4:1	H^+	20	38		1st
400	O_2	4:1	OH^-	1.5	2.1		1st
545	Ar	4:1				0.29	2nd
545	Ar	4:1	H^+			0.22	2nd
630	Ar	AN				1.8	2nd
630	Ar	4:1			5.0		1st
630	Ar	4:1	OH^-			0.18	2nd

[a] Conditions: [BP] = 2 mM, [DTCO] = 20 mM. ϵ_{400}(DTCO) = 5800 M^{-1} cm^{-1} (ref 29), ϵ_{545}(BPH$\cdot$) = 3220 M^{-1} cm^{-1} (ref 28) and ϵ_{630}(BP$^{\cdot-}$) = 5000 M^{-1} cm^{-1} (ref 26). [b] AN is CH_3CN. 4:1 represents 80% CH_3CN/20% H_2O. [c] [H^+] = 1.6 mM; [OH^-] = 10 mM.

($E_{1/2}$ = 0.68 V vs. SCE, acetonitrile)[15] and reduction of the sensitizers, and E_{0-0} is the excitation energy for the particular excited sensitizer species estimated from the intersection of absorption and emission curves. The data (Table I) are consistent with an electron-transfer quenching mechanism in so far as a negative free energy change (ΔG_{et}) suggests an efficient electron transfer for DTCO-sensitizer encounters and near-diffusion-limited quenching rates.[21] For the Ru(II) sensitizer[23] the energetics are not so favorable and a negligible rate of quenching is observed.

Photobleaching and Product Studies. Photoreaction of BP and DTCO in 80% CH_3CN could be followed by measurement of the bleaching of BP absorption (330 nm) on irradiation of samples in quartz tubes in a Rayonet chamber reactor (RUL 3500A lamps). The progress of photolysis could also be followed readily by NMR with reference to peaks associated with reduction of BP (δ 7.7, m) to benzopinacol (δ 7.2, m) and the oxidation of DTCO to DTCS (the latter displaying three well-resolved four-proton multiplets (δ 2.25, 2.65, and 3.15)). Benzopinacol was prepared independently by irradiation of BP in isopropyl alcohol, and DTCS was obtained for direct comparison by periodate oxidation of DTCO.[25] NMR and tlc analysis showed that the reaction was remarkably clean (>95% chemical yield of pinacol and DTCS products). With use of a monochromator–quantum counter apparatus, the quantum efficiency of BP photoreduction was obtained under conditions of >90% quenching of BP triplets (Stern–Volmer analysis, vide supra): ϕ_{bleach} = 0.040 for 4.0 mM BP and 1.3 mM DTCO at λ_{exc} = 334 nm (Ar-purged, 80% CH_3CN solutions).

Laser Flash Photolysis: Two-Component and Three-Component Systems in which Photoregenerated Radicals Are Trapped by Oxygen or Base. Investigation of the mechanism of DTCO oxidation proceeded with the detection of intermediates by laser flash photolysis. Pulsed irradiation of argon-purged acetonitile solutions of BP and DTCO with the frequency-tripled output of a Nd:YAG laser (355 nm, ca. 60 mJ/pulse at 2 Hz) resulted in the appearance of transients (Figure 1) at 610 nm associated with the BP radical anion (BP$^{\cdot-}$)[26] and at 400 nm assigned to DTCO$\cdot^+$ on the basis of data from pulse radiolysis.[16a] The transients took on a more complex appearance for flash photolysis in the presence of water (80% CH_3CN) (Figure 2), where the 400-nm absorption was broadened and the BP$^{\cdot-}$ intermediate was accompanied by a transient at 545 nm assignable to the conjugate acid, BPH$\cdot$.[26] This spectrum was simplified again by addition of a small amount of base or acid which adjusted the BP ketyl equilibrium and altered slightly the appearance of the 400-nm transient (Figure 3).

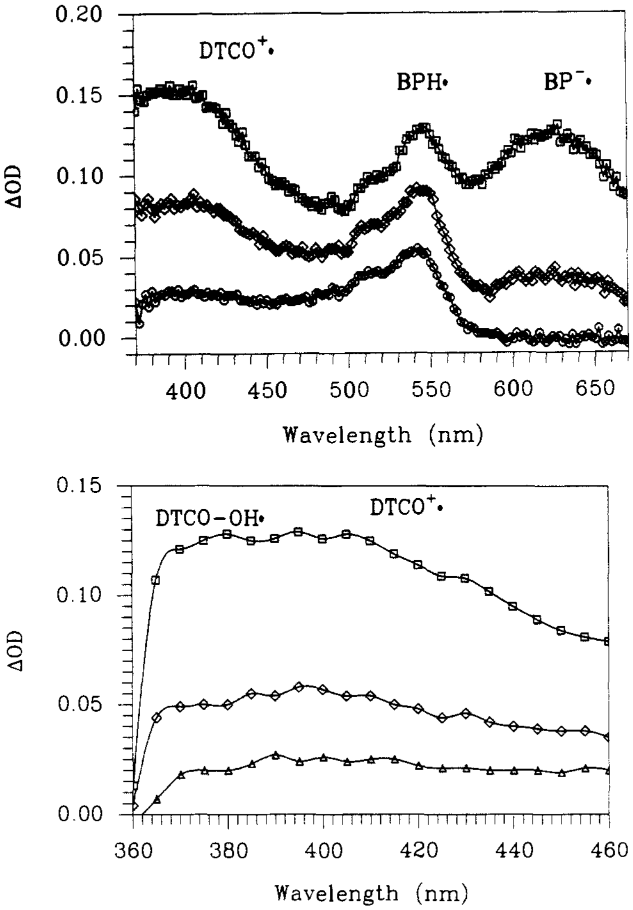


Figure 2. Top: Transient absorption spectra recorded (□) 3, (◇) 9, and (○) 39 μs after laser excitation in an argon-purged solution containing 12 mM BP and 20 mM DTCO in 80% CH_3CN. Bottom: Transient absorption spectra recorded (□) 3, (◇) 15, and (△) 39 μs after the flash. Same conditions as top.

For Ar-purged samples, the BP and DTCO derived transients displayed second-order (or sometimes mixed) decay kinetics and decay half-lives in the 10-μs regime. For kinetic runs, optical density was monitored at the transient absorption maximum, typically to ca. 3 half-lives of decay (10–100 laser shots signal averaged, with 500 points/pulse at 100 ns/point). A second-order decay curve is shown in Figure 4. Representative transient

---

(21) The quenching rates for biacetyl singlet (Table I) and triplet (2.5 × 10^8 M^{-1} s^{-1}) appear anomalously low. The free energy change for electron transfer is favorable, and photobleaching is observed (ϕ_{bleach} = 0.06; λ_{exc} = 405 nm, for 8.8 mM DTCO, where quenching of the biacetyl triplet is >99% complete, and singlet quenching amounts to ca. 12%). We have not studied the system in detail but assume that mechanisms other than outright electron transfer (electron/proton transfer within an exciplex intermediate) could be important.

(22) Turro, N. J.; Engels, R. *J. Am. Chem. Soc.* **1968**, *90*, 2989.

(23) (a) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, 159.

(24) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.; New York, 1973.

(25) Roush, P. B.; Musker, W. K. *J. Org. Chem.* **1978**, *43*, 4295.

(26) Several valls for ϵ(BP$^{\cdot-}$) have been reported: ϵ_{630} = 5000 M^{-1} cm^{-1};[26b] ϵ_{630} = 9500 M^{-1} cm^{-1}. We adopted the former value. (a) Beckett, A.: Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. (b) Patterson, J. I. H.; Perone, S. P. *Anal. Chem.* **1972**, *44*, 1978.

(27) Porter, G.; Wilkinson, F. *Trans. Faraday Soc.* **1961**, *57*, 1686.

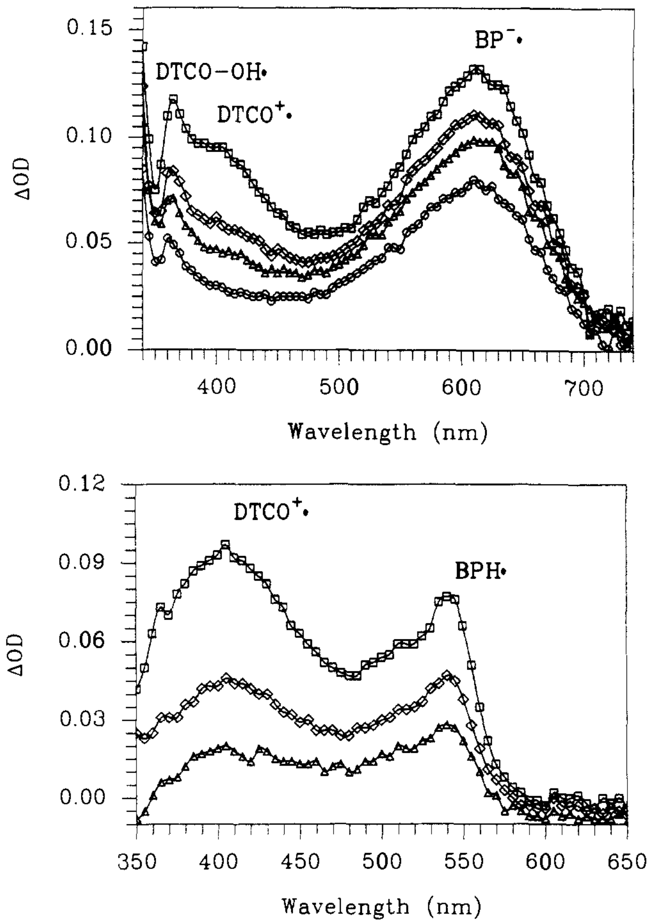


Figure 3. Top: Transient absorption spectra recorded (□) 3, (◇) 9, (△) 15, and (○) 33 μs after laser excitation at 355 nm in Ar purged 80% CH_3CN containing 2 mM BP, 20 mM DTCO, and 10 mM NaOH. Bottom: Transient absorption spectra recorded (□) 3, (◇) 15, and (△) 33 μs after flash. Same conditions as top, except 2 mM HCl instead of NaOH.

absorption and decay data are shown in Table II, including rate constants calculated (for second-order decays) on the basis of previously determined extinction coefficients.[26-29]

An interesting feature of the decay profile for "neutral" (80% CH_3CN) solutions is the evolution of the reduced BP species. The 610-nm transient was observed to decay by first-order kinetics ($k = 3.3 \times 10^5$ s^{-1}) at a rate which was considerably faster than decay of the ketyl radical (BPH·) at 545 nm (Figure 2). This observation is consistent with relatively fast protonation of $BP^{\bullet -}$ (by water) in the vicinity of but on the acid side of the pK_a for BPH· ($pK_a = 9.2$ in water[27]).

For aerated samples the appearance of transients was altered significantly (Figure 5). For example, $BP^{\bullet -}$ and BPH· now appeared only at the shortest time scales and followed a first-order decay ($\tau \sim 50$ ns; Table II). On the other hand, $DTCO^{\bullet +}$ appeared much as before with an accelerated rate of decay which was first order. Steady irradiation under these condtions showed different results as well. Irradiation of 4 mM BP and 50 mM DTCO at 334 nm resulted in negligible photobleaching of benzophenone ($\phi_{bleach} < 0.005$). However, DTCO oxidation to the sulfoxide proceeded with a much higher efficiency than previously observed ($\phi = 0.75$) as determined by NMR analysis of aerated samples in 80% CH_3CN irradiated at 334 nm (50 mM BP, 50 mM DTCO). That BP had acted as a true sensitizer was convincingly demonstrated by calculation of a turnover number (mol of DTCS formed/mol of BP consumed ≥ 600) under conditions of extended photolysis at 334 nm where BP was not consumed (spectrophotometric analysis at 330 nm). For photolysis of aerated samples, H_2O_2 was an expected product (vide infra) but not found ($\phi < 0.005$) on spectrophotometric determination (peroxidase method).

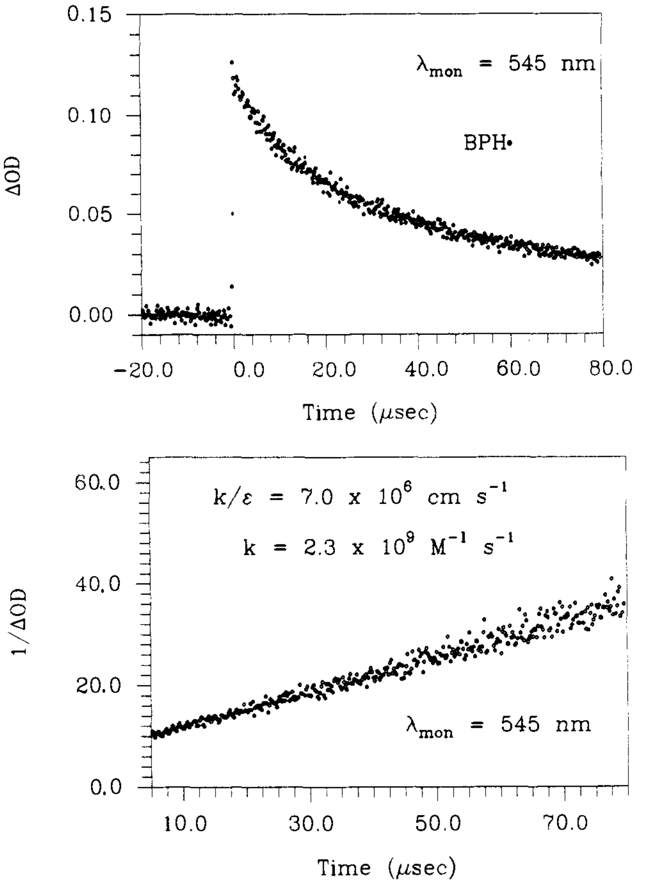


Figure 4. Top: Decay of the absorbance at $\lambda_{mon} = 545$ nm following laser excitation at 355 nm. [BP] = 2 mM, [DTCO] = 20 mM, [HCl] = 2 mM in 80% CH_3CN; argon-purged sample. Bottom: Reciprocal absorbance at $\lambda_{mon} = 545$ nm vs. time. The extinction coefficient for BPH· is assumed to be 3220 M^{-1} cm^{-1}.[28]

A mechanism consistent with the data for photolysis of BP and DTCO is shown in Scheme II. Benzophenone triplet is formed in a conventional fashion and is quenched at a high rate by interaction with DTCO (step 2). Reduced BP species proceed to the pinacol via the ketyl (steps 4 and 5), the $DTCO^{\bullet +}$ yields the sulfoxide (DTCS) via disproportionation and trapping of the dication by water.[17a,30] By using the flash photolysis technique, the yield of net electron transfer ($k_2/(k_2 + k_3)$) could be measured directly. Thus, by comparison with the formation of the benzophenone triplet in benzene ($\epsilon_{535} = 7220$ M^{-1} cm^{-1}),[31] the BPH· radical ($\epsilon_{545} = 3220$ M^{-1} cm^{-1})[28] is generated with a quantum efficiency of 0.73, the value based on transient absorption at 545 nm under identical laser pulse conditions for a 2 mM BP sample ($A_{355} = 0.2$) with 20 mM DTCO in 80% CH_3CN vs. a 1.6 mM BP sample in benzene ($A_{355} = 0.2$).

We conclude that a dominant decay path for Ar-purged solutions involves back reaction of photogenerated radicals (step 6), since the yield of overall BP photoreduction and DTCO oxidation

---

[28] (a) Land, E. J. *Proc. R. Soc.* **1964**, *277*, 549. (b) Amand, B.; Bensasson, R. *Chem. Phys. Lett.* **1975**, *34*, 44.

[29] Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322.

[30] (a) Since the $DTCO^{\bullet +}$ species is clearly intercepted by either I^- or OH^-, a mechanism involving oxidation of DTCO by singlet oxygen is not preferred, but may be a contributor under certain conditions. The mechanism would involve, for example, the recombination of $DTCO^{\bullet +}$ and $O_2^{\bullet -}$ to give DTCO and $^1O_2$, the latter proceeding to react with DTCO via the persulfoxide as previously proposed.[30b-d] This path is not likely to be dominant in the present case since the OH^- (or H_2O) adduct appears to be readily formed in the absence of oxygen. (b) Hovey, M. C. *J. Am. Chem. Soc.* **1982**, *104*, 4196. (c) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (d) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761.

[31] Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

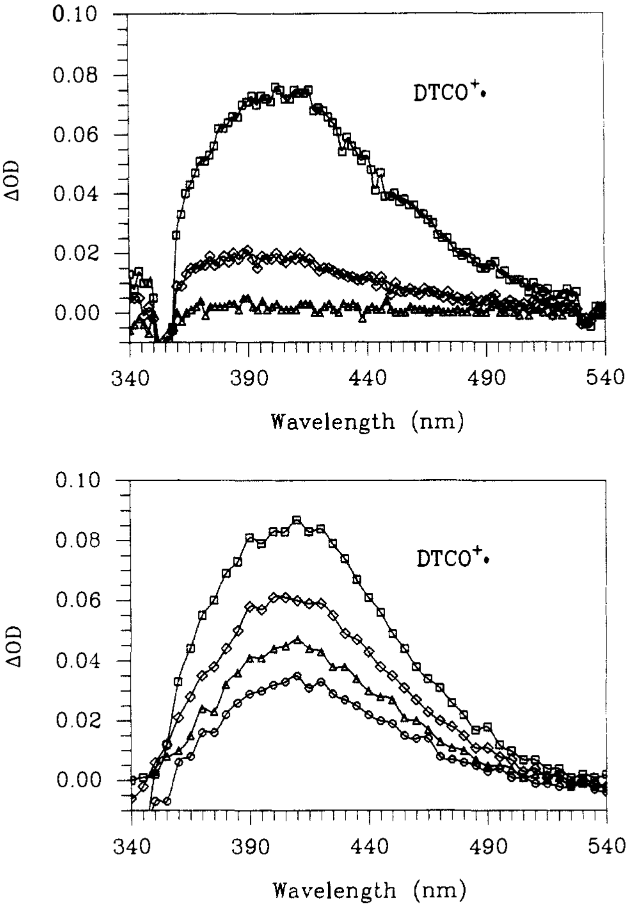
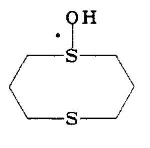
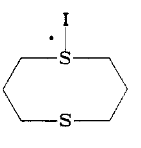


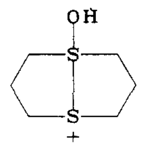
Figure 5. Top: Transient absorption spectra in base and oxygen recorded (□) 1, (◇) 4, and (△) 10 μs after laser excitation at 355 nm in 80% CH_3CN containing 2 mM BP, 20 mM DTCO, and 10 mM NaOH. Bottom: Transient spectra in oxygen recorded (□) 3, (◇) 15, (△) 27, and (○) 39 μs after the flash. [BP] = 2 mM, [DTCO] = 20 mM, [HCl] = 2 mM in 80% CH_3CN.



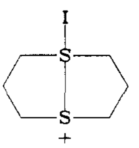
DTCO-OH•



DTCO-I•



DTCO-OH⁺



DTCO-I⁺

is low (ca. 4%). In competition is the forward sequence of radical coupling (step 5), which has a rate constant of $2k = 2.7 \times 10^8$ $M^{-1}\,s^{-1}$ in 80% CH_3CN,[32] and disproportionation of $DTCO^{\bullet+}$ (step 7) for which there is considerable thermodynamic driving force ($\Delta H = -12.6$ kcal/mol, estimated for radical disappearance from the temperature dependence of its EPR signal[19]).[33] An estimate has also been previously made[17b] of the pseudo-first-order rate constant for reaction of $DTCO^{2+}$ with water ($k = 0.06\ s^{-1}$) (step 8).

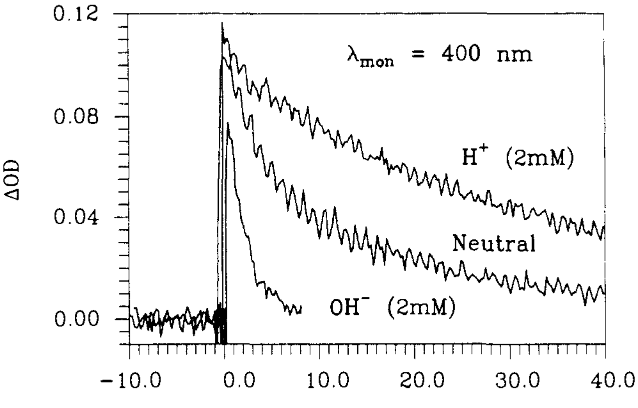


Figure 6. Transient absorption decays at 400 nm following laser excitation at 355 nm in the presence of oxygen, with 2 mM BP and 20 mM DTCO in 80% CH_3CN, with added acid and added base.

Scheme II

$$BP \xrightarrow{h\nu} {}^1BP \rightarrow {}^3BP \qquad (1)$$

$${}^3BP + DTCO \rightarrow BP^{\bullet-} + DTCO^{\bullet+} \qquad (2)$$

$${}^3BP + DTCO \rightarrow BP + DTCO \qquad (3)$$

$$BP^{\bullet-} + H_2O \rightarrow BHP^{\bullet} + OH^- \qquad (4)$$

$$\tfrac{1}{2}[2BPH^{\bullet} \rightarrow (BPH)_2] \qquad (5)$$

$$BPH^{\bullet} + DTCO^{\bullet+} \rightarrow BP + DTCO + H^+ \qquad (6)$$

$$\tfrac{1}{2}[2DTCO^{\bullet+} \rightarrow DTCO + DTCO^{2+}] \qquad (7)$$

$$\tfrac{1}{2}[DTCO^{2+} + H_2O \rightarrow DTCS + 2H^+] \qquad (8)$$

The addition of base to 80% CH_3CN solutions resulted in another alteration of the transient spectrum in the 400-nm region and, on further examination, suggested a novel alternative mechanism for sensitized DTCO oxidation. Solutions of BP and DTCO were prepared with 2–50 mM NaOH and flash photolyzed under Ar at 355 nm as before. A shift of the transient maximum from 400 to 370 nm was clearly perceptible, a change which appeared to be complete on addition of 10 mM base (Figure 3, top). Examination of the decay at 400 nm revealed a mixed kinetic order (improper fit to either first- or second-order plots). The yield of photogenerated radicals was estimated ($\phi = 0.59$), again based on known absorption data for $BP^{\bullet-}$ and $DTCO^{\bullet+}$ for photolysis with added base.

The imposition of a second species absorbing in the 400-nm region was further confirmed on carrying out experiments in the presence of both base and oxygen. On steady photolysis at 334 nm (monochromator apparatus), a solution of 50 mM BP, 50 mM DTCO, and 2.0 mM NaOH gave DTCS with a quantum efficiency of 0.45. For aerated basic solutions, the 630-nm transient associated with $BP^{\bullet-}$ was again absent. The transient spectrum at 1 μs after the flash (Figure 5) shows only the presence of the 400-nm band assigned to $DTCO^{\bullet+}$. It was clear on dissection of the band that decay at 370 and 420 nm in the presence of oxygen (Figure 7) proceeded differently. Unlike the first-order decay observed at 420 nm ($\tau_{1/2} = 1.5$ μs), the decay at 370 nm was bimodal, with a very rapid initial loss ($\tau_{1/2} \sim 30$ ns), followed by a first-order decay similar to the decay at 420 nm. We conclude that the 370-nm band represents a new DTCO derived species which is obtained in the presence of base and which is reactive with oxygen.

---

[32] The dimerization of $BPH^{\bullet}$ has been measured by flash photolysis in a variety of solvents:[26a] $k = 5.9 \times 10^7\ M^{-1}\,s^{-1}$ in isopropyl alcohol. Our value, measured in 80% CH_3CN with 0.2 M benzhydrol quenching 4 mM BP, is $2k = 2.8 \times 10^8\ M^{-1}\,s^{-1}$.

[33] Bimolecular reaction of $DTCO^{\bullet+}$ appears to be complicated. Cyclic voltammetric behavior[15] at high [DTCO] in CH_3CN and EPR data[19] are consistent with formation of a diamagnetic dimer in a reversible step either in sequence with or in parallel to disproportionation (step 7, Scheme I). From the electrochemical data, an estimate was made of the rate of the dimerization step ($2k \sim 8 \times 10^4\ M^{-1}\,s^{-1}$).[15] Disproportionation to $DTCO^{2+}$ permits another possible back reaction of the dication with either $BP^{\bullet-}$ or $BPH^{\bullet}$.

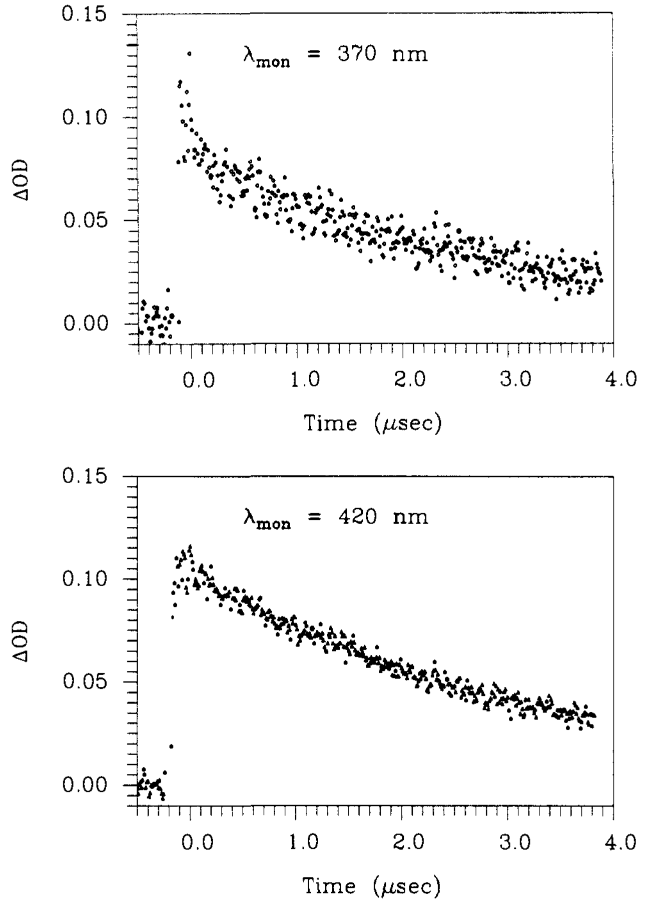


Figure 7. Top: Decay of the absorbance at λ_{mon} = 370 nm following laser excitation at 355 nm in the presence of oxygen. [BP] = 2 mM, [DTCO] = 20 mM, $[\mathrm{OH}^-]$ = 10 mM, in 80% $\mathrm{CH_3CN}$. Bottom: Decay of the absorbance at λ_{mon} = 420 nm. Same conditions as top curve.

The success of quenching BP with DTCO to give $\mathrm{DTCO}^{\bullet +}$ for aerated samples is consistent with an effective competition of DTCO with $\mathrm{O_2}$ for interception of BP triplets (note high rate of quenching for DTCO ≥ 10 mM, Table I). Other important steps indicated by the data for sensitized DTCO oxidation in aerated basic solutions are shown in Scheme III. Trapping of $\mathrm{BP}^{\bullet -}$ by $\mathrm{O_2}$ to give superoxide ($\mathrm{p}K_\mathrm{a}$ = 4.75)[34] may be followed by peroxide formation which proceeds slowly in base (step 14).[35] DTCO oxidation by peroxide (step 16) occurs on the time scale of minutes in the dark (note Experimental Section).

The intriguing result of photooxidation in base is the apparent formation of a new intermediate (370-nm transient) for which we suggest the structure DTCO–OH· (vide infra). The dependence of the decay rate for $\mathrm{DTCO}^{\bullet +}$ on base is highlighted in Figures 5 and 6. The hydroxide adduct of $\mathrm{DTCO}^{\bullet +}$ is expected to be a reducing radical which should be readily intercepted by oxygen, yielding a second equivalent of superoxide and the sulfoxide conjugate acid, $\mathrm{DTCO{-}OH^+}$ (step 12). From the data in Figure 7, it appears that the decay of the adduct radical (λ_{max} = 370 nm, Figure 7, top) is substantial within 200 ns in the presence of $\mathrm{O_2}$ and that a residual decay that may be associated with $\mathrm{DTCO}^{\bullet +}$ (λ_{max} = 400 nm, but also absorbing at 370 and 420 nm) is important at longer times (i.e., >200 ns). Since the one-electron reduction of BP results in 1 equiv of superoxide, and DTCO oxidation ($\mathrm{DTCO}^{\bullet +}$) results in both DTCS and superoxide via the hydroxide adduct (steps 10 and 12), and since peroxide is an oxidant of DTCO, the net stoichiometry (per photon) is as follows

$$\mathrm{2DTCO + O_2 \rightarrow 2DTCS}$$

Scheme III

$$\mathrm{BP^{\bullet -} + O_2 \rightarrow BP + O_2^{\bullet -}} \quad (9)$$

$$\mathrm{DTCO^{\bullet +} + OH^- \rightarrow DTCO{-}OH^{\bullet}} \quad (10)$$

$$\mathrm{DTCO{-}OH^{\bullet} + BP^{\bullet -} \rightarrow DTCO + BP + OH^-} \quad (11)$$

$$\mathrm{DTCO{-}OH^{\bullet} + O_2 \rightarrow DTCO{-}OH^+ + O_2^{\bullet -}} \quad (12)$$

$$\tfrac{1}{2}\mathrm{[2DTCO{-}OH^{\bullet} \rightarrow DTCO + DTCO^{2+} + OH^-]} \quad (13)$$

$$\mathrm{O_2^{\bullet -} + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^-} \quad (14)$$

$$\mathrm{DTCO{-}OH^+ \rightarrow DTCS + H^+} \quad (15)$$

$$\mathrm{DTCO + H_2O_2 \rightarrow DTCS + H_2O} \quad (16)$$

This result is the outcome of the simultaneous one-photon, two-electron oxidation of DTCO and reduction of oxygen which is mediated by the nucleophile, hydroxide, and the ability of peroxide to oxidize a second mole of DTCO. The primary electron-transfer yield approaches 0.5 for aerated basic solutions of BP and DTCO. Since the quantum yield for sulfoxide formation under these conditions is 0.45 (theoretical maximum = 2.0 if primary electron-transfer quantum yield = 1.0), then roughly one-half of liberated radicals result in DTCS product.

DTCO Oxidation in the Presence of Iodide: Alternative Capture of the Dithioether Radical Cation by Nucleophiles. Photolysis of DTCO was carried out in the presence of KI in order to investigate further the tendency of $\mathrm{DTCO}^{\bullet +}$ to react with nucleophiles and to demonstrate the use of DTCO as an oxidation relay. At 10 mM NaI and 20 mM DTCO, the latter remained the primary quencher[35a] of BP triplets, since $k_\mathrm{q} = 3.5 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ for triplet quenching by iodide in 1:4 $\mathrm{CH_3CN/H_2O}$.[36] For deaerated samples, transients assigned to $\mathrm{BPH}^{\bullet}$ and $\mathrm{BP}^{\bullet -}$ appeared as before and decay rates were similar (Figure 8, top). However, the transient at 400 nm which was distinct at up to 4 μs after the flash began to shift to the blue region of the spectrum with time. Within 25 μs, a new band at 365–370 nm had replaced the 400-nm band, and no further spectral shifts were observed at longer times. We assign the structure $\mathrm{DTCO{-}I^{\bullet}}$ to the 370-nm transient, which is clearly distinguishable from the reported spectrum of $\mathrm{I_2}^{\bullet -}$ (λ_{max} = 390 nm).[35b] At 360 nm, the transient grew at about the same rate at which $\mathrm{DTCO}^{\bullet +}$ (monitored at 420 nm) disappeared. The new transient was long lived under these conditions, decaying with a half-life of ca. 80 μs. No evidence for the presence of $\mathrm{I_3^-}$ could be found in either the flash or steady-state experiments. The quantum yield for photobleaching of an Ar-purged solution of 4.0 mM BP, 20 mM DTCO, and 10 mM NaI in 80% AN was 0.14.[37]

A dramatic change was brought about with a four-component system (BP, DTCO, $\mathrm{I^-}$, and $\mathrm{O_2}$). In a typical experiment 10 mM BP, 20 mM DTCO, and 10 mM KI were irradiated in oxygen-purged 80% $\mathrm{CH_3CN}$ (334 nm). NMR analysis showed that BP and DTCO were not consumed under these conditions. Flash photolysis at λ_{exc} = 355 nm showed a fast decay of the $\mathrm{BP}^{\bullet -}$ transient at 630 nm and a permanent growth of absorption in the 350-nm region. At 370 nm, a slight initial decay was followed by a large growth in absorbance with time. Solutions developed the characteristic color of triiodide ($\lambda_{max}(\mathrm{I_3^-})$ = 355 nm)[38] and

---

[34] Bielski, B. H.; Allen, A. O. *J. Phys. Chem.* **1977**, *81*, 1048.

[35] (a) On the basis of the available rate data, iodide (in competition with DTCO) quenches 20% of ^{3}BP. A control experiment (10 mM $\mathrm{I^-}$, 2 mM BP in 80% $\mathrm{CH_3CN}$) clearly produced $\mathrm{I_2^-}$, but the yield was only 5%, so that only 1% $\mathrm{I_2^-}$ should result with 20 mM DTCO present. The finding of a similar blue-shifted band assigned to the $\mathrm{I^-}$ adduct supports the assignment for nucleophilic trapping by $\mathrm{OH^-}$. Less likely is the abstraction from $\mathrm{DTCO}^{\bullet +}$ by $\mathrm{OH^-}$ leading to an alternative sulfur radical. (b) Hug, G. L. *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*; National Bureau of Standards, NSRDS-NBS 69; U.S. Government Printing Office: Washington, DC, 1981.

[36] Shizuka, H.; Obuchi, H. *J. Phys. Chem.* **1982**, *86*, 1297.

[37] NMR analysis showed that benzpinacol formation remained important but other features were more complicated, suggesting some interaction of $\mathrm{I^-}$ with DTCO oxidation product.

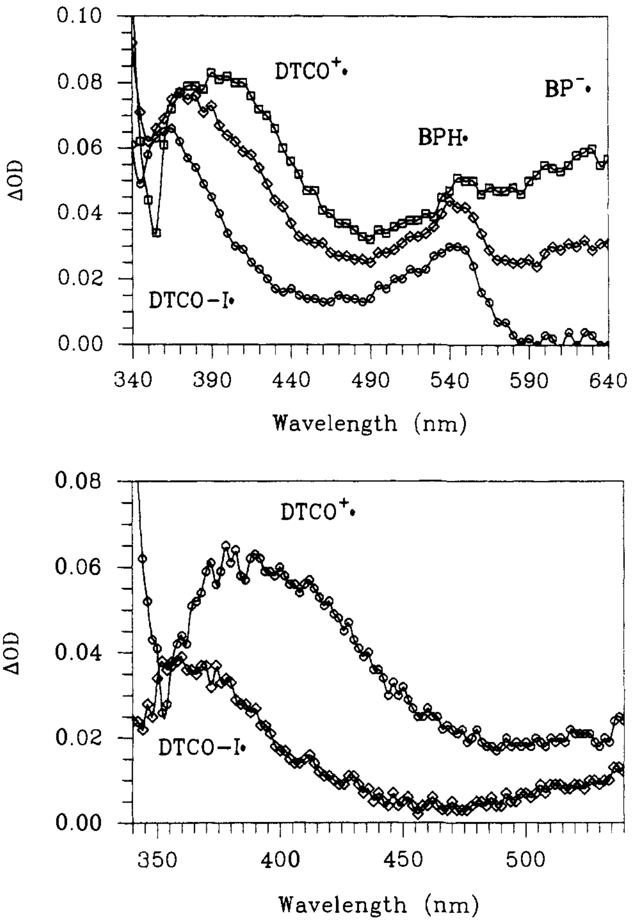


Figure 8. Top: Transient absorption spectra recorded (□) 3, (◇) 9, and (○) 39 μs after the laser flash (355 nm) for an argon-purged solution containing 2 mM BP, 20 mM DTCO, and 10mM KI in 80% CH_3CN. Bottom, Transient absorption spectra recorded (○) 5 and (◇) 26 μs after the laser flash (355 nm). Same conditions as top figure.

gave a positive starch test. The progress of triiodide formation and its quantum yield were a complicated function of the acidity of the medium, the extent of irradiation, and the period of spectrophotometric analysis for I_3^-. Thus, addition of 1.0 mM HCl resulted in an accelerated rate of production of triiodide relative to unacidified 80% CH_3CN solutions, and after irradiation some diminution of the 355-nm product band was observed. On photolysis with 100 mM HCl the rate of I_3^- formation was accelerated further and, in the post irradiation period (ca. 1 h), additional growth in the absorption at 355 nm was observed.

One or more dark reactions are clearly indicated by the profile of DTCO-mediated iodide oxidation. The trend is, in fact, consistent with known chemistry for DTCO and the importance of the following equilibrium which has been implicated by Musker in the iodine oxidation of DTCO[39] and the reduction of DTCS by HI.[17b,40]

$$\text{DTCS} + 3I^- + 2H^+ \rightleftharpoons \text{DTCO} + I_3^- + H_2O$$

The mechanistic steps that are then appropriately added to Scheme II for iodide oxidation involve the trapping of the $\text{DTCO}^{\bullet+}$ intermediate by I^- (step 18, Scheme IV), followed by oxygen trapping of the reducing radical, $\text{DTCO–I}^\bullet$, and forward progress to iodine via the cation, DTCO–I^+ (steps 20 and 21). The latter species has been implicated by Musker[17,39] as in intermediate in the thermal oxidation of iodide by DTCS in mildly acidic solutions.

Scheme IV

$$\text{BPH}^\bullet + O_2 \rightarrow \text{BP} + O_2^{\bullet-} + H^+ \qquad (17)$$

$$\text{DTCO}^{\bullet+} + I^- \rightarrow \text{DTCO-I}^\bullet \qquad (18)$$

$$\text{DTCO-I}^\bullet + \text{BPH}^\bullet \rightarrow \text{DTCO} + \text{BP} + \text{HI} \qquad (19)$$

$$\text{DTCO-I}^\bullet + O_2 \rightarrow \text{DTCO-I}^+ + O_2^{\bullet-} \qquad (20)$$

$$\text{DTCO-I}^+ + I^- \rightleftharpoons \text{DTCO} + I_2 \qquad (21)$$

$$2O_2^{\bullet-} + 2H^+ \rightarrow 2HO_2^\bullet \qquad (22)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (23)$$

$$H_2O_2 + 2HI \rightarrow 2I_2 + 2H_2O \qquad (24)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (25)$$

The iodine–triiodide equilibrium is well established for aqueous media ($K = 710\ M^{-1}$, 25 °C).[38]

The proposal of an unusual adduct of $\text{DTCO}^{\bullet+}$ and iodide is again supported by the transient behavior. Photolysis of BP/DTCO/I^- in 80% AN (Ar) resulted in the time-resolved spectra shown in Figure 8. The blue shift in the 400-nm region noted for the hydroxide adduct is even more pronounced in the case of iodide trapping of $\text{DTCO}^{\bullet+}$. Addition of oxygen reduced both BP- and DTCO-derived transient intensities in later time regimes (rapid coloration with pulsing prohibits acquisition of complete spectra under aerated conditions). However, inspection of the decay at 420 nm, resulting from 10 pulses at 355 nm, revealed a residual transient which was lost with a half-life of ca. 20 μs. Similar interrogation at 370 nm revealed little transient at ca. 500 ns following the flash and a slow growth over 1 ms due to the appearance of triiodide which absorbs in this region. The conclusion again is that the DTCO-derived radical cation transient is efficiently trapped by I^- leading to an adduct, $\text{DTCO–I}^\bullet$, which in turn is trapped by oxygen according to the proposed mechanism (Scheme IV).

The appearance of derivatives of sulfide radical cations resulting from nucleophilic attack has been documented by Asmus in pulse radiolysis studies.[16] The principal findings are that simple dialkyl sulfides on oxidation will provide covalent adducts of the type $R_2S–X$, where X can represent a number of groups including strong and weak nucleophiles (halides, the parent or other sulfide, and even perchlorate). For several systems, high rates of capture of the initial sulfide radial ions ($R_2S^{\bullet+}$) ($k > 10^9\ M^{-1}\ s^{-1}$) were observed.[16c] The adducts have been assessed from a structural point of view in terms of three-electron S–X bonds, and the relative positions of transient absorption for the adducts have been predicted on the basis of the three-electron bond strength (stronger bonds associated with $R_2S–X$ species absorbing more to the blue).[16b]

A remaining point relevant to our study involves the role of water as a potential nucleophile for $R_2S^{\bullet+}$ species.[16,41] Close inspection of Figure 2 leads to the tentative conclusion that a water adduct may indeed be important in "neutral" media where the conjugate base, $\text{DTCO–OH}^\bullet$ (missing in acidified media, Figure 3, top), results from water adduct deprotonation and provides the contribution at 370 nm which broadens the absorption in the 400-nm region. In a recent pulse radiolysis study,[16d] an internal adduct of an alcohol and $R_2S^{\bullet+}$ moieties was identified for the endo-substituted norbornane series. The protonated form, absorbing at 400 nm, and the neutral radical, absorbing at 420 nm, were identified at pH 4 and 8, respectively. A water adduct of a sulfide radical cation has been proposed as an intermediate in the electrochemical oxidation of the aromatic dithioether, thianthrene, via the "half-regeneration mechanism".[41] This

---

(38) Skoog, D. A.; West, D. M. *Analytical Chemistry*, 3rd ed.; Holt, Rinehart, and Winston: New York, 1979; p 332.

(39) Hirschon, A. S.; Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1982**, *104*, 725.

(40) Doi, J. T.; Kessler, R. M.; deLeeuw, D. L.; Olmstead, M. M.; Musker, W. K. *J. Org. Chem.* **1983**, *48*, 3707.

(41) Evans, J. F.; Blount, H. N. *J. Org. Chem.* **1977**, *42*, 976.

mechanism, if operative here, requires a "recombination" of $DTCO^{\cdot+}$ and DTCO–OH·, an interesting alternative step for deaerated media, but not important for samples in which DTCO–OH· is trapped by O_2.

$$\text{DTCO–OH}\cdot + \text{DTCO}^{\cdot+} \rightarrow \text{DTCO–OH}^{+} + \text{DTCO}$$

The quantum yield of sensitized iodide oxidation will depend on the yield of primary electron transfer (which is high in acidified media, Table II), the competitions involving iodide and oxygen trapping (Scheme IV), and the extent of dark reactions of peroxide and DTCO/DTCS which are acid dependent. The operation of Scheme IV again leads to a net reaction stoichiometry per photon as follows.

$$4HI + O_2 \rightleftharpoons 2I_2 + 2H_2O$$

With an initial quantum yield of triiodide of 0.5 at pH 1.5, and after equilibration, a quantum yield of 1.5 (theoretical maximum = 2.0 mol of I_3^-/einstein), the competition of back reactions such as step 19 (Scheme IV) appears minor, since the electron-transfer yield (0.73) and the percentage of free radicals resulting in I_3^- product are substantial.

To demonstrate the potential "two-cycle" aspect of the use of DTCO or similar sulfides as oxidation relays, an experiment was performed in which light and dark processes were separately established. Thus, when 20 mM DTCO and mM 20 BP were irradiated in aerated aqueous acetonitrile to significant conversion followed by separate (dark) reaction on addition of 0.1 mM NaI and 2 mM HCl, a high yield of I_3^- based on DTCS as limiting reagent resulted (NMR analysis of the photochemical step, followed by UV analysis of the triiodide).

The oxidation of halide has been the objective in a number of recent photochemical studies,[42] including cases in which the conversion of halide was coupled with oxygen reduction to peroxide.[43] Schmehl and Whitten[44] reported results similar to our own in which a palladium porphyrin acted as photosensitizer and electron donor and methyl viologen acted as a relay of reducing equivalents. We note, as did the previous authors,[44] that reaction of HI and O_2 (above) is energetically downhill ($\Delta G = -36.6$ kcal/mol; I_2 in water) but that the process fails to occur at a significant rate in the dark near room temperature or in the absence of the benzophenone photosensitizer. The reduction of oxygen to water is a useful reaction in several contexts[45] and is exemplary of processes which require the pooling of redox equivalents.

Summary

The dithioether, DTCO, is a potent quencher of excited species which have good oxidizing properties. In contrast to the behavior of other sulfides, for which electron donor–acceptor quenching leads to polar exciplexes, combination of benzophenone triplet and DTCO results in efficient formation of free radical ions. Careful resolution of the phototransients resulting from reductive quenching by DTCO has led to the identification of novel species, DTCO–X·, adducts of the radical cation $DTCO^{\cdot+}$, and nucleophiles. Study of the BP/DTCO system in the presence of potential reactants, oxygen, OH^-, and I^- has led to unusual results, suggesting a mechanism in which two radicals (ketyl and DTCO–X·) are implicated in O_2 reduction. The data are consistent with a net $4e^-$/photon oxidation of dithioether (2DTCO → 2DTCS) or halide ($2I^- \rightarrow 2I_2$). We are continuing to study the photochemical behavior of sulfur compounds which appear to be capable of multiple electron transfer.

Experimental Section

Materials. 1,5-Dithiacyclooctane (DTCO) was synthesized according to known literature procedures.[46] 1,5-Dithiacyclooctane 1-oxide (DTCS) was synthesized from DTCO and IO_3^-.[25,47] Benzophenone (BP) was recrystallized from hexane, methanol, and petroleum ether. Biacetyl (BIA) was distilled at atmospheric pressure (bp 88 °C). $UO_2(NO_3)_2\cdot 6H_2O$ was Mallinckrodt analytical reagent grade and was used as received. Anhydrous sodium iodide, crystal violet, and leuco-crystal violet were used as received from Aldrich Chemical Co. $Ru(bpy)_3^{2+}$ was purchased from GFS Chemicals (chloride salt) and was used as received. Baker HPLC grade acetonitrile was used as received for the preparation of 80% CH_3CN solutions but was distilled from P_2O_5 and stored over molecular sieve when needed for anhydrous experiments. Horseradish peroxidase was obtained from Sigma Chemical Co.

Laser Flash Photolysis System. The laser flash photolysis apparatus has been previously described.[48] It consists of a Quantel YG-581-10 Nd:YAG laser with frequency doubling and tripling capability, LeCroy Tr8818 100-megasample/s digitizer, an Oriel 150-W xenon monitoring lamp, an RCA 4840 PMT, a H-20 monochromator from Instruments SA, a Kinetic Systems stepping-motor controller for wavelength selection, a Kinetic Systems CAMAC interface crate, and a PDP-11/23 microcomputer for data acquisition and manipulation.

Transient Detection. All samples employed CH_3CN or 80% CH_3CN/H_2O as solvent and were degassed with argon prior to photolysis for at least 15 min when oxygen-free conditions were needed. For examination of the DTCO system under aerobic conditions, oxygen was bubbled continuously through the cell in such a way as to ensure that the bubbles did not interfere with the monitoring beam. The path length of the monitoring beam was 2 cm, while the path length of the laser was 1 cm, with the monitoring beam perpendicular to the laser. Samples were subjected to the smallest number of laser pulses consistent with the necessary signal averaging (decay curves were generated from data points collected for many laser pulses (between 10 and 100 pulses)). Spectra were obtained from five to ten pulses (60 mJ/pulse at $\lambda_{exc} = 355$ nm) at each λ_{mon}. Decay curves (Figure 4) were plotted as both ln ΔOD vs. time and 1/ΔOD vs. time. Correlation coefficients and standard deviations (point to slope, intercept, and slope), which were available from a linear least-squares analysis of the data, were used in the evaluation of the order of reaction. Quantum yields of transients were determined with reference to ^3BP in benzene at $\lambda_{mon} = 535$ nm ($\epsilon = 7220$ M^{-1} cm^{-1}).[31] The actinometer solution and the sample solution had identical $OD_{355} = 0.2$. Actinometer runs were made before, during, and after sample measurements, and ΔOD_{535} agreed within 5%. Each sample was pulsed 25 times and signal averaged to eliminate errors due to pulse-to-pulse instability. For 60 mJ/pulse at 355 nm, $[^3BP] = 5.5 \times 10^{-5}$ M typically.

Luminescence Quenching. Luminescence spectra were recorded on a Perkin-Elmer MPF-44A fluorescence spectrophotometer. The quenching experiments were performed in air by monitoring the change in the intensity of luminescence as a function of added quencher. The slope of I_0/I vs. [DTCO], which equals $k_q\tau$, was graphically determined, with the intercept close to unity in all cases. For $Ru(bpy)_3^{2+}$, $\lambda_{exc} = 450$ nm, $\lambda_{mon} = 610$ mn. For UO_2^{2+}, $\lambda_{exc} = 424$ nm, $\lambda_{mon} = 510$ nm. For biacetyl, $\lambda_{exc} = 417$ nm, $\lambda_{mon} = 460$ nm. The lifetimes of the excited states ($\tau_0(Ru(bpy)_3^{2+})$ and $\tau_0(UO_2^{2+})$), which were needed to determine quenching rate constants, were measured by laser flash photolysis (time-resolved emission); the biacetyl singlet (10 ns)[22] is too short-lived for the detection system used.

The quenching of ^3BP was followed by laser flash photolysis. The decrease in the first-order rate constant of phosphorescence decay at 440 nm was monitored as a function of [DTCO]. All samples were degassed for 30 min prior to excitation; [BP] = 12 mM in 80% CH_3CN. A plot of k_{obsd} vs. [DTCO] was linear.

Product Determinations. Products were identified by ^1H NMR on a 90-MHz JEOL NMR spectrometer. Equal concentrations (both 10 and 50 mM were used) of sensitizer and quencher in 80% CD_3CN/D_2O were charged to an NMR tube into which a long needle was placed. Either O_2 or Ar was bubbled slowly throughout the experiment. The photolysis was run in a Rayonet photochemical reaction chamber equipped with RUL 3500 medium-pressure mercury lamps. NMR analysis was conducted at various times during photolysis, including 25%, 50%, and ≥90% conversion. The progress of the photolysis was followed with reference

---

[42] (a) Neumann-Spallart, M.; Kalyanasundaram, K. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 704. (b) Chen, S.-N.; Lichtin, N. N.; Stein, G. *Science* **1975**, *190*, 879. (c) Simon, R. A.; Ricco, A. J.; Harrison. D. J.; Wrighton. M. S. *J. Phys. Chem.* **1983**, *87*, 4446.

[43] (a) Neyhart, G. A.; Marshall, J. L.; Dressick, W. J.; Sullivan B. P.; Watkins, P. A.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1982**, 915. (b) Dressick, M. J.; Meyer, T. J.; Durham, B.; Rillema, D. P. *Inorg. Chem.* **1982**, *21*, 3451. (c) Pina, F.; Ciano, M.; Moggi, L.; Balzani, V. *Inorg. Chem.* **1985**, *24*, 844.

[44] Schmehl, R. H.; Whitten, D. G. *J. Phys. Chem.* **1981**, *85*, 3473.

[45] Itaya, K.; Shoji, N.; Uchida, I. *J. Am. Chem. Soc.* **1984**, *106*, 3423.

[46] (a) Meadow, J. R.; Reid, E. E. *J. Am. Chem. Soc.* **1934**, *56*, 2177. (b) Leonard, N. J.; Milligan, T. W.; Brown, T. L. *J. Am. Chem. Soc.* **1960**, *82*, 4075. (c) Roush, P. B.; Ph.D. Thesis, University of California, Davis, 1977.

[47] Glass, R. S., private communication.

[48] Malba, V.; Jones, G., II; Poliakoff, E. D. *Photochem. Photobiol.* **1985**, *42*, 451.

[49] Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1276.

to signals at δ 2.1 (m, 4, CH_2) and 2.8 (m, 8, CH_2S) assigned to DTCO,[46c] δ 2.25 (m, 4, CH_2), 2.65 (m, 4, CH_2S), and 3.15 (m, 4, $CH_2S{=}O$) assigned to DTCS,[25] and δ 7.7 (m, 10, CH) assigned to BP. Benzpinacol, δ 7.2 (m, 20, CH), was prepared independently by irradiation of BP in isopropyl alcohol.

The peroxidase method[50] was used to determine the presence of H_2O_2 in samples which had been irradiated in the presence of oxygen. Quantities from 1 to 200 μL of sample were added to a 10-mL solution containing 0.1 mg of peroxidase, 3 mM leuco crystal violet, and 0.2 M acetate buffer at pH 5. The presence of H_2O_2 causes a dark blue color to form (crystal violet). Control solutions easily detected microgram quantities of H_2O_2 in CH_3CN solutions. As an important control, the reaction of DTCO and H_2O_2 was inspected. NMR analysis showed that addition of 30% H_2O_2 solution (40 μL) to 0.5 mL of 0.5 M DTCO in 80% CD_3CN/D_2O resulted in 50% conversion to DTCS within 60 min.

Quantum Yield Determinations. Quantum yields of photobleaching were determined by measuring the absorption spectrum of the sensitizer as a function of irradiation time. Δ[Sens] was measured by determining ϵ_{334}(BP) = 140 in (80% CH_3CN/H_2O). The number of photons incident on the sample was determined by using a quantum counter (Rhodamine B fluorescence in ethanol) to absorb a small, constant percentage of the incident light from a 500-W mercury lamp which had passed through a monochromator. The apparatus has been previously described.[49] The system was calibrated by ferrioxalate actinometry. Benzophenone samples were irradiated and monitored at λ = 334 nm. Quantum yields were obtained from the slope of a plot of Δ[Sens] vs. einsteins absorbed and extrapolated to zero time to correct for the change in the light absorbed as the sensitizer bleached.

Quantum yields of I_3^- production were determined with the same quantum counting apparatus described above. Solutions containing 20 mM DTCO, 10 mM I^-, and 10 mM BP in 80% CH_3CN/H_2O were irradiated at λ_{exc} = 334 nm for periods of 1 to 30 min while O_2 was continually bubbled through a portion of the solution which was not directly irradiated. The concentration of triiodide was determined by measuring ΔOD_{400}, a wavelength at which BP does not absorb. The molar absorptivity, $\epsilon(I_3^-) = 3.71 \times 10^3$ M^{-1} cm^{-1}, was determined in the same solvent system. Corrections were made for the competitive absorbance of the photoproduct, I_3^-.

The quantum yields for sulfoxide production in the presence of oxygen were determined by monitoring the decrease in [DTCO] and the increase in [DTCS] by NMR as a function of irradiation time for samples in which [BP] = 50 mM and [DTCO] = 50 mM in 80% CD_3CN/D_2O (λ_{exc} = 334 nm), with oxygen continuously bubbling through the cell during the experiment. An identical experiment was performed with 8 mM BP and 200 mM DTCO in order to monitor the photobleaching of BP after prolonged irradiation under oxygen and to calculate a turnover number (mol of BP consumed/mol of DTCS formed).

Acknowledgment. Support of this research by the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. We thank Professors W. K. Musker and R. S. Glass for helpful discussions and for providing information prior to publication and also Professors M. Z. Hoffman and K. D. Asmus for their advice and suggestions.

Registry No. UO_2^{2+}, 16637-16-4; DTCO, 6572-95-8; benzophenone, 119-61-9; bracetyl, 431-03-8.

---

(50) Mottola, H. A.; Simpson, B. E.; Gorin, G. *Anal. Chem.* **1970**, *42*, 410.

Communications to the Editor

Reactivity of Mixed Cyclometalated Palladium Compounds Containing the [2-$Me_2NC_6H_4C(H)SiMe_3$] Monoanion.[1] Transmetalation Reaction and Formation of a Novel μ-Alkylidene Compound (X-ray) Bis(μ-chloro)bis{μ-*C*,σ-*N*-[2-(dimethylamino)benzylidene](μ-chloro)(diethyl sulfide)dipalladium(II)}

Fida Maassarani,[2a] Michel Pfeffer,*[2a] Anthony L. Spek,[2b]
Antoine M. M. Schreurs,[2b] and Gerard van Koten*[2c]

Laboratoire de Chimie de Coordination UA 416 CNRS
Université Louis Pasteur
F-67070 Strasbourg Cédex, France
Laboratorium voor Kristal- en Structuurchemie
University of Utrecht
3508 TB Utrecht, The Netherlands
Anorganisch Chemisch Laboratorium
University of Amsterdam, Nieuwe Achtergracht 166
1018 WV Amsterdam, The Netherlands

Received January 3, 1986

The chemistry of metal complexes containing μ-methylene (or μ-alkylidene) bridges is a rapidly growing field[3a] with the number of possible synthetic routes to these complexes still increasing.[3b] It was found that in order to get stable Pd_2– and Pt_2–μ-methylene compounds the absence of a stabilizing metal-to-metal bond had to be compensated for by the use of bridging $R_2PCH_2PR_2$ ligands.[4,5]

The study reported here involves reactions of mixed cyclometalated compounds Pd[2-$Me_2NC_6H_4CH(SiMe_3)$](dmba) (**1**, dmba is 2-$Me_2NCH_2C_6H_4$) with $PdCl_2(SR_2)_2$. Depending on the nature of the SR_2 ligand these reactions provide either transmetalation products or a novel type of dimeric μ-alkylidene dipalladium compound {$Pd_2(\mu\text{-Cl})(\mu'\text{-Cl})(SEt_2)$-[($CHC_6H_4NMe_2$-2)]}$_2$ (**2**). Interesting features of these reactions are (i) the novel way in forming the alkylidene fragment which involves overall 1,2-Me_3SiCl elimination, (ii) the stability of the μ-alkylidene compound **2** in which specific bridging ligands (see above) are absent, and (iii) the influence of the coligand SR_2 on the reaction course.

Reaction of **1**[6a] with *trans*-$PdCl_2(SEt_2)_2$[6b] (1:1 molar ratio) in boiling $CHCl_3$ or toluene afforded in addition to PdCl(dmba)(SEt_2) and $[PdCl(dmba)]_2$ (30% yield calculated on dmba) a red crystalline product **2**, which was isolated from the reaction mixture in 26% yield (recrystallization from CH_2Cl_2/pentane). FD mass spectrometry, elemental analytical, and ^1H and ^{13}C NMR spectrometric[7] data indicated a $Pd_2Cl_2(SEt_2)$[(C(H)$C_6H_4NMe_2$-2)]

---

[1] Part 2. For part 1, see: Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Wehman, E.; van Koten, G. *J. Am. Chem. Soc.* **1984**, *106*, 8002.

[2] (a) Strasbourg, France. (b) Utrecht, The Netherlands. (c) Amsterdam, The Netherlands.

[3] (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. (b) Cf. Figure 9, in: Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319.

[4] Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808. Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

[5] Arnould, D. P.; Bennett, M. A.; McLaughlin, G. M.; Robertson, G. B.; Whittaker, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 32 and 34.

[6] (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; van Koten, G.; Jastrzebski, J. T. B. H., manuscript in preparation. (b) With *trans*-$PdCl_2(SPr_2)_2$ the corresponding μ-benzylidene compound {$Pd_2(\mu\text{-Cl})(\mu'\text{-Cl})(SPr_2)$-[($CHC_6H_4NMe_2$-2)]}$_2$ is formed.

[7] ^1H NMR of **2** ($CDCl_3$, Me_4Si internal): δ NMe_2 3.03, 3.44 and 3.06, 3.44; CH 5.96 and 5.94; SCH_2 2.3 m; CH_3 1.24 (mole ratio diastereomers 3:2). ^{13}C NMR ($CDCl_3$, Me_4Si internal): δ NMe_2 53.7 and 53.3; CH 76.7; SCH_2 30.7; CH_3 13.2.

[8] The structure was solved by Patterson and Fourier methods (SHELX 84) and refined (SHELX 76) with anisotropic thermal parameters of the non-hydrogen atoms to R = 0.042, R_{wF} = 0.0497, w = 1. Hydrogen atoms were introduced on calculated positions. A disorder model was used to include CH_2Cl_2 molecules on 0,0,0 and 0,0,$^1/_2$ positions. Full details will be given elsewhere.