of the plot in the potential region below 0.4 V in Figure 9, which is notably absent in the plot derived from the complete kinetic situation presented in Figure 5a.

Peak Broadening of the CV Wave and the Nature of the Electrochemical Reversibility. In the kinetics of Scheme III, the disappearance of the electrogenerated intermediate A_0^+ depends on the overall rate constant k_2'. Actually, two pathways exist for the depletion of A_0^+, viz., the diffusion rate constant k_d in eq 32 and the chemical reaction rate constant k_r in eq 33.

Diffusion is known to be proportional to the square root of the sweep rate,[24] whereas k_r will be a constant that is specific to the chemical system, i.e., the chemical identity of A_0^+. Both processes operate simultaneously in the inhomogeneous concentration profile extant at the electrode surface. Nonetheless, it has been shown that the net effect k_2' may be described as a simple sum of the two rate processes, i.e.,[18,60]

$$k_2' = k_r + k_d \tag{41}$$

The results in Figure 2 indicate that the net forward rate constant k_e in eq 36 is independent of the sweep rate varying over 4 orders of magnitude. This is consistent with the generation of a highly unstable intermediate in which k_2' is dominated by k_r over the entire range of accessible sweep rates.[61] This result has important implications. Thus, the CV waves in Figure 1 are observed to broaden (as measured by $E_p - E_{p/2}$) substantially at higher sweep rates. This broadening is not due to a decrease in the electrochemical reversibility.[62] For example, if k_2' were controlled by k_d, the maximum slope of the plot of log k vs. log v would be 0.5 for systems in which electrochemical reversibility (as defined by eq 37 and 38) is determined by the sweep rate.

Furthermore, we can conclude that the broadening of the CV waves in Figure 1 is not due to an experimental artifact such as an uncompensated cell resistance.[63] Thus at any constant value of the applied potential, the current increases as the square root of the sweep rate. Yet the value of the measured rate constant is invariant, as shown by the horizontal rows in Figure 2. Therefore, uncompensated iR drops have a minimal influence on the rate data. Indeed, the slopes in Figure 2 in conjunction with eq 42 may be used to estimate an upper limit on the uncompensated cell resistance,

$$\mathrm{d} \log k_e = (\beta n \mathcal{F}/2) V_{cell}\, \mathrm{d} \log v \tag{42}$$

where $V_{cell} = iR_{cell}$. Since the slopes in Figure 2 are all close to zero, the uncompensated cell resistance must also be close to zero, according to eq 42. Indeed, this conclusion accords well with the results obtained from Table III.

We can thus conclude that the broadening of the CV waves with sweep rate is not due to (1) changes in degree of electrochemical reversibility or (2) experimental artifacts such as uncompensated cell resistance. However, such a peak broadening could result directly if the transfer coefficient β_e were itself a function of the applied potential. Thus standard electrochemical theory indicates that the width of the CV wave will be given by eq 30. Indeed the plot of k_e vs. E in Figure 3 indicates a substantial degree of curvature, consistent with a potential dependence of β.[49]

Acknowledgment. We wish to thank the National Science Foundation for support of this research and funds to purchase the electrochemical equipment and the computer and Professor C. Walling for helpful comments of the manuscript.

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Supplementary Material Available: Tabulation of the experimental rate constants k_e and electrochemical data used (27 pages). Ordering information is included on any current masthead page.

(61) In other words, the electrochemical irreversibility induced by the fast following chemical reaction is already so large that the reversibility of the system cannot be significantly altered, even by employing sweep rates as high as 1000 V s^{-1}.

(62) The interpretation of the broadening and concurrent shifting of the CV wave as due to changes in the electrochemical reversibility of the system while a constant value of the transfer coefficient is maintained is the basis of the method proposed by Nicholson[63] for obtaining the data for heterogeneous rate constants.

(63) The broadening effect of CV waves arising from uncompensated cell resistance is known. See: Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

Micellar Photochemistry. Photooxidations with Intramicellar-Generated Singlet Oxygen

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Abstract: Pyrex-filtered irradiation of an aerated 5% aqueous sodium dodecyl sulfate ($NaDodSO_4$) solution of 2.8 mM 10-methylphenothiazine (MPT) and 2.8 mM benzyl sulfide resulted in formation of a 39% yield of benzyl sulfoxide. The reaction was general for transformation of a variety of sulfides to sulfoxides and for triphenylphosphine to triphenylphosphine oxide and was catalytic with respect to MPT. Also effective in promoting the photooxidation were 10-acetylphenothiazine, 10-benzoylphenothiazine, 10-(2-cyanoethyl)phenothiazine, 10-methyl-2-(trifluoromethyl)phenothiazine, and 3-bromo-10-methylphenothiazine. The photooxidation also took place in microemulsion media. Singlet oxygen was implicated as the primary oxidizing agent and is thought to arise by the intramicellar recombination of the transient $MPT^{+\cdot}/O_2^{-\cdot}$ ion pair. The rates of quenching of $^1O_2$ by benzyl sulfide and MPT were measured in chloroform solution. The quenching rate, k_Q, was 6.4×10^6 M^{-1} s^{-1} for benzyl sulfide and 2.9×10^6 M^{-1} s^{-1} for MPT. The reaction of singlet oxygen with benzyl sulfide in the presence of MPT in the micelle was discussed in terms of the greater tendency of the MPT to quench singlet oxygen rather than react to form 10-methylphenothiazine 5-oxide.

Aqueous micellar medium effects on photophysical processes have seen much attention recently.[1] The use of micelles to promote synthetically useful photochemical reactions is an area of rapidly increasing interest. Some examples of synthetic reactions include photocycloadditions,[2] substitutions,[3] isotopic enrichment,[4] and remote functionalization.[5] In contrast to those in homogeneous solution, products and yields often change dra-

(1) J. K. Thomas, *Chem. Rev.*, **80**, 283–299 (1980).

(2) (a) K.-H. Lee and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 493–495 (1979); (b) Y. Nakamura, Y. Imakura, T. Kato, and Y. Morita, *ibid.*, 887–888 (1977); (c) Y. Nakamura, Y. Imakura, and Y. Morita, *Chem. Lett.*, 965–968 (1978).

(3) (a) R. R. Hautala and R. L. Letsinger, *J. Org. Chem.*, **36**, 3762–3768 (1971); (b) J. B. S. Bonilha, H. Chaimovich, V. G. Toscano, and F. Quina, *J. Phys. Chem.*, **83**, 2463–2470 (1979).

(4) (a) N. J. Turro, B. Kraeutler, and D. R. Anderson, *J. Am. Chem. Soc.*, **101**, 7435–7437 (1979); (b) *Tetrahedron Lett.*, 3–6 (1980); (c) B. Kraeutler and N. J. Turro, *Chem. Phys. Lett.*, **70**, 266–269 (1980).

(5) (a) R. Breslow, S. Kitabatake, and J. Rothbard, *J. Am. Chem. Soc.*, **100**, 8156–8160 (1978); (b) M. Mitani, T. Suzuki, H. Takeuchi, and K. Koyama, *Tetrahedron Lett.*, 803–804 (1979).

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Table I. Phenothiazine-Promoted Micellar Photooxidation Products and Yields

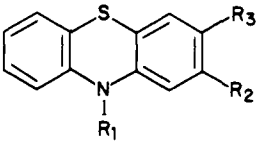
phenothiazine	substrate	irrad time, h	product	yield, %
MPT	$PhCH_2SCH_2Ph$	3.0	$PhCH_2S(=O)CH_2Ph$	39
		2.5		45[a]
		2.2		24[b]
		2.1		22[c]
	$PhCH_2SCH_2CH_2CH_2CH_3$	2.7	$PhCH_2S(=O)CH_2CH_2CH_2CH_3$	40
	$PhCH_2SCH_2CH=CH_2$	4.2	$PhCH_2S(=O)CH_2CH=CH_2$	17
	$PhCH_2SPh$	4.2	$PhCH_2S(=O)Ph$	29
	PhSPh	4.0	PhS(=O)Ph	2.5
	$(i\text{-}C_3H_7)_2S$	2.5	*d*	
	$(PhCH_2)_3N$	3.0	*d*	
	$PhCH_2SePh$	4.0	...	0
	Ph_3P	2.0	Ph_3PO	39
3a	$PhCH_2SCH_2Ph$	2.5	$PhCH_2S(=O)CH_2Ph$	50
3b		3.0		50
3c		3.0		32
3d		2.4		27
3e		2.2		12
3f		3.8		0

[a] In microemulsion media (5% $NaDodSO_4$ + 4.4% 1-pentanol + 1.5% hexadecane). [b] In *tert*-butyl alcohol solution. [c] In cyclohexane solution. [d] Product was too water soluble to isolate (see text). [e] MPT was a byproduct (see text).

matically when a reaction is carried out in a detergent solution because of the order imposed on a system by the micellar structure.

Above the critical micelle concentration (cmc), surfactant molecules associate into spherical micelles approximately 30 Å in diameter and containing 50–70 monomers each.[6] Inside is a hydrophobic "core" consisting of the coiled hydrocarbon chains of the surfactant molecules. Organic compounds normally insoluble in water can be solubilized in aqueous detergents by incorporating them into this hydrophobic region. This "oil droplet" can serve as a miniature reaction vessel confining the reactant molecules to a very small volume and greatly enhancing bimolecular reaction rates. Further, the "skin" of the micelle, which consists of the surface layer of the polar surfactant head groups (the Stern layer), can provide a boundary across which charged species can mediate interactions between the micellar contents and ions in the bulk aqueous phase. This latter feature of micellar structure gives rise to such phenomena as phase-transfer catalysis, emulsion polymerization, etc.

Anionic micelles can promote photoionization of electron-rich aromatic molecules such as pyrene, phenothiazine, and tetramethylbenzidine. The highly charged Stern layer drastically reduces the ionization potential of these micelle-bound molecules from their gas-phase values, and the entrapped aromatic cation radical which results is stabilized by the electrostatic barrier, preventing the return of the photoejected electron. For example, 10-methylphenothiazine (MPT, **1**), which has a gas-phase ionization potential of 6.5 eV, can be photoionized in aqueous sodium dodecyl sulfate ($NaDodSO_4$) by 347-nm (3.57eV) light.[7] Use of laser flash photolysis enables the observation of the MPT cation radical and the solvated electron in such systems.



1, $R_1 = CH_3$, $R_2 = H$, $R_3 = H$;
3a, $R_1 = CH_3CO$, $R_2 = H$, $R_3 = H$;
3b, $R_1 = PhCO$, $R_2 = H$, $R_3 = H$;
3c, $R_1 = NCCH_2CH_2$, $R_2 = H$, $R_3 = H$,
3d, $R_1 = CH_3$, $R_2 = CF_3$, $R_3 = H$;
3e, $R_1 = CH_3$, $R_2 = H$, $R_3 = Br$;
3f, $R_1 = CH_3$, $R_2 = Cl$, $R_3 = H$

The ease of generation and the stability of the micelle-bound MPT cation radical suggested to us that it might exhibit unusual chemical reactivity. Indeed, ion-driven photoredox couples in micelles are being increasingly studied as solar energy storage systems or hydrogen generators.[8] In this paper we report the discovery and properties of an organic electron-transfer couple which employs micelle-solubilized MPT and its photogenerated cation radical as an oxidizing agent for a wide variety of substrates.

Results

One liter of 5% aqueous sodium dodecyl sulfate ($NaDodSO_4$) solution solubilized 615 mg of MPT. The concentration of MPT was 2.8 mM, and the average occupation number of each micelle was unity.[9a] Irradiation of this clear, colorless solution afforded no change when purged with nitrogen. When air was bubbled through the solution during the photolysis, a deep red color rapidly formed which persisted for several days after the lamp was shut off. The ESR spectrum of the red solution was characteristic of MPT cation radical[10] and was, except for the fine structure, identical with the spectrum produced by a solution of MPT in concentrated sulfuric acid (see Figure 1).

Irradiation of micellar MPT as above with an equimolar amount of benzyl sulfide cosolubilized[9b] again afforded no reaction when nitrogen purged. When air bubbled, however, a 39% yield of benzyl sulfoxide was obtained, and the MPT was recovered essentially quantitatively.[11] This oxidation reaction was found to be applicable to sulfides in general (see Table I). Photolysis of benzyl *n*-butyl or allyl benzyl sulfide likewise afforded the corresponding sulfoxides. The photooxidation of phenyl sulfide occurred in much lower yield.[12]

Attempts to extend this photooxidation method to other substrates met with partial success (see Table I). The choice of

(6) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975, p 30.

(7) Y. Moroi, A. M. Braun, and M. Graetzel, *J. Am. Chem. Soc.*, **101**, 567–572 (1979).

(8) (a) N. J. Turro, M. Graetzel, and A. M. Braun, *Angew. Chem., Int. Ed. Engl.*, **19**, 675 (1980); (b) M. S. Tunuli and J. H. Fendler, *J. Am. Chem. Soc.*, **103**, 2507 (1981).

(9) (a) It was assumed that each micelle consisted of 60 surfactant molecules. Thus, 1 L of 5% $NaDodSO_4$ was 2.8 mM in micelles. (b) Poisson statistical analysis (see ref 9c) indicated that 63% of the micelles contained at least one molecule of either MPT or benzyl sulfide. Thus, the fraction of micelles containing at least one each of both molecules was $(0.63)^2$ or 0.39. (c) R. C. Dorrance and T. F. Hunter, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1572 (1972).

(10) S. Odiot and F. Tonnard, *J. Chem. Phys.*, **61**, 382 (1964).

(11) (a) Extractive isolation of organics from $NaDodSO_4$ solutions resulted in intractible emulsion formation unless the micellar structure was first broken down by binding the surfactant to render it insoluble. The resulting heterogeneous mixture could then be extracted with an organic solvent such as ether or dichloromethane. Binding agents which were effectively used with $NaDodSO_4$ include magnesium chloride[11b] or a cationic ion-exchange resin such as Rexyn 202,[3a] the latter being more efficient. (b) N. J. Turro, private communication.

(12) Sulfides without α-hydrogens have been shown to oxidize slowly in many systems. See T. Tezulea, H. Miyazaki, and H. Suzuki, *Tetrahedron Lett.*, 1959–1960 (1978).

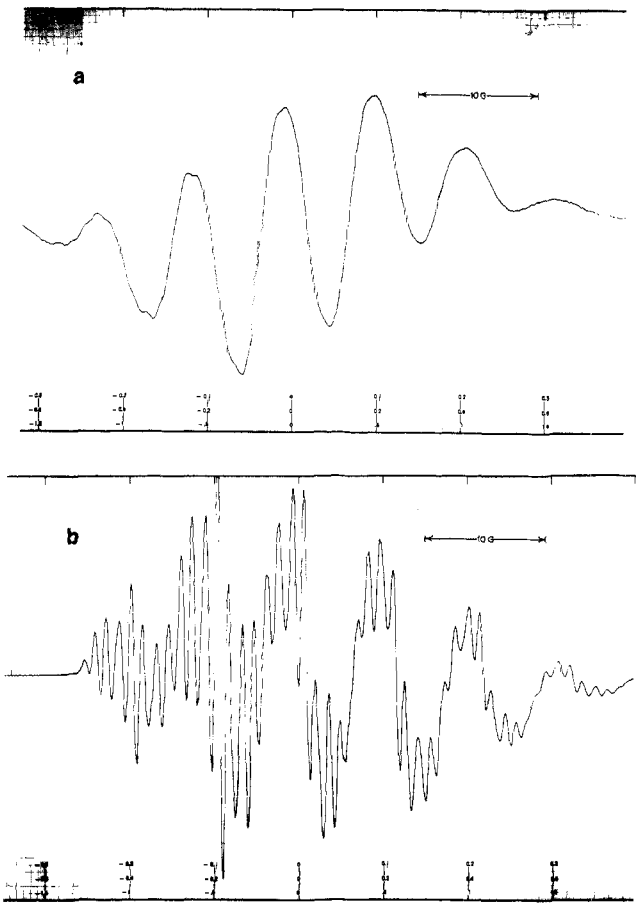
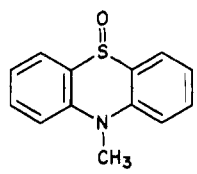


Figure 1. ESR spectra of MPT cation radical: (a) 2.8 mM MPT in 5% aqueous $NaDodSO_4$ irradiated 2 h; (b) 11 mM MPT in concentrated sulfuric acid.

oxidizable substrate was found to be crucial because of the increase in water-phase solubility which generally accompanies oxidation reactions. Isopropyl sulfide, for example, affords a sulfoxide which is too hydrophilic to be detected or extracted from the bulk aqueous phase. Triphenylphosphine yielded triphenylphosphine oxide upon aerated irradiation with micellar MPT. Benzyl phenyl selenide was unreactive in this system.[13] Attempts to oxidize various amines to amine oxides encountered experimental difficulties because of the extreme water solubility of the products which prevented extractive isolation.

Photooxidation of sulfides promoted by MPT also took place in nonmicellar homogeneous solution, but the reactions were not as clean, yielding many resinous byproducts and degradation of the MPT. Irradiation of MPT and benzyl sulfide in *tert*-butyl alcohol solution gave a 24% yield of benzyl sulfoxide, accompanied by 17% of 10-methylphenothiazine 5-oxide (**2**), 26% of insoluble,



2

uncharacterizable material, and 18% of an unidentified compound. In cyclohexane solution destruction of the MPT was complete, and a 22% yield of benzyl sulfoxide was seen.

Variation in the phenothiazine substituents was done in order to explore possible effects on the photooxidation reaction (see Table I). Benzyl sulfide was oxidized to benzyl sulfoxide in 50% yield by either 10-acetyl- or 10-benzoylphenothiazine (**3a** or **3b**).

(13) L. Hevesi and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **15**, 381 (1976).

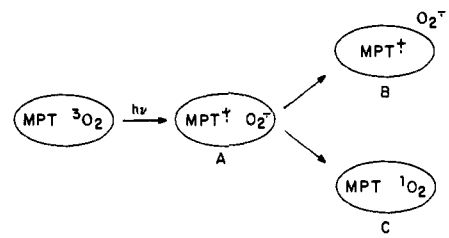


Figure 2. MPT photoionization showing reaction pathways available to the micelle-contained ion pair A. Oval denotes micellar boundary.

Substitution of 10-(2-cyanoethyl)phenothiazine (**3c**) for MPT resulted in a 33% yield of benzyl sulfoxide. In contrast, ring substitution of the phenothiazine nucleus brought on undesired side reactions. Benzyl sulfide was oxidized in 27% yield by using 10-methyl-2-(trifluoromethyl)phenothiazine (**3d**). In this case, however, the phenothiazine **3d** was degraded to an unknown product during the reaction. Likewise, 3-bromo-10-methylphenothiazine (**3e**) afforded a quantitative yield of MPT in addition to 12% benzyl sulfoxide, the former arising through photoscission of the bromine atom. 2-Chloro-10-methylphenothiazine (**3f**) was destroyed by the photolysis conditions and produced no benzyl sulfide oxidation.

Further generality of the MPT-promoted photooxidation was shown when carried out in microemulsion media. Addition of 1-pentanol and hexadecane to an aqueous $NaDodSO_4$ solution causes the micelle to expand in size while preserving its spherical shape. The clear solution which results is termed a microemulsion.[14] The greater micellar volume enables solubilization of larger amounts of organic hydrophobic solutes than in simple micelles. Irradiation of MPT and benzyl sulfide in such a microemulsion afforded 40% benzyl sulfoxide and recovered MPT in a fashion completely parallel to the process in $NaDodSO_4$ alone.

Mechanistic Studies and Discussion

Solubilization of MPT and benzyl sulfide in aqueous $NaDodSO_4$ at the specified concentrations results in an average occupation of one molecule of each per micelle. Irradiation of nitrogen-purged micellar MPT, with or without added sulfide, results in no detectable photoionization. The requirement for both ultraviolet light and MPT in order for oxidation of a sulfide to a sulfoxide to occur was elucidated by appropriate control experiments in which each factor was in turn omitted. Oxygen is apparently necessary not only to oxidize the sulfide but also to effect photoionization of the MPT (Figure 2).

Graetzel and co-workers found that the addition of an electron sink such as duroquinone to micellar phenothiazine greatly enhanced its photoionization. Electron transfer from phenothiazine to duroquinone took place on a nanosecond time scale, and this was followed by slow electron back-transfer to form neutral species, both processes occurring within the interior of the micelle.[15]

In the present system oxygen serves as an electron acceptor for the excited MPT molecule. Initially, the ion pair $MPT^+\cdot/O_2^-\cdot$ (A in Figure 2) is formed inside the micelle, and, in a fraction of the micelles, the superoxide thus formed can escape into the bulk aqueous phase before electron back-transfer can occur (B in Figure 2). The negatively charged skin of the $NaDodSO_4$ micelle prevents reentry of the superoxide anion or its excess electron, making the entrapped MPT cation radical exceedingly long-lived. These micelles account for the deep red color of the solution.

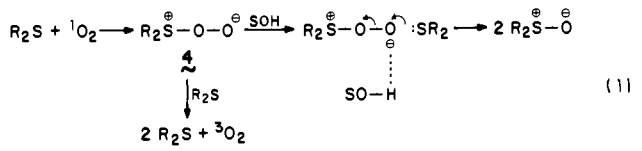
Further control experiments elucidated the catalytic role of the phenothiazine. Irradiation of micellar MPT under the standard conditions but in the absence of sulfide afforded a 5% yield of **2**. Photolyzing **2** and benzyl sulfide in aqueous $NaDodSO_4$ under nitrogen-purging conditions resulted in no oxidation to benzyl sulfoxide. These two experiments show that **2** is not an inter-

(14) M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **102**, 3188–3193 (1980).

(15) S. A. Alkaitis, M. Graetzel, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **79**, 541 (1975).

mediate in the oxidation of benzyl sulfide and that sulfide reacts much more efficiently than MPT with whatever oxidizing species is present.

In homogeneous media 1 mol of singlet oxygen oxidizes 2 mol of dialkyl sulfide to form sulfoxide.[16] The mechanism proposed involves the intermediacy of a persulfoxide, structure **4**, and requires a second molecule of sulfide to convert the persulfoxide to two sulfoxide molecules (eq 1).



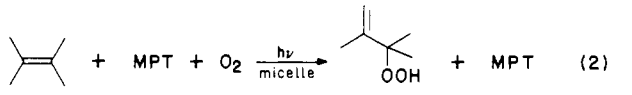
(1)

The photooxidation of sulfides in micellar media, however, showed no second-order dependence of reaction rate on sulfide concentration. When the MPT-promoted micellar photooxidation was run with one-tenth the amount of benzyl sulfide, oxidation proceeded normally, and a 40% yield of benzyl sulfoxide was obtained. The mechanism of the reaction of benzyl sulfide with singlet oxygen in the micellar photooxidation is not known. Clearly, two molecules of sulfide are not involved since in the dilution experiment only 1% of the micelles contain two or more sulfide molecules.[9c] Involvement of the MPT is feasible, as is that of the ubiquitous water, though several tests failed to detect any hydrogen peroxide.

Tests for Superoxide. The superoxide formed upon electron transfer from the excited MPT molecule is probably only a transient species which rapidly exits the micelle (B in Figure 2) or annihilates the MPT cation radical forming singlet oxygen (C in Figure 2—see discussion below). Chemical reactions of the superoxide moiety were not observed, when, for instance, an electrophile such as 1-iodooctane was cosolubilized in the MPT/$NaDodSO_4$ system. Photolysis with aeration afforded none of the expected 1-octanol or 1-hydroperoxyoctane.[17] This proved only that superoxide, if formed, was not trappable in this competition experiment.

Potassium superoxide, which cleaves and oxidizes sulfur–sulfur bonds (e.g., in compounds such as disulfides, thiolsulfinates, and thiolsulfonates),[18] was unreactive toward benzyl sulfide in pyridine solution. A mixture of benzyl sulfide and potassium superoxide in pyridine, with a catalytic amount of dicyclohexyl-18-crown-6, afforded only recovered benzyl sulfide. Thus, in the micellar photooxidation of sulfides catalyzed by MPT, the oxidizing agent is not superoxide.

Tests for Singlet Oxygen. Strong evidence has been obtained that singlet oxygen is the active oxidizing agent in the micellar photooxidation. Irradiation of aerated micellar MPT and tetramethylethylene resulted in rapid formation of 2,3-dimethyl-3-hydroperoxy-1-butene (eq 2). The latter is the product of the ene reaction between tetramethylethylene and singlet oxygen and is diagnostic of the presence of singlet oxygen.[19]



(2)

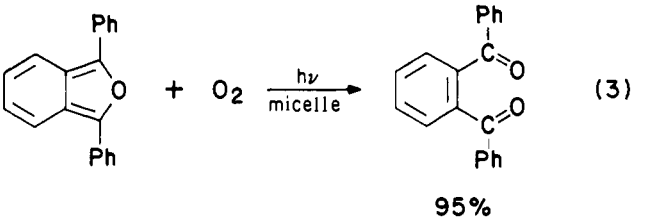
1,3-Diphenylisobenzofuran proved unusable as a singlet oxygen trap because of its large extinction coefficient at the 320-nm maximum of the MPT, thus absorbing most of the incident UV light. Irradiation of aerated micellar 1,3-diphenylisobenzofuran alone caused rapid bleaching of the fluorescent blue-yellow color

Table II. Rates of Reaction of Singlet Oxygen with Compounds Used in This Study

compd	rate ($10^5 k_q$, M^{-1} s^{-1})	compd	rate ($10^5 k_q$, M^{-1} s^{-1})
$PhCH_2SCH_2Ph$	64	MPT	29
$PhCH_2SPh$	8.5	$PhCH_2SePh$	60
PhSPh	0.8[a]	Ph_3P	85

[a] Reference 23b.

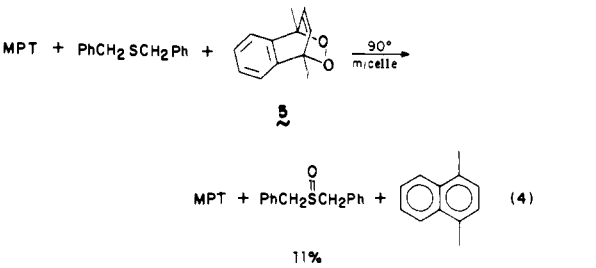
and afforded the singlet oxygen product 1,2-dibenzoylbenzene in 95% yield (eq 3).[20,21]



(3)

95%

The behavior of singlet oxygen inside the $NaDodSO_4$ micelle was examined in detail by utilizing a process known to afford $^1O_2$ by nonphotochemical means. Generation of intramicellar singlet oxygen was effected by Turro's method of pyrolysis of an aromatic endoperoxide.[22] Thus an $NaDodSO_4$ solution of equimolar amounts of MPT, benzyl sulfide, and 1,4-dimethylnaphthalene 1,4-endoperoxide (**5**) was heated to 90 °C for 45 min, affording an 11% yield of benzyl sulfoxide as well as recovered benzyl sulfide and MPT (eq 4). We note, as observed during the micellar photolysis, that MPT is inert to singlet oxygen in the presence of benzyl sulfide.



(4)

11%

Rates of Reaction of Singlet Oxygen. In order to quantify the greater proclivity of alkyl sulfides to react with singlet oxygen, we used the method of Monroe[23] to measure the rate of reaction of MPT and substrates with singlet oxygen (see Table II). The Monroe method measures a compound's rate of quenching (k_Q) of the self-sensitized photooxidation of rubrene. The resultant rate is the sum of the rates of all processes which remove $^1O_2$ from the solution, including reaction to sulfoxide and quenching. Note that k_Q for MPT is 2.9×10^6 M^{-1} S^{-1}, almost half that of k_Q for benzyl sulfide. Yet in the micellar photooxidation, MPT is only slowly photooxidized, and it is not oxidized in the presence of benzyl sulfide.

For sulfides in micellar environments where water molecules are known to penetrate the hydrophobic interior region exten-

(16) (a) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); (b) M. Casagrande, G. Gennari, and G. Cauzzo, *Gazz. Chim. Ital.*, **104**, 1251 (1974); (c) C. S. Foote and J. W. Peters, *J. Am. Chem. Soc.*, **93**, 3795, (1971).

(17) J. San Filippo, C. Chern, and J. S. Valentine, *J. Org. Chem.*, **40**, 1678–1680 (1975).

(18) T. Takata, Y. H. Kim, and S. Oae, *Tetrahedron Lett.*, 821 (1979).

(19) (a) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1969); (b) J. L. Zupancic, K. A. Horn, and G. B. Schuster, *J. Am. Chem. Soc.*, **102**, 5279 (1980).

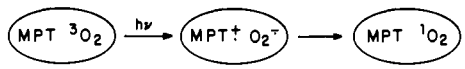
(20) H. H. Wasserman, J. R. Scheffer, and J. L. Couper, *J. Am. Chem. Soc.* **94**, 4991 (1972).

(21) (a) This ability of 1,3-diphenylisobenzofuran to self-sensitize the formation of singlet oxygen is not generally appreciated (see ref 21b–d). Thus, experimenters who would use the compound as diagnostic of the presence of singlet oxygen must be cautioned not to allow any absorption of incident light by the 1,3-diphenylisobenzofuran, lest self-promoted photooxidation occur. (b) T. Wilson, *J. Am. Chem. Soc*, **88**, 2898 (1966); (c) J. Olmstead and T. Akashah, *ibid.*, **95**, 6211 (1973); (d) R. K. Haynes, J. M. Peters, and I. D. Wilmot, *Aust. J. Chem.*, **33**, 2653 (1980).

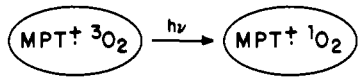
(22) N. J. Turro, M. Chow, S. Kanfer, and M. Jacobs, *Tetrahedron Lett.*, 3–6 (1981).

(23) (a) B. M. Monroe, *J. Phys. Chem.*, **81**, 1861 (2077); (b) *Photochem. Photobiol.*, **29**, 761 (1979).

Scheme I



Scheme II



sively,[24] k_Q is a measure of reaction to sulfoxide since quenching is a minor process in protic media.[25] For the phenothiazines studied, however, the picture is more complex. The rate of reaction of diaryl sulfides with singlet oxygen is very low ($k_Q = 8 \times 10^4$ M^{-1} s^{-1} for phenyl sulfide[23b]). The simultaneous presence of a diarylamine function in phenothiazines increases the tendency of the latter to quench singlet oxygen rather than react with it, since amines are known to quench singlet oxygen 90% of the time and react to form amine oxide the remaining 10%.[26] This accounts for the discrepancy between the complete inertness of MPT in the presence of benzyl sulfide in the micellar photooxidation despite the fact that the k_Q of MPT is half that of benzyl sulfide (see Table II). MPT, as a diaryl sulfide, reacts to form its sulfoxide very slowly in analogy to diphenyl sulfide. MPT as a diaryl tertiary amine quenches singlet oxygen rapidly, though steric hindrance probably mitigates this acceleration somewhat.[21a] MPT, as an electron-rich phenothiazine, then, functions as a rapid quencher of singlet oxygen, slow to react to form its 5-oxide. Therefore its high k_Q reflects not a rapid rate of reaction but rather of quenching of singlet oxygen because of the presence of the amine moiety plus the electron-rich phenothiazine ring system.

Direct comparison of the sulfoxide reaction rates of MPT and benzyl sulfide was provided by an experiment in which equimolar amounts of these two compounds were photooxidized in chloroform by using the singlet oxygen sensitizer methylene blue. The reaction yielded a 7:1 ratio of benzyl sulfoxide and 10-methylphenothiazine 5-oxide (**2**). In micellar media the reactivity ratio is probably even higher.

Source of Singlet Oxygen. Two mechanisms for the production of intramicellar singlet oxygen in the MPT-promoted photooxidation of sulfides seemed plausible: electronic excitation via the energy of recombination of the MPT cation radical and superoxide anion radical or dye-sensitized conversion of triplet to singlet oxygen, where the deeply red colored MPT cation radical functioned in much the same manner as classical singlet oxygen sensitizers such as methylene blue or rose bengal. Both mechanisms are depicted in Schemes I and II.

Reaction of cation and anion radicals was carried out in acetonitrile solution to attempt to test Scheme I. Addition of potassium superoxide to a solution of methyl phenothiazine radical cation perchlorate and benzyl sulfide afforded a 5% yield of benzyl sulfoxide plus recovered benzyl sulfide and MPT (eq 5a). Since

$$\text{MPT}^+\ ClO_4^- + PhCH_2SCH_2Ph + KO_2 \xrightarrow{CH_3CN} \underset{5\%}{\text{MPT} + PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph} + KClO_4 \quad (5a)$$

it is known that superoxide does not react directly with benzyl sulfide, the sulfoxide must arise from intermediate production of $^1O_2$ resulting from the energy of recombination of MPT$^{+}\cdot$ and $O_2^{-}\cdot$. Interestingly, no oxidation of the MPT is seen, even if the benzyl sulfide is omitted, a reactivity pattern parallel to that of the MPT micellar photooxidation. This contrasts with the analogous reaction of KO_2 with thianthrene cation radical perchlorate, affording singlet oxygen and a 1:1 mixture of neutral thianthrene and thianthrene 5-oxide.[27]

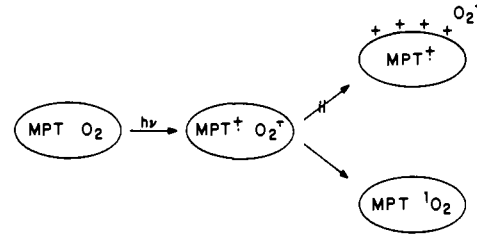


Figure 3. MPT-promoted photooxidation processes in cationic CTAB micelles.

The methyl phenothiazine cation radical is similar in both structure and charge to methylene blue, an efficient sensitizer of singlet oxygen. Therefore, a test was made of the second mechanistic possibility, i.e., the propensity of MPT$^{+}\cdot$ to function as a singlet oxygen sensitizer (Scheme II). Irradiation of an aerated acetonitrile solution of methyl phenothiazine radical cation perchlorate and benzyl sulfide resulted in no oxidation to benzyl sulfoxide (eq 5b).

$$\text{MPT}^+\ ClO_4^- + PhCH_2SCH_2Ph \xrightarrow[O_2]{h\nu,\ CH_3CN} \text{N.R.} \quad (5b)$$

Additional evidence for the cation radical/anion radical annihilation mechanism for production of singlet oxygen was furnished by carrying out the MPT-promoted photooxidation in a cationic surfactant solution. In such positively charged micelles, photoionization of MPT does not occur directly since the micelle skin, now positively charged, does not prevent fast return of the photoejected electron.[14] When a saturated aqueous solution of cetyltrimethylammonium bromide (CTAB) containing MPT and benzyl sulfide was aerated and irradiated, oxidation to 9% benzyl sulfoxide was observed. Figure 3 depicts the processes thought to occur within the CTAB micelle.

As in the case of the anionic micellar solution, irradiation of MPT and oxygen cosolubilized in the CTAB micelle generates the MPT$^{+}\cdot/O_2^{-}\cdot$ ion pair. Subsequent cation/anion radical annihilation produces singlet oxygen as in the SDS micelle. Here, however, the expulsion of a small fraction of the superoxide anion radicals from the micelles (e.g., B in Figure 2) does not occur because of the attraction of the positively charged surfactant head groups of the CTAB. Indeed, no red color was seen during the photooxidation run in CTAB, proving the absence of micelles containing the MPT cation radical.

Conclusion. Intramicellar generation of singlet oxygen occurred when aerated aqueous detergent solutions of MPT or a number of 10-alkylphenothiazines were irradiated with ultraviolet light. A series of experiments indicated that the singlet oxygen was formed from the energy of recombination of the initially formed MPT$^{+}\cdot/O_2^{-}\cdot$ ion pair. The singlet oxygen could be used to cleanly oxidize sulfides, phosphines, or phenothiazines cosolubilized in the micelles. The expanded micelles of a microemulsion also promoted the MPT-assisted photooxidation. Several control experiments excluded superoxide from consideration as the active oxidizing agent; others showed a first-order dependence of reaction rate on sulfide concentration, which is contrary to the present widely accepted mechanism of oxidation by singlet oxygen. Singlet oxygen quenching rates of the substrates used in this study were determined and discussed in relation to quenching/reaction preferences. These rates were compared to competitive rates separately established for MPT and benzyl sulfide in a methylene blue sensitized oxidation experiment performed in the same solvent.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary apparatus. Proton nuclear magnetic resonance spectra were obtained by using a Varian A60, EM360, or EM390 spectrometer. Ultraviolet and infrared

(24) M. A. J. Rodgers and M. E. Da Silva E. Wheeler, *Chem. Phys. Lett.*, **43**, 587 (1976).
(25) M. L. Kacher and C. S. Foote, *Photochem. Photobiol.*, **29**, 765 (1979).
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(27) W. Ando, Y. Kabe, S. Kobayashi, C. Takyu, A. Yamagishi, and H. Inaba, *J. Am. Chem. Soc.*, **102**, 4526–8 (1980).

spectra were obtained on a Cary 219 and a Perkin-Elmer 283B spectrometers, respectively. High-resolution mass spectra were obtained by using a Varian VG ZAB-2F instrument at 70 eV. Gas chromatography was performed on a Hewlett-Packard 5710A FID instrument using a Supelco 10% SP-2250 1.8 mm × 1.8 m glass column. High-performance liquid chromatography was performed on a Beckman/Altex 110A chromatograph employing a Model 153 UV detector at 254 nm and a Rheodyne 20 microliter loop injector using a Rainin 0.46 × 25 cm Ultrasil ODS reverse-phase packed column eluted with 65:35 acetonitrile/water. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) slurry packed into Pyrex columns.

Water was doubly distilled and sodium dodecyl sulfate (Aldrich) was ether-washed and recrystallized from ethanol. Tetramethylethylene (Aldrich) was freshly distilled from lithium aluminum hydride under an inert atmosphere. The following phenothiazines were prepared by the literature methods: 10-methylphenothiazine (MPT),[28] 10-acetylphenothiazine,[29] 10-benzoylphenothiazine,[29] 10-(2-cyanoethyl)phenothiazine,[30] 3-bromo-10-methylphenothiazine,[31] and 2-chloro-10-methylphenothiazine.[32]

Preparative workup of 1 L of 5% aqueous $NaDodSO_4$ solutions was accomplished by stirring for 18 h with 125 g of Rexyn 202 ion-exchange resin. The mixture was filtered, and the solids were washed five times with 200-mL portions of ether. The filtrate was ether extracted, and the combined organic phases were concentrated in vacuo.

Analytical workup of 3-mL aliquots of 5% $NaDodSO_4$ solutions was accomplished by addition of 1 g of magnesium chloride[11b] and 3 mL of methylene chloride and by vigorously stirring. The lower layer was decanted and 1 g of sodium chloride added to it to break up the emulsion. This mixture was swirled and allowed to stand briefly to allow the layers to separate. The bottom organic layer was then suitable for GLPC or HPLC analysis.

Preparative photolyses were done by using a Hanovia 450-W medium-pressure mercury arc lamp in a water-cooled quartz immersion apparatus with a Pyrex sleeve filter. The 1-L immersion well was fitted with a rubber septum/polyethylene tube for aeration and a wide-mouth funnel (to allow breakup of the resulting foam) and was wrapped in aluminum foil to maximize light capture.

10-Methyl-2-(trifluoromethyl)phenothiazine (3d). A solution of 10.0 g of 2-(trifluoromethyl)phenothiazine (37 mmol), 3.0 mL of methyl iodide (50 mmol), and 7.5 g of 33% aqueous sodium hydroxide solution in 50 mL of methyl sulfoxide was heated to 90 °C for 20 min with stirring. The reaction mixture was cooled, poured into 500 mL of water, and ether extracted twice. The combined ether layers were water washed, dried with magnesium sulfate, and concentrated in vacuo, affording an oily solid. Recrystallization of this material using ethanol afforded 10.0 g (96%) of pale yellow prisms, mp 58–59.5 °C.

The spectral data were as follows: 60-MHz NMR ($CDCl_3$) 3.38 (s, 3 H, CH_3), 6.67–7.30 (m, 7 H, arom) ppm; IR (KBr) 3058, 2968, 2871, 2808, 1596, 1562, 1462, 1424, 1407, 1328, 1243, 1162, 1152, 1140, 1109, 1072, 1033, 900, 860, 811, 746, 738, 729, 719, 638 cm^{-1}; high-resolution MS calcd for $C_{14}H_{10}F_3NS$ m/e 281.0485, found m/e 281.0476.

Anal. Calcd for $C_{14}H_{10}F_3NS$: C, 59.78; H, 3.59; N, 4.98. Found: C, 59.46; H, 3.47; N, 4.87.

Photooxidation of Benzyl Sulfide in $NaDodSO_4$ with MPT. A 1-L aqueous 5% $NaDodSO_4$ solution of 615 mg of MPT (2.9 mmol) and 615 mg of benzyl sulfide (2.8 mmol) was stirred, aerated, and irradiated for 3.0 h. The usual workup of the resulting deep red photolysate afforded 900 mg (74%) of a dark solid which was chromatographed on a 1.2 × 32 cm silica gel column slurry packed and eluted with 1:1 hexane/chloroform. The following 50-mL fractions were collected: 1, nil; 2, 501 mg (41%) of a 1:1 mixture of MPT and benzyl sulfide; 3, nil; 4–8, 290 mg (24%) of benzyl sulfoxide. The benzyl sulfoxide was recrystallized twice from hexane/chloroform and identified by its spectrum and mixed melting point.

Photooxidation of Benzyl *n*-Butyl Sulfide in $NaDodSO_4$ with MPT. A 1-L 5% $NaDodSO_4$ solution of 514 mg of MPT (2.41 mmol) and 448 mg of benzyl *n*-butyl sulfide (2.5 mmol) was aerated and irradiated 2.67 h. The usual workup afforded 761 mg (79%) of a red oil which was chromatographed on a 1.5 × 32 cm silica gel column slurry packed and eluted with 3:2 hexane/chloroform in the following 50-mL fractions: 1, 1:1 mixture of benzyl *n*-butyl sulfide and MPT; 2 and 3, benzyl *n*-butyl sulfide; 4–10, 184 mg of benzyl *n*-butyl sulfoxide (identified by spectral comparison to an authentic sample).

Photooxidation of Allyl Benzyl Sulfide in $NaDodSO_4$ with MPT. A 1-L 5% $NaDodSO_4$ solution of 631 mg of MPT (3.0 mmol) and 562 mg of allyl benzyl sulfide (3.43 mmol) was aerated and irradiated 4.17 h. The usual workup afforded deep reddish crystals which were chromatographed on a 1.5 × 32 cm silica gel column slurry packed and eluted with 1:1 hexane/chloroform in the following 25-mL fractions: 1–5, a 1:1 mixture of MPT and allyl benzyl sulfide; 6 and 7, nil; 8–15, 105 mg (17%) of allyl benzyl sulfoxide, identified by comparison to an authentic sample.

Photooxidation of Benzyl Phenyl Sulfide in $NaDodSO_4$ with MPT. A 1-L 5% $NaDodSO_4$ solution of 611 mg of MPT (2.9 mmol) and 574 mg of benzyl phenyl sulfide (2.6 mmol) was aerated and irradiated 4.2 h. The usual workup afforded 1.0 g of a red crystalline solid which was chromatographed on a 1.5 × 32 cm silica gel column slurry packed and eluted with 10% chloroform in hexane in the following 50-mL fractions: 1 and 2, nil; 3. 820 mg of a 1:1.1 mixture of benzyl phenyl sulfide and MPT; 4, nil; 5 and 6, 160 mg (29%) of benzyl phenyl sulfoxide (identified by spectral comparison to an authentic sample).

Photooxidation of Phenyl Sulfide in $NaDodSO_4$ with MPT. A 1-L 5% $NaDodSO_4$ solution of 628 mg (2.9 mmol) of MPT and 1.50 g (8.1 mmol) of phenyl sulfide was aerated and irradiated for 4 h. The usual workup afforded a deep red oil which was chromatographed on a 1.5 × 32 cm silica gel column slurry packed in petroleum ether. The following fractions were obtained: 1, 150 mL petroleum ether, nil; 2, 100 mL of 10% ether, MPT, and phenyl sulfide; 3, 100 mL of 20% ether, phenyl sulfide; 4, 300 mL of 1:1 petroleum ether/chloroform, 152 g of a deep red oil.

Fraction 4 was analyzed by preparative HPLC on a 25 × 0.62 cm Zorbax SIL chromatograhic packing silica gel column eluted with 10% acetonitrile in methylene chloride at 4 mL/min. Estimation of the major peak (retention time, 6 min) in comparison to calibration curves using an authentic sample revealed that fraction 4 was 25% (w/w) diphenyl sulfoxide, representing a 2.5% overall yield.

Photooxidation of Benzyl Sulfide in $NaDodSO_4$ with Other Phenothiazines. (a) With 10-Acetylphenothiazine (3a). A 1-L 5% $NaDodSO_4$ solution of 726 mg (3.0 mmol) of 10-acetylphenothiazine and 648 mg (3.0 mmol) of benzyl sulfide was aerated and irradiated for 2.5 h. The usual workup afforded a 3:3:1 mixture of sulfoxide/sulfide/10-acetylphenothiazine.

(b) With 10-Benzoylphenothiazine (3b). A 1-L 5% $NaDodSO_4$ solution of 478 mg (1.6 mmol) of 10-benzoylphenothiazine and 605 mg (2.8 mmol) of benzyl sulfide was aerated and irradiated 3.0 h. The usual workup afforded 1.09 g of a yellow crystalline solid. NMR analysis revealed a 1:1:1.9 ratio of sulfide/sulfoxide/10-benzoylphenothiazine.

(c) With 10-(2-Cyanoethyl)phenothiazine (3c). A 1-L 5% $NaDodSO_4$ solution of 728 mg (2.9 mmol) of 10-(2-cyanoethyl)phenothiazine and 653 mg (3.0 mmol) of benzyl sulfide was aerated and irradiated 3.0 h. The usual workup afforded 1.26 g of a yellow crystalline solid. The mass balance was 91%. NMR analysis revealed a 1:2:1.2 mixture of sulfoxide/sulfide/10-(2-cyanoethyl)phenothiazine.

(d) With 10-Methyl-2-(trifluoromethyl)phenothiazine (3d). A 1-L 5% $NaDodSO_4$ solution of 811 mg (2.8 mmol) of 10-methyl-2-(trifluoromethyl)phenothiazine and 610 mg (2.8 mmol) of benzyl sulfide was aerated and irradiated for 2.4 h. The usual workup afforded a tan solid which was analyzed by NMR spectroscopy. The sulfide/sulfoxide ratio was 43:16.

(e) With 3-Bromo-10-methylphenothiazine (3e). A 1-L 5% $NaDodSO_4$ solution of 806 mg (2.8 mmol) of 3-bromo-10-methylphenothiazine and 614 g (2.9 mmol) of benzyl sulfide was aerated and irradiated 2.25 h. The usual workup afforded a brown oil which was analyzed by preparative HPLC and NMR spectroscopy. The crude product was a 5.5:40:22 mixture of sulfoxide/sulfide/MPT.

(f) With 2-Chloro-10-methylphenothiazine (3f). A 1-L 5% $NaDodSO_4$ solution of 714 mg (2.9 mmol) of 2-chloro-10-methylphenothiazine and 618 mg (2.9 mmol) of benzyl sulfide was aerated and irradiated 3.75 h. The usual workup afforded a black oily solid which was chromatographed on silica gel and analyzed by NMR spectroscopy. No benzyl sulfoxide nor 10-methyl-2-chlorophenothiazine was detected.

MPT Photooxidation in a Microemulsion. A 1-L solution of 5% $NaDodSO_4$ was treated with 44 mL of 1-pentanol and 15 mL of hexadecane, affording a clear, colorless solution. A benzene solution of 615 mg (2.9 mmol) of MPT and 772 mg (3.6 mmol) of benzyl sulfide was added and stirred for 18 h. The clear solution was aerated and irradiated 2.5 h. The usual workup afforded a brown oil which was distilled at 45 °C in vacuo. The residue was cooled and the liquid (hexadecane, benzyl sulfide, and MPT identified by NMR) decanted from a solid mass of crystals. The solid was chromatographed on a 1.5 × 32 cm silica gel column with 3:2 hexane/chloroform in 50-mL fractions. Fractions 1–4

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(30) E. F. Godefroi and E. L. Wittle, *J. Org. Chem.*, **21**, 1163 (1956).
(31) E. R. Biehl, T. Daniel, P. C. Reeves, and S. Lapie, *J. Heterocycl. Chem.*, **11**, 247 (1974).
(32) K. Fujii, *Yakugaku Zasshi*, 77, 247 (1957). See: *Chem. Abstr.*, **51**, 12102 (1957).

contained hexadecane and 5–7 contained 300 mg of benzyl sulfoxide, identified by NMR spectroscopy.

Photooxidation of Triphenylphosphine in $NaDodSO_4$ with MPT. A 1-L 5% $NaDodSO_4$ solution of 613 mg (2.9 mmol) of MPT and 755 mg (2.9 mmol) of triphenylphosphine was aerated and irradiated 2.0 h. The usual workup afforded a brown solid which was chromatographed on a 1.5 × 32 cm silica gel column. Elution with 140 mL of hexane yielded MPT plus triphenylphosphine. Elution with 1:1 hexane/chloroform afforded 300 mg of triphenylphosphine oxide, identified by its NMR spectrum.

Nonmicellar Irradiation of MPT/Benzyl Sulfide. (a) In *tert*-Butyl Alcohol. A *tert*-butyl alcohol (1-L) solution of 642 mg of MPT (3.01 mmol) and 692 mg of benzyl sulfide (3.23 mmol) was aerated and irradiated for 2.2 h. The orange photolysate was concentrated in vacuo, affording 1.28 g (96%) of a black oily solid which was extracted with chloroform and filtered to remove 335 mg (26%) of insoluble matter. The resulting oil (945 mg) was chromatographed on a 1.5 × 38 cm silica gel column slurry packed with 1:1 hexane/chloroform, and the following fractions collected: 1, 40 mL of 1:1 hexane/chloroform, nil; 2, 50 mL of 1:1 hexane/chloroform, 275 mg (18%) of an unidentified compound, mp 95–96 °C; 3, 100 mL of 1:1 hexane/chloroform, 305 mg (24%) of benzyl sulfoxide; 4, 300 mL of chloroform, 215 mg (17%) of MPT 5-oxide (**2**), identical with an authentic sample.

(b) In Cyclohexane. A cyclohexane (1-L) solution of 393 mg of MPT (1.8 mmol) and 401 mg of benzyl sulfide (1.9 mmol) was aerated and irradiated 2.1 h. The resulting slurry of black solids and brown solution was concentrated in vacuo, treated with $CDCl_3$, and filtered to remove insoluble matter. NMR analysis revealed a 1:3.6 ratio of benzyl sulfoxide/benzyl sulfide. No MPT was detected.

Control Experiments. (a) Intermediacy of 10-Methylphenothiazine 5-Oxide. A 1-L 5% $NaDodSO_4$ solution of 65 mg of 10-methyl-phenothiazine 5-oxide (0.28 mmol) and 600 mg of benzyl sulfide (2.8 mmol) was purged with nitrogen and irradiated for 1.25 h. The usual workup afforded a reddish oil which was NMR analyzed. No benzyl sulfoxide was detected.

(b) Photooxidation of Micellar MPT. A 1-L 5% $NaDodSO_4$ solution of 600 mg of MPT (2.8 mmol) was aerated, irradiated 2.5 h, and worked up as usual. NMR analysis of the crude photolysate revealed a 5% conversion to MPT 5-oxide plus a number of other unidentified products.

(c) Absence of MPT. A 1-L 5% $NaDodSO_4$ solution of 623 mg of benzyl sulfide (2.9 mmol) was aerated, irradiated 2.0 h, and worked up as usual. NMR analysis of the crude photolysate indicated no reaction had occurred.

(d) Effect of Sulfide Concentration. A 1-L 5% $NaDodSO_4$ solution of 612 mg of MPT (2.87 mmol) and 60.3 mg of benzyl sulfide (0.281 mmol) was aerated and irradiated 2.1 h. The usual workup afforded reddish crystals which NMR analyzed as a 1:1.5:13 mixture of sulfoxide/sulfide/MPT.

Tests for Superoxide. (a) A 1-L 5% $NaDodSO_4$ solution of 625 mg of MPT (2.9 mmol) and 5.35 g (22.2 mmol) of 1-iodooctane was aerated and irradiated 22.8 h. At intervals, an aliquot was removed and analyzed by GLPC (10% SP-2250 at 150 °C). No 1-octanol or 1-hydroperoxyoctane was detected in this manner.

(b) A pyridine (20 mL) solution of 3.91 g of benzyl sulfide (18.2 mmol), 1.37 g of potassium superoxide (19.3 mmol), and 1.47 g of dicyclohexyl-18-crown-6 (4.0 mmol) was stirred 80 min. The reaction mixture was added to ice and chloroform extracted. The extracts were washed with 10% aqueous hydrochloric acid and dried ($MgSO_4$). Removal of the solvent in vacuo afforded a yellow solid which was analyzed by NMR. No benzyl sulfoxide was detected.

Tests for Singlet Oxygen. (a) A 1-L 5% $NaDodSO_4$ solution of 625 mg of MPT (2.9 mmol) and 1.17 g of tetramethylethylene (13.9 mmol) was aerated and irradiated 4.0 h. An aliquot of the photolysate was analyzed by GLPC, and a peak corresponding to 2,3-dimethyl-3-hydroperoxy-1-butene was detected.

(b) A 1-L 5% $NaDodSO_4$ solution of 635 mg of MPT (3.0 mmol), 640 mg of benzyl sulfide (3.0 mmol), and 501 mg of 1,4-dimethyl-1,4-*endo*-peroxynaphthalene (2.7 mmol)[33] was stirred and heated to 90 °C for 45 min. The usual workup afforded 1.31 g of a yellow oily solid (74% mass balance). NMR analysis indicated an 11% conversion of benzyl sulfide to benzyl sulfoxide. No MPT 5-oxide (**2**) was detected.

(c) An acetonitrile (10-mL) solution of 940 mg of 10-methylphenothiazyl cation radical perchlorate (3.0 mmol)[34] and 615 mg of benzyl sulfide (2.9 mmol) was stirred, and 610 mg of pulverized potassium superoxide (8.6 mmol) was added portionwise. Vigorous effervescence occurred, and the color quickly changed from deep red to gray. The reaction mixture was filtered, and the solids were washed with tetrahydrofuran. Concentration of the filtrate in vacuo afforded a crystalline solid which was separated into components by preparative HPLC. Benzyl sulfoxide constituted 2.2% of the crude mixture (w/w).

(d) An acetonitrile (200-mL) solution of 1.04 g of 10-methylphenothiazyl cation radical perchlorate (3.3 mmol) and 1.57 g of benzyl sulfide (7.3 mmol) was aerated and irradiated 3.0 h. Concentration in vacuo afforded a dark solid which was percolated through a short silica gel column using chloroform. Evaporation of the solvent yielded 1.5 g of a solid identified as benzyl sulfide by its spectral data and mixed melting point.

(e) A 1-L saturated CTAB solution of 619 mg of MPT (2.9 mmol) and 618 mg of benzyl sulfide (2.9 mmol) was aerated and irradiated 3.0 h. The usual workup (Bio-Rex 70, an anionic exchange resin, was substituted for the Rexyn 202) afforded a dark oil which was analyzed by NMR spectroscopy. The crude material was a 1:10:6.9 mixture of benzyl sulfoxide/benzyl sulfide/MPT.

Photooxidation of Micellar 1,3-Diphenylisobenzofuran. A 1-L 5% $NaDodSO_4$ solution of 783 mg of 1,3-diphenylisobenzofuran (2.9 mmol) was aerated and irradiated 2 h. The usual workup afforded 784 mg (95%) of 1,2-dibenzoylbenzene, identified by mixed melting point and comparison of its spectral data to those of an authentic sample.

Registry No. **3a**, 1628-29-1; **3b**, 38076-73-2; **3c**, 1698-80-2; **3d**, 77195-43-8; **3e**, 52853-38-0; **3f**, 19607-03-5; MPT, 1207-72-3; $PhCH_2SCH_2Ph$, 538-74-9; $PhCH_2SCH_2CH_2CH_2CH_3$, 5184-47-4; $PhCH_2SCH_2CH{=}CH_2$, 6937-97-9; $PhCH_2SPh$, 831-91-4; PhSPh, 139-66-2; $(i\text{-}C_3H_7)_2S$, 625-80-9; $(PhCH_2)_3N$, 620-40-6; $PhCH_2SePh$, 18255-05-5; Ph_3P, 603-35-0; MPT cation radical, 34510-35-5; oxygen, 7782-44-7.

(33) H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.* 253 (1972).

(34) M. H. Litt and J. Radovic, *J. Phys. Chem.*, **78**, (17), 1750 (1974).