compared to the other three, was attributed to a reversibility of reaction 2 owing to the proximity of the $E°$ of the $R^+/R·$ couple.

Knowing the equilibrium constant of reaction 2 from the value of $E°_{R^+/R·} - E°_{DDQ}$ and the value of k_1, k_2, and k obtained previously, we introduce the backward reaction constant k' and we can generate the curves which give the catalytic efficiency. For example, if $E°_{R^+/R·} - E°_{DDQ} = 210$ mV keeping $k = 2 \times 10^{10}$ M^{-1} s^{-1}, we must have $k' \simeq 7 \times 10^6$ M^{-2} s^{-1}. Simulation with these values for $\gamma = 4.9$ and $v = 0.02$ V/s give $i_p/\gamma i_p° = 0.30$ (experimental value 0.289). It is noted that with the three other catalysts the value of k' does not modify significantly, the determination of k_1.

Concluding Remarks

The above described study of the direct and mediated reduction of two highly reactive benzylic chlorides shows the possible importance of pre-activation pathways in electron transfer reactions. While in the present case this route appears as very inefficient in the direct electrochemical reduction, it gives rise to significant catalytic efficiencies in the mediated reaction. Homogeneous redox catalysis can thus be carried out at potentials that can be 2 V more positive than the potential where the direct electrochemical reduction occurs. Notably, the direct and mediated processes lead to different reaction products, the carbanions or free radical, respectively, in the present case. It has also been shown that the kinetic analysis of the system by means of cyclic voltammetry allows the determination of the equilibrium and rate constants of the preceding chemical step. The same procedures, here illustrated by the reduction of benzylic-type chlorides, can be applied to any other systems where a preceding reaction mechanism occurs.

Acknowledgment. We acknowledge support of this work by the CNRS (Equipe de Recherche Associée 309 "Electrochimie Moleculaire") on the French side, and by the Deutsche Forschungsgemeinschaft, the Fond der Chemischen Industrie and the Deutscher Akademischer Austauschdienst on the German side.

Registry No. 1, 72087-83-3; **3**, 20685-16-9; FC, 1282-37-7; MFC, 88946-23-0; EFC, 88946-24-1; PFC, 88946-25-2; DMFC, 52649-35-1; CLA, 118-75-2; TCNE, 670-54-2; TCNQ, 1518-16-7; DDQ, 84-58-2.

(25) These figures are reasonable compared to some findings in the SN1 behavior of trityl chloride, a structure which is related to **3**. The forward rate constant is quite similar to the first-order solvolysis rate of trityl chloride in a solvent mixture of comparable polarity.[26a] Also, it has been observed that the dissociation constant of trityl chloride is extremely small in acetonitrile, but that SN1 reactions do rapidly occur when the chloride ion is removed from the equilibrium.[26b]

(26) (a) Swain, G.; Scott, C. B.; Lohmann, K. H. *J. Am. Chem. Soc.* **1953**, *75*, 136. (b) Baaz, M.; Gutmann, V.; Kunze, O. *Monatsh. Chem.* **1962**, *93*, 1142.

Spin Trapping in SDS Micelles

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Abstract: By the use of spin traps of differing solubility, radical reactions in the aqueous phase or the micellar interior of SDS micelles can be probed. Sodium 2-sulfonatophenyl *tert*-butyl nitrone (2-SSPBN) is useful for investigating the bulk aqueous phase, while 4-dodecyloxyphenyl *tert*-butyl nitrone (4-DoPBN) can be used to monitor the micellar interior. The effect of SDS on the line widths and hyperfine splitting constants of spin adducts of 2-SSPBN, 4-trimethylaminophenyl *tert*-butyl nitrone (4-M_3APBN), 4-DoPBN, and PBN have been investigated. ESR line shapes reveal a micelle/spin adduct charge association using 4-M_3APBN. Distinct asymmetry of the ESR spectra indicates premicellar aggregation.

Introduction

Perhaps the most exciting advance in spin trapping is the recent finding that in vivo detection of free radicals is possible by this method. Thus trichloromethyl radicals have been detected by phenyl *tert*-butyl nitrone (PBN) in the liver of rats exposed to carbon tetrachloride,[1] and a carbon-centered radical has been trapped by PBN in the lung of goats when subjected to small amounts of 3-methylindole.[2] A large amount of in vitro work preceded these experiments where the right conditions for spin trapping have been investigated and the assignments of various ESR spectra of spin adducts verified. In this connection it has been found that nitrones[3] are much more useful spin traps than nitroso compounds,[4] PBN and 5,5-dimethylpyrroline *N*-oxide (DMPO) receiving the most attention. Although DMPO is the trap of choice for the detection of hydroxyl radicals,[3,5] it has been

(1) Lai, E. K.; McCay, P. B.; Noguchi, T.; Fong, K. L. *Biochem. Pharm.* **1979**, *28*, 2231. Poyer, J. L.; McCay, P. B.; Lai, E. K.; Janzen, E. G.; Davis, E. R. *Biochem. Biophys. Res. Commun.* **1980**, *94*, 1154. See also: Albano, E.; Lott, K. A. K.; Slater, T. F.; Stier, A.; Symons, M. C. R.; Tomasi, A. *Biochem. J.* **1982**, *204*, 593.

(2) Kubow, S.; Janzen, E. G.; Bray, T. M. *J. Biol. Chem.*, in press. Kubow, S.; DuBose, C. M.; Janzen, E. G.; Carlson, J. R.; Bray, T. M. *Biochem. Biophys. Res. Commun.* **1983**, *114*, 168.

(3) For reviews of spin trapping in biological systems see: Janzen, E. G. *Free Radicals Biol.* **1980**, *4*, 115. Kalyanaraman, B. *Rev. Biochem. Toxicol.* **1982**, *4*, 73. For reviews of spin trapping with nitrones see: Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. Perkins, M. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 1.

(4) Nitroso compounds should not be used as detectors of radicals in any system containing olefinic bonds because the "ene reaction" produces the hydroxylamine by a molecular reaction which gives detectable amounts of aminoxyls upon oxidation: Sullivan, A. B. *J. Org. Chem.* **1966**, *31*, 2811. Knight, G. T. *Chem. Commun.* **1970**, 1016. Floyd, R. A.; Soong, L. M.; Stuart, M. A.; Reigh, D. L. *Arch. Biochem. Biophys.* **1978**, *185*, 450. Sridhar, R.; Hampton, M. J.; Steward, J. E.; Floyd, R. A. *Appl. Spectrosc.* **1980**, *34*, 289. Sridhar, R.; Floyd, R. A. *Can. J. Chem.* **1982**, *60*, 1574. Floyd, R. A. *Ibid.* **1982**, *60*, 1577.

(5) Finkelstein, E.; Rosen, G. M.; Rauckman, E. J. *Arch. Biochem. Biophys.* **1980**, *200*, 1. Marriott, P. R.; Perkins, M. J.; Griller, D. *Can. J. Chem.* **1980**, *58*, 803.

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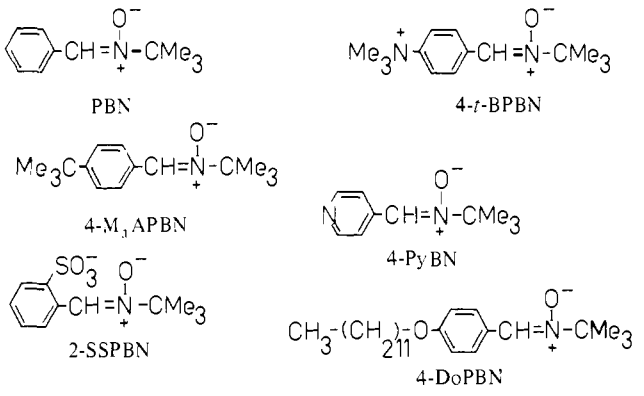
completely unsuccessful in in vivo experiments.[6] This is probably due to its high water solubility and because the spin adducts are not very persistent aminoxyls (nitroxides).[7]

In order to investigate systematically the question of solubility and diffusion of spin traps and spin adducts in biological systems, we have initiated a study into the spin-trapping chemistry of micellar solutions, hoping subsequently to extend our findings to better membrane models such as vesicles and liposomes. In this paper the following spin traps have been used to trap radicals in sodium dodecyl sulfate (SDS) micellar solutions: phenyl *tert*-butyl



nitrone (PBN),[8] sodium 2-sulfonatophenyl *tert*-butyl nitrone (2-SSPBN),[9] 4-trimethylaminophenyl *tert*-butyl nitrone (4-M$_3$APBN),[10,11] 4-*tert*-butylphenyl *tert*-butyl nitrone (4-*t*BPBN), and 4-dodecyloxyphenyl *tert*-butyl nitrone (4-DoPBN).

Spin trapping in micellar systems has received only limited attention. Bakalik and Thomas[12] used 2-methyl-2-nitrosopropane to detect the formation of carbon-centered radicals from the reactions of hydroxyl radicals produced in radiolysis of SDS solutions. Harbour and Bolton[13] photolyzed TRITON X-100 micelles containing DMPO and chromophores such as chlorophyll (BChl, or Chla) and detected the superoxide radical anion. Later Lukac and Harbour,[14] using dioctadecyldimethylammonium bromide (DODAB) and dihexadecyl phosphate (DHP) vesicles, trapped hydroxy radicals with DMPO upon irradiation of solubilized phthalocyanine. Walter et al.[15,16] showed that phenyl radicals could be trapped by 4-DoPBN in SDS micelles whether the phenyl source was water soluble (phenyldiazonium tetrafluoroborate) or hydrocarbon soluble (phenylazotriphenylmethane).

Experimental Section

All spin traps used were available in our laboratory and their synthesis is described elsewhere except for 4-*t*BPBN and 4-DoPBN. Both nitrones were produced by condensation of the appropriate aldehyde with *tert*-butylhydroxylamine. CHN analysis and NMR spectra indicated the desired products: mp 159–161 °C (4-*t*BPBN), mp 60–62 °C (4-DoPBN). PA-4-PD has been synthesized by condensation of phenylhydrazine with 4-pyridyldiphenylmethyl chloride followed by oxidation to the azo compound with hydrogen peroxide. NMR data indicated the desired product. CHN analysis was unavailable owing to the highly hygroscopic nature of the compound. SDS (electrophoresis grade) was purchased from Biorad and used as received. All solutions were prepared from deionized water distilled from an all-glass apparatus.

Samples were prepared by stirring spin traps in the appropriate concentration of SDS for 10 min at 45 °C. The resulting optically clear solutions were cooled and placed in one arm of an ESR H-cell.[17] The appropriate initiator was placed in the other arm. The solution cell was sealed with septa and the trap/SDS solution outgassed with a stream of N_2 for 15 min. The initiator was mixed with trap solution and the resulting mixture shaken into a standard ESR flat cell.

All ESR spectra were recorded on a Varian E-104 spectrometer calibrated with alkaline Fremy's salt. Coupling constants quoted are av-

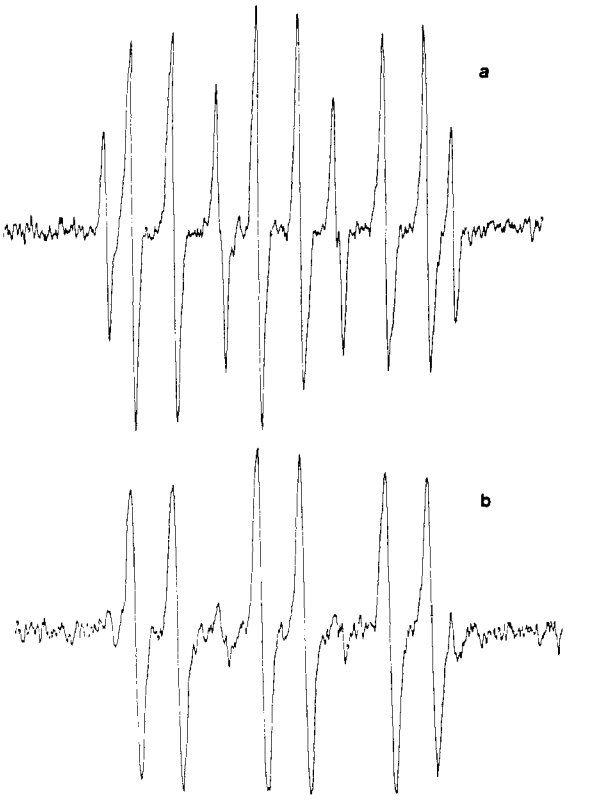


Figure 1. ESR spectrum of the hydroxyl radical spin adduct of 2-SSPBN produced by thermolysis of sodium persulfate: (a) in water, (b) in 250 mM SDS.

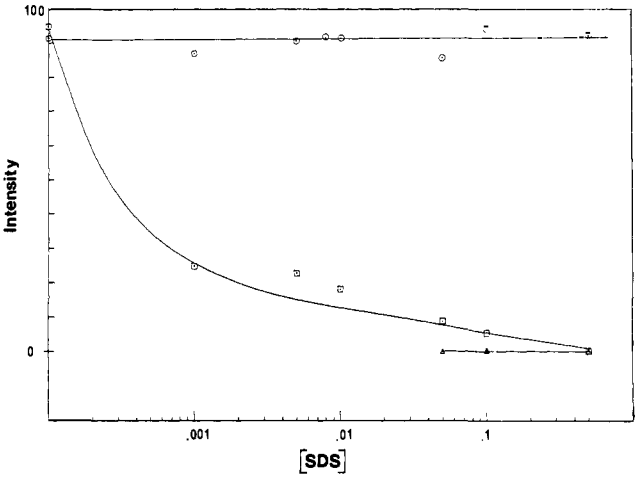


Figure 2. Plot of relative spin adduct intensity vs. concentration of SDS for the hydroxyl radical adduct of 2-SSPBN (circles), PBN (squares), and 4-DoPBN (triangles).

(6) Private communication from P. B. McCay and co-workers.
(7) We are attempting to remedy this problem by synthesizing more hydrophobic sterically hindered cyclic nitrones: (a) Janzen, E. G.; Shetty, R. V.; Kunanec, S. M. *Can. J. Chem.* **1981**, *59*, 756. (b) Haire, D. L.; Janzen, E. G. *Ibid.* **1982**, *60*, 1514.
(8) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1968**, *90*, 5909; **1969**, *91*, 4481.
(9) Janzen, E. G.; Shetty, R. V. *Tetrahedron Lett.* **1979**, 3229.
(10) 4-M$_3$APBN was first synthesized as the percholate salt by R. D. Goodin (see ref 11).
(11) Goodin, R. D. Ph.D. Dissertation, University of Texas, Austin, Texas, 1975.
(12) Bakalik, D. P.; Thomas, J. K. *J. Phys. Chem.* **1977**, *81*, 1905.
(13) Harbour, J. R.; Bolton, J. R. *Photochem. Photobiol.* **1978**, *28*, 231.
(14) Lukac, S.; Harbour, J. R. *J. Chem. Soc., Chem. Commun.* **1982**, 154.
(15) Walter, T. H.; McIntyre, G. L.; Bancroft, E. E.; Davis, E. R.; Gierasch, L. M.; Blount, H. N. *Biochem. Biophys. Res. Commun.* **1981**, *102*, 1350.
(16) Walter, T. H.; Bancroft, E. E.; McIntyre, G. L.; Davis, E. R.; Gierasch, L. M.; Blount, H. N.; Stronks, H. J.; Janzen, E. G. *Can. J. Chem.* **1982**, *60*, 1621.
(17) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.

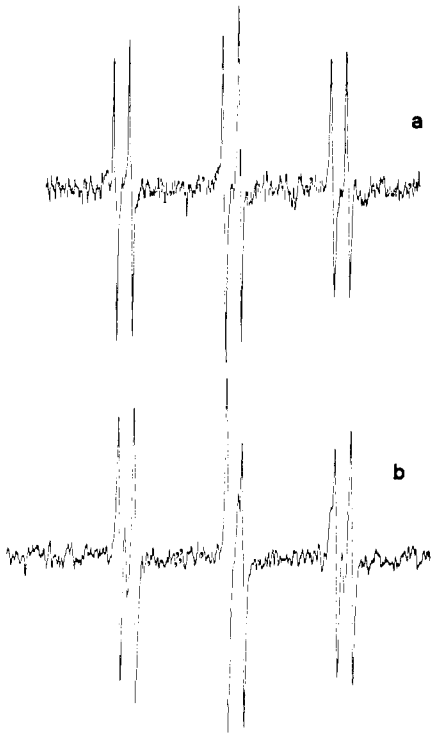


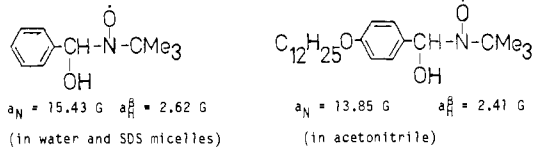
Figure 3. (a) ESR spectrum of the hydroxyl radical adduct of 4-M_3APBN from photolysis of H_2O_2 in water. (b) ESR spectrum of hydroxyl and sulfate radical spin adducts of 4-M_3APBN from photolysis of aqueous $Na_2S_2O_8$.

erages measured as many times as possible from one spectrum and are accurate to ±0.05 G. Photolysis was carried out in the ESR cavity using a "home-built" low-pressure Hg lamp.

Results and Discussion

Sodium Persulfate. When aqueous solutions of sodium persulfate ($Na_2S_2O_8$) react with 2-SSPBN, an ESR spectrum consisting of a triplet of doublets is obtained (a_N = 15.71 G, a_H^β = 5.28 G; see Figure 1a). This spectrum has previously been assigned to the hydroxyl radical adduct produced from the photolysis of H_2O_2[9] (a_N = 15.68 G, a_H^β = 5.20 G). In addition a four-line spectrum is also seen which is due to the *tert*-butyl aminoxyl: $C_4H_9N(O\cdot)H$. Trace amounts of silver ion ($AgNO_3$) or photolysis of the persulfate mixture greatly enhances the signal due to the hydroxyl adduct of 2-SSPBN.

The intensity of the HO/2-SSPBN spectrum produced from 5 mM spin trap and 0.1 mM $Na_2S_2O_8$ remains unchanged upon addition of SDS up to a concentration of 500 mM SDS (14% by weight) as shown in Figure 2. The ESR lines remain sharp and no increase in line width is found upon addition of SDS at any concentration (see Figure 1b). With 5 mM PBN exposed to the same concentration of $Na_2S_2O_8$ the intensity of the spectrum due to the hydroxyl adduct[18] decreases markedly upon the addition of SDS, dropping essentially to zero at 500 mM SDS (Figure 2).



4-DoPBN is soluble only in SDS solutions above the critical micelle concentration (cmc). No ESR signals can be detected when 0.1 mM $Na_2S_2O_8$ is present in solutions of SDS micelles containing 5 mM 4-DoPBN (Figure 2). There is no reason to believe that the hydroxyl adduct of 4-DoPBN is not persistent enough for detection. In acetonitrile a typical triplet of doublets obtained from the photolysis of H_2O_2 is assigned to the hydroxyl adduct of 4-DoPBN (see above).

(18) Janzen, E. G.; Nutter, D. E.; Davis, E. R.; Blackburn, B. J.; Poyer, J. L.; McCay, P. B. *Can. J. Chem.* **1978**, *56*, 2237.

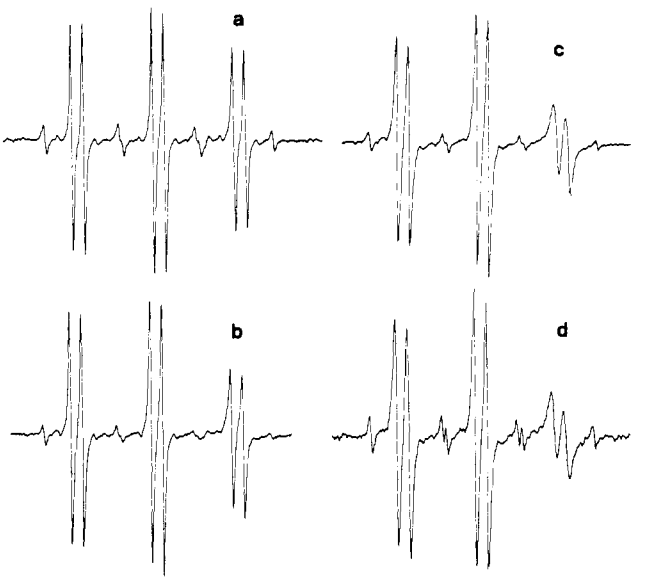


Figure 4. ESR spectra of hydroxyl radical spin adduct of 4-M_3APBN from Ag^+-catalyzed thermolysis of $Na_2S_2O_8$ in SDS: (a) 2.5 mM SDS, (b) 10 mM SDS, (c) 25 mM SDS, (d) 250 mM SDS.

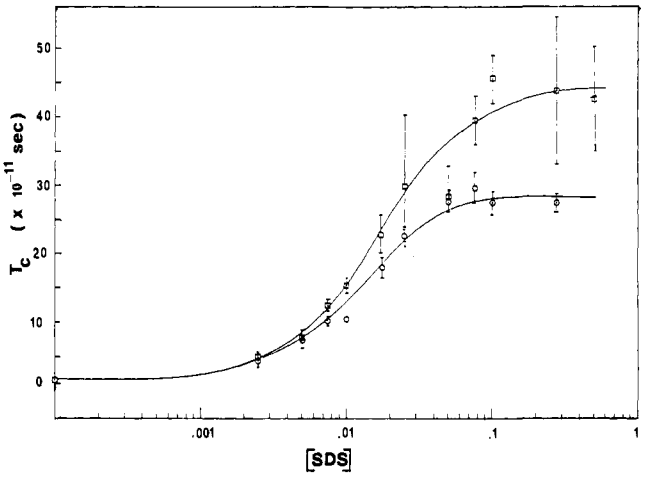
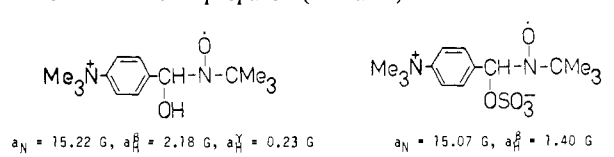


Figure 5. Plot of correlation time vs. concentration of SDS for the spin adducts of 4-M_3APBN from reaction with sodium persulfate by Ag^+ catalysis (circles) and photolysis (squares).

The hydroxyl adduct of 4-M_3APBN can be made by photolysis of H_2O_2 in water and like 4-pyridyl *N*-oxide *tert*-butyl nitrone[19] shows a small γ-H hyperfine splitting due to the hydroxyl hydrogen (Figure 3a). This adduct is very short lived in solutions of $Na_2S_2O_8$. However, upon photolysis of 5 mM 4-M_3APBN in 0.1 mM $Na_2S_2O_8$, both the hydroxyl and sulfate adducts are observed[20] (Figure 3b). Trace amounts of $AgNO_3$ give a strong signal due to the hydroxyl adduct of 4-M_3APBN and *tert*-butyl aminoxyl, but the former spectrum decays rapidly depending on the kind of solution prepared (see later).



Upon addition of SDS, the spectra due to HO/4-M_3APBN show line broadening due to immobilization of the spin adduct.

(19) Janzen, E. G.; Wang, Y. Y.; Shetty, R. V. *J. Am. Chem. Soc.* **1978**, *100*, 2923.

(20) For previous detection of sulfate adducts, see ref 7a and 11.

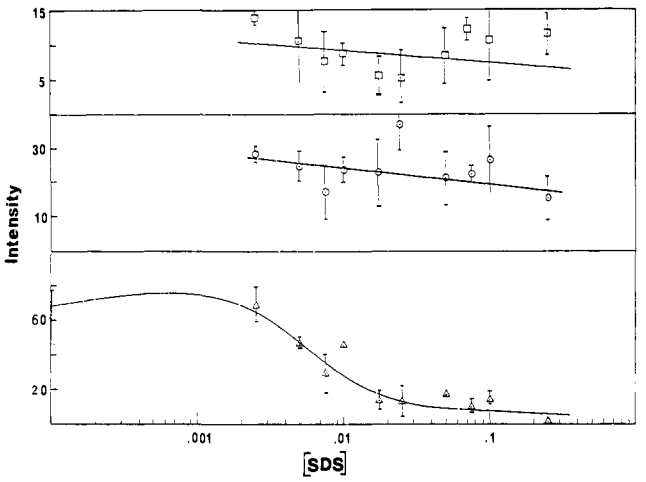


Figure 6. Plot of relative spin adduct intensity vs. concentration of SDS for the spin adducts of 4-M_3APBN with $Na_2S_2O_8/h\nu$ (squares), 4-M_3APBN with $Na_2S_2O_8/Ag^+$ (circles), and 2-SSPBN with $Na_2S_2O_8/Ag^+$ (triangles).

The extent of line broadening is most marked in the high-field wing of the nitrogen triplet and is independent of the method used to prepare the spectrum (photolysis or $AgNO_3$-catalyzed thermal decomposition of $Na_2S_2O_8$; Figure 4). If the rotational correlation time $\tau_c = AW_{+1}[(H_{+1}/H_{-1})^{1/2} - 1]$ (where $A = 6.6 \times 10^{-10}$ s, W_{+1} = line width of low-field line, H_{-1} and H_{+1} = the height of the low-field and high-field line, respectively)[21] is plotted against SDS concentration, an S-shaped curve is obtained (Figure 5). It is clear from inspection of Figures 4 and 5 that hindrance to free rotation of the HO/4-M_3APBN spin adduct sets in before the cmc of SDS. Also of interest is the observation that the relative strength of the ESR signal due to the HO/4-M_3APBN adduct does not change upon addition of SDS when the adduct is made by photolysis (Figure 6). Considerable scatter is present in both plots because of the decay of the signal with time. In comparison the HO/2-SSPBN adduct prepared in the presence of $AgNO_3$ shows marked intensity dependence on SDS concentration (Figure 6). The signal is weaker with increased amounts of SDS.

In discussing the observed results in the case of the room-temperature thermal decomposition of $Na_2S_2O_8$ in the presence of the spin traps 2-SSPBN, PBN, and 4-DoPBN, a number of points need clarification: namely, (a) what is the source of the hydroxyl adduct in each case; (b) where is $S_2O_8^{2-}$ located (aqueous phase, micellar interior or at the interface); (c) where is the spin trap located; and (d) where is the spin adduct formed and located.

The hydroxyl adducts could have been produced either by the trapping of free hydroxyl radicals formed in the oxidation of water by sulfate radicals

$$S_2O_8^{2-} \rightarrow SO_4^{-}\cdot \xrightarrow{H_2O} HSO_4^- + HO\cdot$$

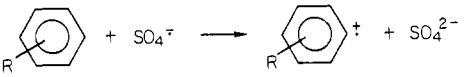
or by hydrolysis of the radical cation of PBN produced in the electron-transfer oxidation of PBN by sulfate radicals or persulfate itself:

$$PBN \xrightarrow[SO_4^{-}\cdot]{S_2O_8^{2-}} PBN^+\cdot$$

$$PBN^+\cdot \xrightarrow[-H^+]{H_2O} PBN/OH$$

In a flash photolysis study of persulfate ions in aqueous solutions, Dogliotti and Hayon[22] concluded that sulfate radicals are relatively stable with respect to hydrolysis in aqueous solutions at pH 0.1–8.5. Decay was found to be bimolecular with a rate constant of approximately 4×10^8 M^{-1} s^{-1} and relatively insensitive to the acidity of the solution in this pH range.

The absolute rate constants for reactions of $SO_4^{-}\cdot$ with substituted benzenes have been determined by pulse radiolysis[23] and found to be very fast (e.g., 5×10^9 M^{-1} s^{-1} for anisole and 1.2×10^8 M^{-1} s^{-1} for benzonitrile). Since the slope of a Hammett plot was found to be negative ($\rho = -2.4$), an electron-transfer mechanism was proposed as the first step of the reaction:



Therefore, thermally produced sulfate radicals either recombine or react with aromatic substrates like PBN:

$$S_2O_8^{2-} \underset{k \sim 10^8}{\rightleftharpoons} 2SO_4^{-}\cdot \xrightarrow[k \sim 10^8]{PBN} PBN^+\cdot$$

The reaction of water with sulfate radicals to give hydroxyl radicals would not compete favorably with these two processes at the pH used in this work. Thus, on the basis of available literature, it is possible to conclude that the source of the hydroxyl adduct is $PBN^+\cdot$.

The sodium persulfate is undoubtedly located in the bulk aqueous phase of the micellar solution because the solubility of $Na_2S_2O_8$ in hydrocarbon solvents is negligible. Whether $S_2O_8^{2-}$ or $SO_4^{-}\cdot$ ions associate with the polar charged layer of the SDS micelles was considered in the interpretation of the observed results (see next paragraph).

The location of the spin traps must depend on the nature of the substituents attached to PBN and the solubility of PBN itself. 2-SSPBN is completely insoluble in hydrocarbon solvents. None of this compound is extracted by benzene in a benzene–water mixture. PBN can be dissolved in water to approximately 0.1 M concentration. About 80% of the dissolved PBN is found in the benzene layer of a benzene–water mixture. 4-DoPBN is insoluble in water (less than 10^{-6} M in H_2O). Walter et al.[15] have reported that 4-DoPBN can be dissolved in SDS micelles up to a ratio of 1:5 4-DoPBN to SDS and that the nitronyl function resides in a region approximately as polar as ethanol.

From this information we conclude that 2-SSPBN must reside only in the bulk aqueous phase (the possibility that this spin trap is also located in the charged layer of the micelle could be ruled out; see below). 4-DoPBN in contrast must reside in the interior of the micelles with the polar nitronyl function in or near the charged layer on the periphery of the micelle.[15] A (very) small amount of 4-DoPBN (less than 10^{-6} M) may be dissolved in the bulk aqueous phase in equilibrium with the material dissolved in the micelle, but the spin-trapping method is not sensitive enough to detect radicals under conditions where the spin trap concentration is this low. PBN is expected to be distributed between the bulk aqueous phase and the interior of the micelles. Since micellar solutions are dynamic systems, exchange between these PBN molecules is expected with the ratio of the amounts inside to outside being about 4:1.

$$PBN_{(micelle)} \rightleftarrows PBN_{(H_2O)}$$

On the basis of the reported work on 4-DoPBN,[15] the polar nitronyl function of PBN is also expected to be located in the charged layer of the micelle.

The reaction of $SO_4^{-}\cdot$ with 2-SSPBN could occur in the bulk aqueous phase or in the charged layer of the micelle if either or both reactants happened to reside in this region. However, the rate of these reactions would be expected to be different. Thus four possibilities exist:

$$SO_4^{-}\cdot_{(H_2O)} + \text{2-SSPBN}_{(H_2O)} \rightarrow$$

$$SO_4^{-}\cdot_{(H_2O)} + \text{2-SSPBN}_{(micelle)} \rightarrow$$

$$SO_4^{-}\cdot_{(micelle)} + \text{2-SSPBN}_{(H_2O)} \rightarrow$$

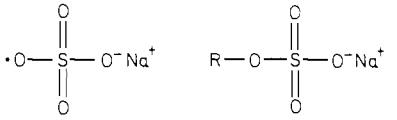
$$SO_4^{-}\cdot_{(micelle)} + \text{2-SSPBN}_{(micelle)} \rightarrow$$

(21) Martinie, J.; Michon, J.; Rassat, A. *J. Am. Chem. Soc.* **1975**, *97*, 1818.

(22) Dogliotti, L.; Hayon, E. *J. Phys. Chem.* **1967**, *71*, 2511.

(23) Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 163. See also Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res.* **1983**, *16*, 27.

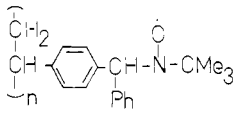
Since no spin adducts were obtained from $Na_2S_2O_8$ and 4-DoPBN dissolved in micellar solution, it seems unlikely that $SO_4^{-}\cdot$ radical ions are associated or concentrated in any way in the charged micelle layer in spite of the structural similarity:



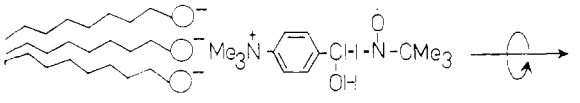
Because of the intensity of the hydroxyl adduct of 2-SSPBN is unaffected by the addition of SDS molecules to a concentration well beyond the cmc, it is possible to conclude that 2-SSPBN is free to react with $SO_4^{-}\cdot$ at the same rate as in the absence of SDS molecules and micelles. This means that 2-SSPBN is likely not associated with the charged layer of the micelle and only resides in the bulk aqueous phase. The reaction of $SO_4^{-}\cdot$ and 2-SSPBN then occurs in the aqueous phase. By the same argument, the reaction of PBN with $SO_4^{-}\cdot$ only occurs in the aqueous phase, and no reaction is observed with 4-DoPBN because of low solubility in water.

The formation of the hydroxyl spin adducts of 2-SSPBN and PBN determines their immediate location by the above arguments. However, the spectra obtained may come from spin adducts which have diffused into other regions of the micellar system. The hyperfine splitting parameters of the hydroxyl spin adduct of PBN strongly indicate residency in the aqueous phase only, and no case was found where two spectra of the same spin adduct were observed (as in the case of the phenyl adduct; see later). Although the hydroxyl adduct of PBN can be produced in hydrocarbon solvents such as benzene,[18] the solubility of this species must be such that the aqueous environment is preferred. The hydroxyl adduct of 2-SSPBN is undoubtedly in the bulk aqueous phase since the solubility must be very similar to that of 2-SSPBN itself. No broadening due to immobilization of this spin adduct is detected, and therefore no association with the micellar surface is apparent.

In contrast to HO/2-SSPBN the spectrum of HO/4-M_3APBN becomes slightly immobilized at low concentrations of SDS, indicating significant ion-pair aggregation before micellization begins. More immobilization occurs as the concentration of SDS increases. The plot of τ_c vs. [SDS] gives a smooth line through the cmc and levels off after a point. Thus it appears that the "time average size" of the aggregate that HO/4-M_3APBN is associated with increases continuously even beyond the point of micellization. However, even at 500 mM SDS the immobilization of HO/4-M_3APBN is not serious enough to completely destroy the doublet structure in the spectrum (Figure 4d; $\tau_c \simeq 2.7 \times 10^{-10}$ s). Considerable freedom of motion still exists for the nitroxide. An association suggests itself where the charged end of the molecule is held by coulombic attraction to the SDS aggregate, leaving the nitroxyl free to rotate around the long axis of the molecule.[24]



Indeed the spectrum obtained from trapping phenyl radicals with "poly-PBN"[25] is not unlike that in Figure 4d.



We assume that 4-M_3APBN itself is held to an aggregate or to the surface of a micelle in the same way as HO/4-M_3APBN. This would make the trap available for one-electron oxidation by

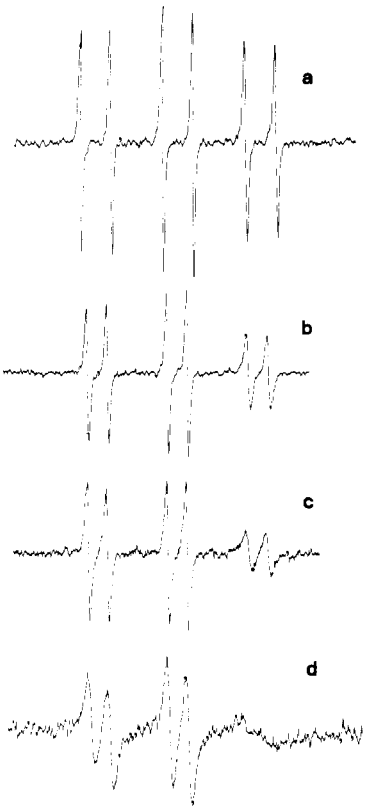
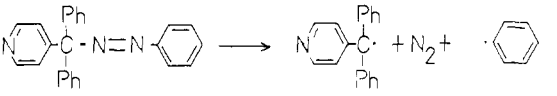


Figure 7. ESR spectra of the phenyl radical spin adduct of (a) 2-SSPBN in water, (b) PBN in micelles, (c) 4-*t*BPBN in micelles, and (d) 4-DoPBN in micelles.

$S_2O_8^{2-}$ or $SO_4^{-}\cdot$ followed by hydrolysis to HO/4-M_3APBN. In this connection it is interesting to find that when silver ion is used to catalyze the production of HO/4-M_3APBN some decrease in the amount of this spin adduct is observed with increase in [SDS]. This effect is dramatic with 2-SSPBN. The explanation for this result is complicated by the probable difference in rates of the electron-transfer reactions between $SO_4^{-}\cdot$ and the bound or unbound 4-M_3APBN with aggregated or micellar SDS molecules.

Phenylazo-4-pyridyldiphenylmethane (PA-4-PD). Since phenylazotriphenylmethane (PAT, the most commonly used phenyl radical source) is essentially water insoluble,[26] a new water-soluble phenyl radical source has been synthesized: phenylazo-4-



pyridyldiphenylmethane. This compound gives phenyl radicals, but 4-pyridyldiphenylmethyl radicals are not detected under the conditions used. Although PA-4-PD is water soluble, partitioning experiments between water and benzene show that 98% of this compound is dissolved in the hydrocarbon phase.

An aqueous solution of 0.1 mM PA-4-PD containing 50 mM 2-SSPBN gives a triplet of doublets assigned to the phenyl adduct: a_N = 15.98 G, a_H^β = 5.90 G (Figure 7a). When the concentration of SDS is increased from 0 to 500 mM, the amount of Ph/2-SSPBN detected is essentially constant until the cmc (Figure 8); then the intensity of the spectra drops continuously so that at 500 mM SDS almost nothing is observed. With PBN the opposite is found. Although the signal intensity of Ph/PBN is smaller than for Ph/2-SSPBN in water at the same concentration, it increases with increase in [SDS] up to a maximum at the cmc (Figure 8). With 4-DoPBN phenyl radicals are detected in increasing amounts from 75 to 500 mM SDS.

(24) Charged spin labels attached via coulombic attraction to vesicles show line broadening of ESR spectra (Chen, W. L.; Hsia, J. C. *Biochemistry* **1974**, *13*,, 4948) and correlation times of 2.7×10^{-10} s (Lim, Y. Y.; Fendler, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4023).

(25) Janzen, E. G.; Wang, Y. Y. *J. Phys. Chem.* **1979**, *83*, 894.

(26) When large amounts of PAT are used, phenyl radicals can be detected in the aqueous phase by PBN: unpublished results of D. L. Haire in these laboratories.

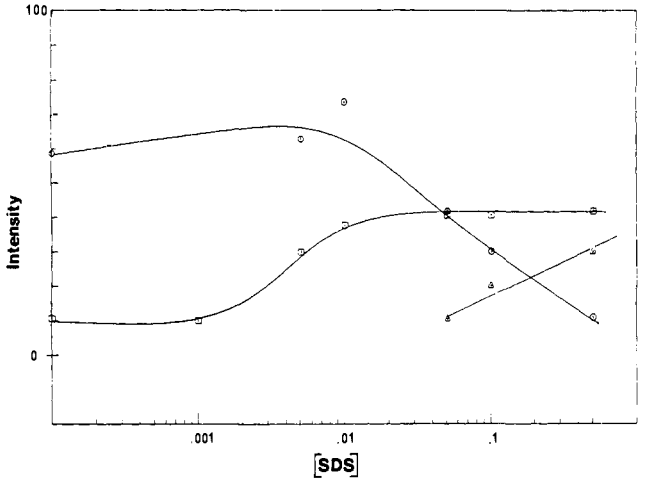


Figure 8. Plot of relative spin adduct intensity vs. SDS concentrations for the phenyl spin adduct to 2-SSPBN (circles), PBN (squares), and 4-DoPBN (triangles).

In the interpretation of these results the following reactions will be considered:

$$\text{PA-4-PD}_{(H_2O)} \rightleftarrows \text{PA-4-PD}_{(\text{micelle})}$$

$$\text{PA-4-PD}_{(H_2O)} \rightarrow \text{Ph}^{\bullet}_{(H_2O)}$$

$$\text{PA-4-PD}_{(\text{micelle})} \rightarrow \text{Ph}^{\bullet}_{(\text{micelle})}$$

$$\text{Ph}^{\bullet}_{(H_2O)} \rightleftarrows \text{Ph}^{\bullet}_{(\text{micelle})}$$

$$\text{PBN}_{(H_2O)} \rightleftarrows \text{PBN}_{(\text{micelle})}$$

$$\text{Ph}^{\bullet}_{(H_2O)} + \text{2-SSPBN}_{(H_2O)} \rightarrow \text{Ph/2-SSPBN}_{(H_2O)}$$

$$\text{Ph}^{\bullet}_{(\text{micelle})} + \text{4-DoPBN}_{(\text{micelle})} \rightarrow \text{Ph/4-DoPBN}_{(\text{micelle})}$$

$$\text{Ph}^{\bullet}_{(H_2O)} + \text{PBN}_{(H_2O)} \rightarrow \text{Ph/PBN}_{(H_2O)}$$

$$\text{Ph}^{\bullet}_{(\text{micelle})} + \text{PBN}_{(\text{micelle})} \rightarrow \text{Ph/PBN}_{(\text{micelle})}$$

We assume firstly that the initiator PA-4-PD is equilibrated between the two phases at the beginning of the experiment and that only a relatively small amount of the initiator is consumed during the course of the experiment. Since PA-4-PD is much more soluble in hydrocarbon solvents than in water, this initiator will be almost entirely dissolved in the micelles. Phenyl radicals produced in the bulk aqueous phase by PA-4-PD in the aqueous phase are trapped by 2-SSPBN, but in the presence of micelles it is expected that a significant fraction of the phenyl radicals produced in the aqueous phase also disappears rapidly into the micelles because the rate of the entry of aromatic hydrocarbons into SDS micelles has been determined at almost diffusion-controlled rates (e.g., 7×10^9 M^{-1} s^{-1} for benzene[27]). The reverse reaction (exit rate from SDS micelles) is slower (e.g., 4.4×10^6 s^{-1} for benzene[27]). Thus the drop in intensity of the signal due to Ph/2-SSPBN with increase in [SDS] could be due to these two reasons. For a quantitative analysis the rate constant of spin-trapping phenyl radicals in the bulk aqueous phase by 2-SSPBN would be needed, but this value is not known at this time.

The observation that the signal due to Ph/4-DoPBN increases with increase in [SDS] supports the above interpretation since this trap monitors the number of phenyl radicals released in the interior of the micelle. The situation with PBN is more complex since all three components, initiator, radical, and spin trap, are partitioning between the two phases. However, since all are more soluble in the hydrocarbon phase than in bulk water, the shape of the curve observed in Figure 8 would be expected.

Of interest to note is that the ESR spectra of Ph/2-SSPBN consist of sharp lines at all concentrations of SDS. The phenyl adduct of PBN, on the other hand, gives a spectrum which indicates that the spin adduct is slightly immobilized in the presence of SDS (Figure 7b). Since the coupling constants are smaller than found when the spin adduct is in water, the nitroxyl function must be confined to a less polar region of the micelle. In fact, concentration conditions can be found where Ph/PBN is detectable in both phases (Figure 9). From computer simulations it can be deduced that 35% of Ph/PBN resides in a less polar region at 5 mM SDS (5 mM PBN and 0.1 mM PA-4-PD). Under the same conditions 69% is in the micellar phase when [SDS] = 10 mM. At higher concentrations of SDS no spectrum due to Ph/PBN in the aqueous phase can be detected.

These observations show that exchange of spin adducts between bulk aqueous phase and micellar surface or interior is relatively slow. Such conclusions have been reached by others.[28]

The spectra of Ph/4-DoPBN show that this spin adduct is somewhat more immobilized than Ph/PBN (Figure 7d). The

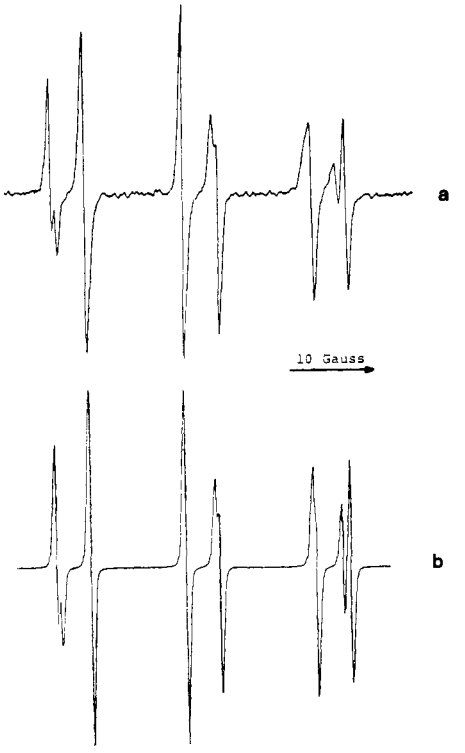


Figure 9. (a) ESR spectrum of the phenyl radical spin adduct to PBN in 5 mM SDS. (b) Computer simulation of the above spectrum.

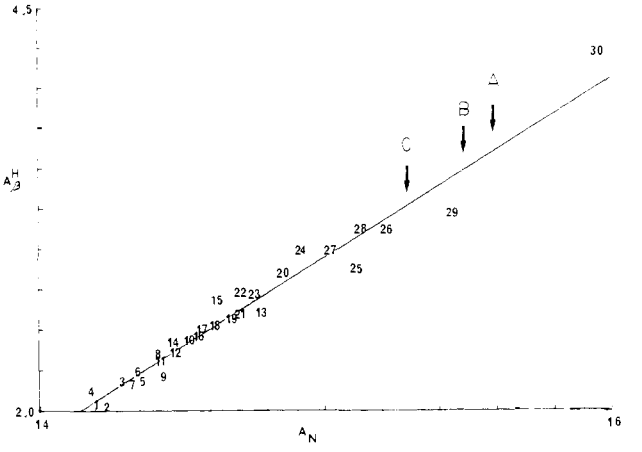


Figure 10. Plot of a_N vs. a^{β}_H for the phenyl radical spin adduct of PBN in 30 solvents including points for micelle solubilized (a) PBN/Ph, (b) 4-*t*BPBN/Ph, (c) 4-DoPBN/Ph.

(27) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

(28) Atherton, N. M.; Strach, S. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1. Jolicoeur, C.; Friedman, H. L. *J. Solution Chem.* **1978**, *11*, 813.

spectrum due to the phenyl adduct of 4-*tert*-butyl PBN (4-*t*-BPBN) in 1% SDS is included for comparison (Figure 7c). The steady increase in line width of the high-field branch of the aminoxyl triplet in comparing Ph/PBN, Ph/4-*t*-BPBN, and Ph/4-DoPBN is evidence of increased immobilization with increase in size of the hydrocarbon group in the 4 position of PBN.

In a recent study of the solvent effect on Ph/PBN, a plot of a_H^β vs. a_N was shown to be linear.[29] This plot is given here with a few extra points included (Figure 10). If one assumes that the 4-*tert*-butyl or the 4-dodecyloxy group will not noticeably affect the hyperfine coupling constants of Ph/PBN, the values for these spin adducts can be placed on the line of best fit and the polarity of the environment of the SDS micelle where these spin adducts find themselves deduced. The arrows of Figure 10 show the positions of the following a_H^β and a_N values:

adduct	a_N, G	a_H^β, G
Ph/PBN (H_2O)	15.98	4.21
Ph/PBN (micelle)	15.60	3.87
Ph/4-*t*BPBN (micelle)	15.50	3.62
Ph/4-DoPBN (micelle)	15.29	3.56

Although the region where the phenyl spin adducts reside in the SDS micelle becomes more hydrophobic with substitution of hydrocarbon groups, the environment probed by the nitroxyl function is still very polar and approximately that of pure methanol. The same conclusion was reached by Walter et al.[16] for the spin trap-4-DoPBN itself; namely, the nitrone function appears to reside in a region of the micelle with a polarity of that of ethanol.

Conclusions

Spin-trapping experiments indicate that 2-SSPBN can be used to probe radical events in the aqueous phase of SDS micelles whereas 4-DoPBN is useful for detecting radicals produced in the hydrocarbon phase. Since the nitronyl function of 4-DoPBN is believed to reside in the polar region of the micelle,[16] radicals which are formed here or which diffuse in from the aqueous phase will be detected by this trap. PBN traps radicals both in the aqueous phase as well as in the interior of the micelle. Sulfate radicals ($SO_4^{-}\cdot$) do not penetrate SDS micelles and are not detected by 4-DoPBN. No evidence of radicals derived from hydrogen atom abstraction from SDS molecules was found.

Although undoubtedly other spin traps will be found which can be used to study radical events in the aqueous exterior or hydrocarbon interior of SDS micelles, 2-SSPBN and 4-DoPBN appear to be the only pair of spin traps (with peristent spin adducts) which because of their solubility will not "cross-over" and complicate the observed results. PBN is soluble in both phases where 4-M_4A PBN already associates with SDS before cmc.

Acknowledgment. This work is being supported by the Natural Sciences and Engineering Research Council of Canada. Grateful acknowledgment is hereby made. The authors wish to express their appreciation for the substantial help and encouragement provided by Professor Henry N. Blount, particularly during the early stages of this work. Also some synthetic work on the first preparations of certain spin traps carried out by Dr. Raghav Shetty is gratefully acknowledged. E.G.J. is also grateful for an invitation to spend one month leave at the Oklahama Medical Research Foundation Laboratory in Oklahoma City (Nov 1982) where the first draft of this manuscript was written. Finally, this manuscript has been substantially influenced and hopefully improved by questions and comments by a referee.

Registry No. PBN, 3376-24-7; 2-SSPBN, 73475-11-3; 4-PyBN, 69396-90-3; 4-*t*-BPBN, 88888-33-9; 4-M_3APBN, 88888-34-0; 4-DoPBN, 80311-20-2; Ph/PBN, 21572-75-8; Ph/2-SSPBN, 88888-37-3; Ph/4-*t*-BPBN, 88888-38-4; HO/PBN, 55482-05-8; Ph/4-DoPBN, 82981-31-5; HO/2-SSPBN, 88888-39-5; HO/4-M_3APBN, 88888-36-2; HO/4-DoPBN, 88888-40-8; SO_4/4-M_3APBN, 88904-41-0; $Na_2S_2O_8$, 7775-27-1; H_2O_2, 7722-84-1; PA-4-PD, 88888-35-1; Ph·, 2396-01-2; $SO_4^{-}\cdot$, 12143-45-2; HO·, 3352-57-6; $C_4H_9N(O\cdot)H$, 22665-15-2; SDS, 151-21-3.

(29) Janzen, E. G.; Coulter, G. A.; Oehler, U. M.; Bergsma, J. P. *Can. J. Chem.* **1982**, *60*, 2725.

Effect of High Pressure on Intramolecular Electron-Transfer Luminescence of 9,9′-Bianthryl in Different Solvents

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Abstract: The effects of high pressure on the fluorescence from the intramolecular electron-transfer state of 9,9′-bianthryl were investigated in different solvents. In low-viscosity solvents an increase of pressure affects the emission similarly to an increase of solvent polarity. In moderately viscous solvents the formation of the electron-transfer state is quenched as pressure is increased. In highly viscous solvents, as in glycerol, the emission is only from the locally excited state at atmospheric pressure, and no change except for peak shift is observed with pressure increase. Freezing of solvents at high pressure strictly quenches the formation of the electron-transfer state.

Introduction

There is a possibility that electron transfer occurs between molecules in the excited state and in the ground state even in the case where it does not occur between the ground-state molecules. This is because the ionic potential of molecules in the excited state becomes smaller and the electron affinity becomes larger than those in the ground state. For the excited-state complex (so-called "excimer" or "exciplex"), the two molecules are considered to interact spacially to form a sandwich-like conformation with a separation of 3.0–3.5 Å. Also possible is an intramolecular interaction such as reported for α,ω-diarylalkanes,[1] aryl-ω-N,N'-

(1) (a) Okada, T.; Migita, M.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Am. Chem. Soc.* **1981**, *103*, 4715, and references cited therein. (b) Wang, Y.; Crawford, M.; Eisental, K. B. *J. Phys. Chem.* **1980**, *84*, 2696, and references cited therein. (c) Chandross, E.; Thomas, H. *Chem. Phys. Lett.* **1971**, *9*, 393. (d) Davidson, R.; Whelan, T. *J. Chem. Soc., Chem. Commun.* **1977**, *11*, 361. (e) Davidson, R. S.; Bonneau, R.; Joussot-Dubien, J.; Toyne, K. J. *Chem. Phys. Lett.* **1979**, *63*, 269.

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