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- Abbreviations: TPP = dianion of meso-tetraphenylporphyrin; Bu₄N⁺ = tetra-*n*-butylammonium; Im⁻ = imidazolate anion, C₃N₂H₃⁻; 1-Melm = 1-methylimidazole; 2-MeIm = 2-methylimidazole; THF = tetrahydrofuran.
- Anal. Calcd for C₅₁H₃₉N₆O₂Mn: C, 75.92; H, 4.87; N, 10.42; Found: C, 75.60; H, 4.86; N, 9.93. NMR integration solvate analysis from acid decomposition: calcd for THF, 8.9; found, 9.8.
- Crystal data and refinement results: [Mn(N₄C₄₄H₂₈(C₃N₂H₃)_n)]_n; monoclinic; *a* = 20.033 (3), *b* = 16.851 (3), and *c* = 22.545 (5) Å; β = 104.36 (2)°; space group C2/c; Z = 8; ρ_{calcd} = 1.324, ρ_{obsd} = 1.32 g/cm³; R₁ = 0.090, R₂ = 0.089; 4320 unique observed data (F_o > 3σ(F_o), 2θ < 55°, Mo Kα radiation).
- Another explanation, albeit less likely, is that a Jahn Teller or Peirls distortion causes a symmetry lowering alternation of Mn-N_{im} bond lengths. The pseudo S = 3/2 spin state would then have to be rationalized by an all high-spin complex with complete coupling of one unpaired electron per Mn(III) atom by overlap of the d_{z²} orbitals via the σ bonding system of imidazolate.
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- For example, comparison of low-spin Fe(1-Melm)₂(TPP) to high spin Fe(2-Melm)(TPP) reveals differences of 0.09 and 0.15 Å in Fe-N_{porph} and Fe-N_{im}, respectively. No significant difference in Mn-N_{porph} is expected between high- and low-spin Mn(III) since in both states d_{x²-y²} is unoccupied. W. R. Scheidt, *Acc. Chem. Res.*, **10**, 339 (1977).
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John T. Landrum, Christopher A. Reed*²⁹

Department of Chemistry, University of Southern California
Los Angeles, California 90007

K. Hatano, W. Robert Scheidt

Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556
Received December 23, 1977

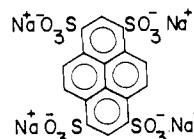
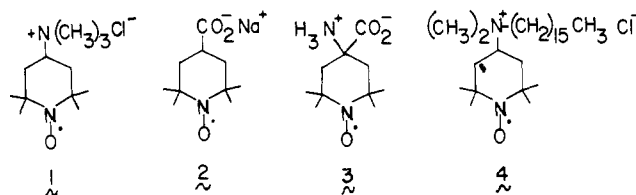
Fluorescence Quenching by Nitroxyl Radicals in Micellar Environments. A Useful Probe for Studying Micelle-Substrate Interactions

Sir:

Although it is now well established that micelles can catalyze or inhibit chemical reactions in aqueous solutions,¹ detailed descriptions of these effects are lacking. With the goal of elucidating such mechanisms, we have been investigating the fluorescence quenching of pyrene and pyrene derivatives by nitroxyl radicals in micelle environments.²

Previously, we showed that di-*tert*-butylnitroxide (a stable radical) quenches the fluorescence from a series of aromatic hydrocarbons at, or near, the diffusion limit with an interaction distance of 5-7 Å.³ We find that this reaction is equally as efficient in aqueous media. If the mechanism does not change in going from nonpolar to aqueous solutions,⁴ quenching still occurs over collisional distances so that the relative quenching efficiencies will reflect relative encounter frequencies between the excited fluorophores and quenchers. In this paper we show that the encounter frequency is strongly influenced by the micelle surface charge and that examples of both micelle-catalyzed and micelle-inhibited fluorescence quenching reactions can be realized.

The quenching of the fluorescence from 1.0 × 10⁻⁵ M tetrasodium pyrenetetrasulfonate (PTS)⁶ by nitroxyl radicals 1,⁷ 2,⁸ 3,⁹ and 4¹⁰ was studied in aqueous solutions in the ab-



PTS

sence and presence of cetyltrimethylammonium chloride (CTAC) and sodium dodecylsulfate (SDS) micelles. The apparent *k*_q's in Table I were calculated from the essentially linear Stern-Volmer slopes observed between 1.0 × 10⁻⁴ M

Table I. PTS Fluorescence Quenching Results at 25 °C

Quencher	$"k_Q" \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ ^{a, b}		
	Water	In the presence of CTAC micelle ^c	In the presence of SDS micelle ^c
1	70	$\leq 1.0^d$	$\leq 1.0^d$
2	2.6	66	2.4
3	5.0	5.0	5.0
4		320	$\leq 1.0^d$

^a Apparent k_Q 's from the steady-state Stern-Volmer slopes using measured τ_f 's as follows: water, 13 ns; CTAC micelle, 8 ns; SDS micelle, 16 ns. All experiments were carried out on nondegassed samples.

^b Estimated error limits $\pm 10\%$. ^c [CTAC] = 1.0×10^{-2} M which is well above the critical micelle concentration of 1.0×10^{-3} M. [SDS] = 1.5×10^{-2} M which is well above the critical micelle concentration of 8.0×10^{-3} M. P. Mukerjee and K. Mysels, "Critical Micelle Concentration of Surfactant Systems", National Bureau Standards Reference Data Series, National Bureau of Standards, Washington, D.C., 1971. ^d No quenching was observed but upper limit was estimated from the sensitivity limit of the steady-state experiment.

$< [Q] < 1.0 \times 10^{-2}$ M using independently measured τ_f 's.

The fluorescence quenching order is $1 \gg 3 > 2$ in pure water, $2 \gg 3 > 1$ in the presence of CTAC micelles and $3 > 2 > 1$ in the presence of SDS micelles. The results in the absence of micelles show the expected influence of electrostatic interactions between the excited fluorophor and the charged quenchers. In the presence of the CTAC micelles, where PTS is bound to the micelle surface^{11,12} the reactivity order is determined by the relative binding efficiencies of the nitroxyl radicals to the micelle. In the environment of the cationic micelle, the reaction between the similarly charged reactants (PTS and 2) is strongly enhanced and that between the two oppositely charged reactants (PTS and 1) is strongly retarded relative to the results in pure water.

In the presence of the SDS micelle, PTS appears to be dissociated from the micelle surface. Under this condition, 2 and 3 quench the excited PTS as efficiently as they do in pure water. The striking result is the inhibition of the reaction between excited PTS and 1 which presumably results because of strong binding of the latter to the anionic micelle.

The results obtained with the surfactant nitroxyl radical 4 support the interpretations given above. This quencher is incorporated into both the CTAC and SDS micelles¹³ and is a model for the micelle-bound quencher. In the presence of the CTAC micelle, where the fluorophor also is associated with the micelle, very efficient fluorescence quenching is observed. However, in the presence of the SDS micelle, where the fluorophor is dissociated, very inefficient fluorescence quenching is noted.¹⁴

At this time, we stress only the qualitative interpretation of these results. Because both static-like and dynamic quenching mechanisms¹⁵ can operate, the absolute magnitudes of the k_Q 's in Table I should be cautiously interpreted. Further work is in progress to sort out these pathways and to explore the usefulness of this quencher system for studying interactions between fluorophors solubilized in the hydrophobic core of micelles and reactants in the aqueous medium.

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- (11) We estimate that PTS has an association constant with the CTAC micelle sufficiently large ($K > 10^5 \text{ M}^{-1}$) for it to be essentially completely incorporated into the micelle under the reaction conditions. This estimate is based on the report that potassium 2,4-dinitrophenylsulfate binds to cetyltrimethylammonium bromide (CTAB) with $K \sim 1.9 \times 10^5 \text{ M}^{-1}$. See table 4.1 in J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, N.Y., 1975.
- (12) The absorbance of a 1.0×10^{-5} M PTS solution initially decreases with added CTAC until $\sim 1.0 \times 10^{-3}$ M surfactant. Thereafter, the absorbance increases sharply and levels off $\geq 5 \times 10^{-3}$ M added surfactant. In addition, the λ_m for PTS shifts from 375.5 nm in pure water to 380 nm in the presence of 5×10^{-4} M CTAC and finally to 377 nm $\geq 1 \times 10^{-3}$ M CTAC. These observations indicate some interaction between PTS and CTAC below the cmc point. However, the abrupt spectral changes described near 1×10^{-3} M and the invariance of the PTS electronic absorption spectrum over a wide CTAC concentration range above the cmc strongly argue for association of PTS with the CTAC micelle under the conditions of the fluorescence quenching experiments. For similar observations on acridine-type dyes with SDS, see B. H. Robinson, N. C. White, C. Mateo, K. J. Timmins, and A. James in "Chemical and Biological Applications of Relaxation Spectrometry", E. Wyn-Jones, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1975, p 201.
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- (14) Inefficient fluorescence quenching by 4 in the presence of the SDS micelle system could also result from precipitation of aggregates of 4 and SDS. No turbidity was apparent to the eye over the concentrations used in this study. Further, the fluorescence of SDS micelle solubilized pyrene, under experimental conditions similar to the PTS study, is very efficiently quenched by 4, " k_Q " $\approx 8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is consistent with the conclusion presented in the paper.
- (15) We use the term "static-like" to describe quenching of micelle-bound excited PTS by quenchers already associated with the same micelle. An example is the quenching of excited PTS by 4 in the presence of CTAC micelles. "Dynamic" quenching results from diffusional encounter of excited fluorophor and quencher where at least one of the two reactants is dissociated from the micelle.

Samir Atik, Lawrence A. Singer*

Department of Chemistry
University of Southern California
Los Angeles, California 90007

Received January 9, 1978

Stereochemistry of the 1,3-Proton Loss from a Chiral Methyl Group in the Biosynthesis of Cycloartenol as Determined by Tritium Nuclear Magnetic Resonance Spectroscopy

Sir:

The biosynthesis of sterols by photosynthetic organisms¹ proceeds through cyclization of 2,3-oxidosqualene (1) to yield cycloartenol (2) in contrast to nonphotosynthetic organisms² where the cyclization product is lanosterol (3) (Scheme I). The last step in the biosynthetic pathway leading to 2 involves a 1,3-proton loss from a methyl group to form the cyclopropane ring. A priori, this process could take in one of two stereochemically defined ways—retention or inversion of configuration around the C-6 methyl group (Scheme II). We now report our results on the stereochemistry of the 1,3-proton loss as determined by ³H NMR spectroscopy.³

The labeled, chiral substrate 12 for cyclization studies was prepared from D-malic acid (4) according to Scheme III. ³H NMR spectra of 10 (Figure 1) confirm the fact that each molecule of 10 labeled with a tritium atom at C-7 was also labeled with one deuterium atom (and one hydrogen atom) at C-7. Approximately thirty percent of all molecules were la-