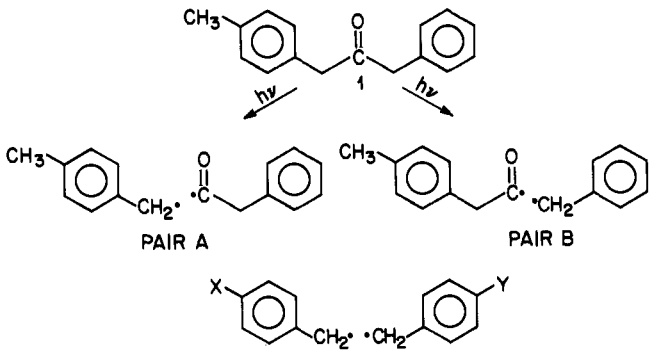
before they recombine.

When the same reaction is carried out in an aqueous solution containing hexadecyltrimethylammonium chloride (HDTCl) a similar polarization pattern is observed (Figure 2). However, in this case only a single benzylic methylene peak, that of 1-(*p*-tolyl)-2-phenylethane (**2b**), is observed, even though the chemical shifts of the three bibenzyls in aqueous HDTCl are sufficiently different to allow **2a** and **2c** to be detected separately if they were formed in any significant amount. These results confirm the selectivity of bibenzyl formation from an unsymmetrical ketone in a micellar environment.[5]

The observation of nuclear spin polarization as a result of a radical-pair reaction in micellar solution implies a spin sorting mechanism different from the one operating in homogeneous solutions. Most commonly, spin sorting occurs as



a) X,Y = H
b) X=H, Y=CH_3
c) X,Y = CH_3

a result of a hyperfine dependent intersystem crossing and a subsequent competition between an electron spin dependent radical-pair reaction (recombination) and an electron spin independent reaction (separation by diffusion). In the photolysis of dibenzyl ketone, for example, the nuclear spin states which allow fast intersystem crossing will be overrepresented in the recombination product, the ketone, whereas those causing slower intersystem crossing will be overrepresented in the escape products, the bibenzyls.

In the micellar environment separation is precluded and coupling is the only available alternative. In this situation the decarbonylation reaction provides for spin selection: the nuclear spin states which allow fast intersystem crossing will predominate in the regenerated starting material whereas those causing slower intersystem crossing will accumulate in the decarbonylated product. In order to allow efficient spin selection, the decarbonylation must occur at a rate comparable with that of the hyperfine induced intersystem crossing. It is noteworthy that the ratio of bibenzyl to ketone polarization is higher in the micelle than in homogeneous solution and is close to the ratio expected on the basis of the spin lattice relaxation times of **1** and **2b**, 2.1 and 1.5 s, respectively. Apparently, the lifetime of the secondary pair is not long enough to allow any significant relaxation of the nuclear spin polarization before coupling.

The CIDNP spectra observed in either cyclohexane or aqueous HDTCl reveal an additional mechanistic detail which would be difficult to determine by classical photochemical techniques. Both spectra show different intensities for the two methylene groups of the regenerated ketone; in both solutions the signal of the *p*-tolylmethylene group is ~1.5 times as large as that of the benzyl group. Since the spin lattice relaxation times of these protons are identical within experimental error (2.1 ± 0.2 s), we interpret the different signal intensities as evidence for a preferential cleavage of the *p*-methylbenzyl bond (to form pair A).

A more detailed analysis of the benzylic polarization reveals that the preference for the formation of pair A may be slightly higher than the 3:2 ratio of the two benzylic signals. This is due to the fact that each pair generates polarization in both benzylic methylene groups. In addition to the main polarization induced in the α protons of the benzyl radicals ($a = -16.3$ G;[7] $\Delta g > 0$), a smaller effect of the same direction is induced in the β protons of the acyl radicals ($a \sim 1$ G;[8d] $\Delta g < 0$). However, the ^1H hyperfine coupling in the β position of acyl radicals is small so that the contribution of these nuclei to the overall polarization must be minor.

The results reported here reveal several details of the photoreactions of dibenzyl ketones and allow an insight into the behavior of radical pairs in the restrictive environment of the micelle. Other aspects of this interesting system, including the fate of a chiral center and of specifically ^{13}C-labeled ketones are under investigation.

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Oxidations and Oxygen Transfers Effected by a Flavin *N*(5)-Oxide. A Model for Flavin-Dependent Monooxygenases

Sir:

The flavin-dependent monooxygenases bind and activate molecular oxygen, ultimately transferring one oxygen atom to substrate and releasing the second as water.[1] Among the reactions catalyzed by the flavin monooxygenases are the hydroxylation of *p*-hydroxybenzoate,[2] the oxidative decarboxylation of salicylate,[3] and a variety of amine oxidations mediated by the mixed-function amine oxidase system.[4] Although flavin monooxygenations have been the object of extensive investigation, the structure of the flavin oxygenating species remains unknown. Recent work strongly implicates the 4a-hydroperoxyflavin as an initial intermediate in the enzymic oxidations; this intermediate and derived species have been offered to explain the reactivity of the flavin, oxygen-transferring systems.[5] Herein we present a study of nonenzymic oxidations and oxygenations effected by flavin *N*(5)-oxides

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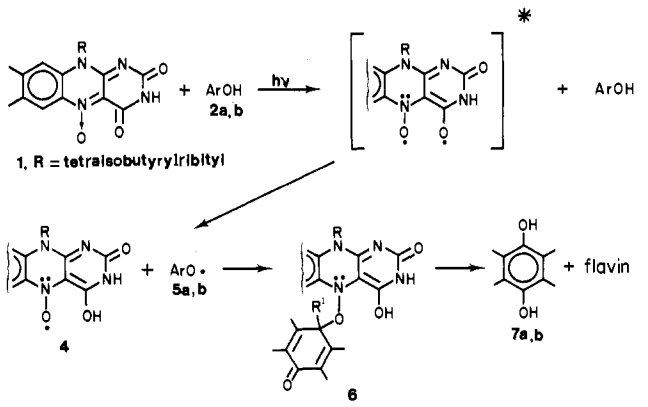
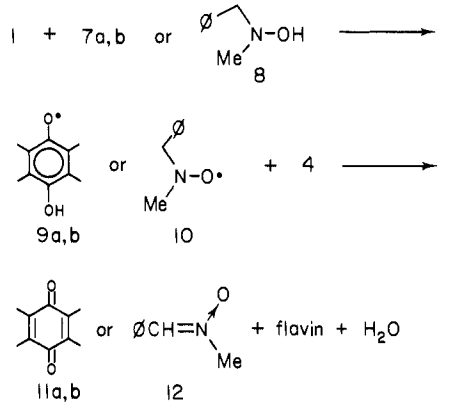
Scheme I



Scheme II



(e.g., **1**, Scheme I).[6] Based on our results we suggest that flavin nitroxyl radical **4** may play a role in flavoenzyme chemistry and suggest a mechanism whereby **4** may be derived from enzyme-bound 4a-hydroperoxyflavin.

Under conditions of ambient temperature and illumination, flavin *N*(5)-oxide **1** oxidizes 2,3,5,6-tetramethylphenol (**2a**) and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (**2b**) to the corresponding benzoquinones **11a,b** (see Table I). The mechanism depicted for these oxidations (Schemes I and II) is suggested by several observations. (1) Photoexcitation of *N*-oxide **1** in the presence of phenols leads to the generation of phenoxy radicals (Scheme I). This is shown by the accumulation of the long-lived radical from 3,5-di-*tert*-butyl-4-hydroxytoluene[7] (**2c**, see Table I) when a mixture of **1** and **2c** are illuminated in the cavity of an ESR spectrometer. Further, the phenoxy radical is not seen under similar conditions, in the absence of **1**, and the transformations **1** + **2a,b** → flavin + **11a,b** do not proceed in the dark. (2) The oxygen atom transferred to **2a,b** is derived from the *N*-oxide (Scheme I). Thus (a) the oxidations proceed in rigorously degassed solutions, (b) the deoxygenated flavin is isolated after photolysis, and (c) ^{18}O is transferred quantitatively from labeled **1**[8] to phenol **2a** (see Table I). (3) The hydroquinones **7a,b** are likely intermediates in the conversion of the phenols **2a,b** into quinones **11a,b.** This is indicated by (a) the rapid reaction of hydroquinone **7a** with **1** (Scheme II) in the dark, producing quinone **11a** (95% GLC yield) and flavin (72% isolated) and (b) the stoichiometry of the oxidation—two molecules of *N*-oxide **1** are required for each phenol converted into quinone.

Thus, Scheme I shows reaction of a photoexcited state of **1**[9] (**3**) with a phenol generating phenoxy radical **5a,b** and the flavin nitroxyl radical **4.** Coupling of **5a,b** with **4,** heterolytic fragmentation of the resulting adduct **6,** and proton loss or decarboxylation (see R′ in structure **6**) would produce oxidized flavin and hydroquinone **7a,b.** Similar phenolic oxidations are effected by Fremy's salt[10a] and other isolable nitroxyl radicals.[10b] The products from other phenol photooxidations are presented in Table I; all products are thought to arise via the corresponding phenoxy radicals generated as in Scheme I.

Table I. Oxidations and Oxygenations Effected by Flavin *N*(5)-Oxide **1.**

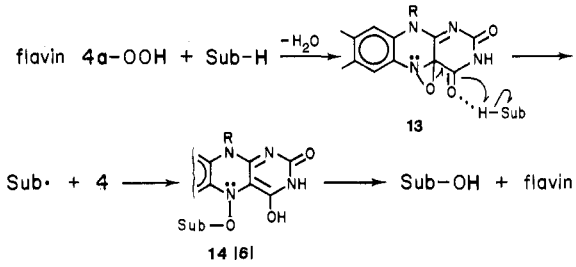
Starting Materials (molar ratio)	Reaction Conditions[a]	Identified Products (yield)[b]	Yield of Flavin
2a + **1** (1:1)	hν,[c] in pyridine-d_5	**11a** (23-30%)[d]	67-77%[e]
repeated with ^{18}O-**1** (57% ^{18}O)	same	**11a** containing 56% ^{18}O	not recovered
2b + **1** (2:1)	hν,[c] in $CDCl_3$	**11b** (34-39%)[d]	not recovered
7a + **1** (1:1)	in the dark, in pyridine-d_5	**11a** (95%)[d]	72%[e]
2c + **1** (2:1)	hν,[c] in $CDCl_3$	(42-45%)[d]	66-70%[e]
+ **1** (2.5:1)	hν,[c] in $CDCl_3$	(61-67%)[d,f]	72-79%[e]
N-OH (**8**) + **1** (2:1)	in the dark, in $CDCl_3$	**12** (not isolated)[g]	quantitative[g]
8 + **1** (1:1)	hν,[c] in $CDCl_3$	**12** (33-41%)[h]	not recovered
+ **1** (2:1)	hν,[c] in $CDCl_3$[i]	NH (75-86%)[d]; ØCHO (82-92%)[d]; CH_3COCH_3 (4.0-5.2%)[d]	73-79%[e]
repeated with ^{18}O-**1** (57% ^{18}O)	same	ØCHO containing 49% ^{18}O	not recovered
n-$C_7H_{15}N$ + **1** (2:1)	hν,[c] in $CDCl_3$[i]	NH (61-70%)[d]; n-$C_6H_{13}CHO$ (56-66%)[d]; CH_3COCH_3 (9.2-12%)[d]	74-86%[e]
+ **1** (2:1)	hν,[c] in $CDCl_3$[i]	NH (41-44%)[d]; ØCHO (26-35%)[d]	66-72%[e]
repeated with ^{18}O-**1** (57% ^{18}O)	same	ØCHO containing 48% ^{18}O	not recovered
· **1** (2:1)	hν,[c] in $CDCl_3$[i]	(42-53%)[d]	49-54%[e]

[a] All reactions were performed in freeze–thaw degassed solution. [b] Range represents results from multiple runs. [c] Light source: tungsten-halogen slide projector lamp (Sylvania, EMM-EKS, 24 V, 250 W) operated at 10 V, used with two filters, Corning CS No. 4-96 plus CS No. 3-74 (transparent from 420 to 580 nm). [d] GLC yield was based on limiting reagent; all products were indistinguishable from authentic samples. [e] Isolated, recrystallized yield. [f] Quantum yield, $\phi \simeq 0.5$, by the procedure in note 20. [g] Complete conversion of **1**, into flavin is seen by ^1H NMR; roughly half of **8** is converted into **12.** [h] Yield was determined by GLC after hydrolysis to PhCHO. [i] Amine/**1** photolyses proceed similarly in pyridine-d_5.

Scheme II depicts a likely course for the conversion of hydroquinone **7a,b** to benzoquinone **11a,b** as well as the similar thermal or photochemical oxidation of hydroxylamine **8** to nitrone **12** (also see Table I). The precedented[11] formation of nitrones from nitroxyl radicals bearing α hydrogens (see **10**) supports the mechanism of Scheme II.

The similarity of the transformations of Scheme I to the biological, flavin-mediated conversions, *p*-hydroxybenzoate → 3,4-dihydroxybenzoate,[2] and salicylate → catechol,[3]

Scheme III



suggests that mechanistic similarities may also exist. Certainly, the biological hydroxylations are not mediated by flavin *N*-oxide and light; yet the nitroxyl radical **4** is a viable candidate for the flavin oxygenating species. A possible mode of enzymic generation of nitroxyl radical **4** is shown in Scheme III. In the presence of substrate (Sub-H)[12] 4a-hydroperoxyflavin (flavin 4a-OOH) would undergo heterolytic cleavage of the weak hydroperoxide O-O bond, as suggested by Orf and Dolphin,[5b] with formation of oxaziridine **13**.[13] Hydrogen bonding of the substrate to the carbonyl at C-4 would induce *concerted* homolysis of the oxaziridine C-O bond and hydrogen atom abstraction from substrate. The homolysis of the C-O bond would achieve the generation of stabilized radicals **4** and Sub· (cf. Schemes I and II) while releasing the ring strain of the oxaziridine. The enzyme-bound, proximate radicals Sub· and **4** would couple rapidly[14] giving adduct **14** (cf. **6**, Scheme I) which, in turn, would fragment to products.[15] The postulated, enzymic radical coupling and subsequent fragmentation of Scheme III find precedent in the model reactions of Scheme I and in other phenol oxidations.[16] The radical-pair mechanism (Scheme III) avoids the need to invoke a specialized form of oxenoid mechanism[2,5b,c] during flavoenzyme oxygen transfer.

The mixed-function amine oxidase system[4] mediates the conversion of hydroxylamine **8** (Scheme II) into nitrone **12.** As chemically precedented,[11] the oxidation may proceed on the enzyme via nitroxyl radicals **10** and **4,** generated as shown in Scheme III (**13** → Sub· + **4**).

The mixed-function amine oxidase system serves as well in the oxidations of secondary amines to hydroxylamines, and tertiary amines to tertiary amine oxides. These oxidations and the reported[17] "essentially quantitative", nonenzymic conversion of brucine into its tertiary amine oxide by 2-*tert*-butyl-3-phenyloxaziridine in refluxing methylene chloride had prompted us to suggest that the Orf and Dolphin flavin oxaziridine **13** functions in the mixed-function amine oxidase system. As precedented by the alleged brucine oxidation, the flavin-oxaziridine (**13**) might directly mediate the oxidations of secondary and tertiary amines. In our hands, however, 2-*tert*-butyl-3-phenyloxaziridine does not transfer oxygen to brucine. As reported,[17] refluxing of the oxaziridine and brucine in methylene chloride leads to the precipitation of a white crystalline solid. Yet the material is formed as well upon refluxing brucine *alone* in methylene chloride. The product[18] is the adduct of brucine with one solvent molecule; a similar adduct forms from Me_3N plus CH_2Cl_2.[19] Whether or not suitably activated oxaziridines can transfer oxygen to amines, enzymically or nonenzymically, must be ascertained by further study.

Table I shows details of amine photooxidations effected by flavin *N*(5)-oxide **1.** The oxidative dealkylations proceed efficiently[20] and the source of oxygen in the carbonyl product is the *N*(5)-oxide oxygen (see Table I). Similar amine oxidative dealkylations are mediated by the flavin-dependent enzymes, monoamine oxidase and D-amino acid oxidase.[21] The photochemical reactions of flavin *N*(5)-oxides would seem to bear no mechanistic relationship, however, to these biological oxidations which are mediated directly by flavins rather than flavin-oxygen adducts.

Further studies into the mechanism of flavin *N*(5)-oxide mediated oxidations are underway. In particular, we pursue syntheses of flavin based nitroxyl radicals and the syntheses of oxaziridines related to **13** in order to study their thermal reactions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to the National Institutes of Health for support of this work. We thank Professor E. Solomon and co-workers for assistance with ESR experiments and Professors M. Wrighton and C. Walsh for valuable discussions. We are particularly grateful to Dr. W. Ashton (Merck Sharp & Dohme) for providing chemical procedures and materials for the synthesis of **1.**

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(2) See Entsch, B.; Ballou, D. P.; Massey, V. *J. Biol. Chem.* **1976,** *251,* 2550.

(3) See White-Stevens, R. H.; Kamin, H. *J. Biol. Chem.* **1972,** *247,* 2358, and references therein.

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(7) The ESR spectrum was indistinguishable from the published spectrum: Becconsall, J. K.; Clough, S.; Scott, G. *Trans. Faraday Soc.* **1960,** *56,* 459.

(8) Made by the procedure for unlabeled material (note 6) utilizing $NO^+BF_4^-/H_2{}^{18}O/Et_2O$ for the final nitrosative closure.

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(11) For a review of nitroxyl chemistry, see Keana, J. F. W. *Chem. Rev.* **1978,** *78,* 37.

(12) Substrate induced formation of oxaziridine from 4a-hydroperoxyflavin is compatible with the observed release of H_2O_2 from the flavin when no substrate or when a poor substrate is bound to *p*-hydroxybenzoate hydroxylase or salicylate hydroxylase; see ref 2 and 3 and references therein.

(13) Ironically, Orf and Dolphin[5b] cite examples of "stable arene oxaziridines" in support of their postulated flavin oxaziridine. Indeed, the species responsible for aromatic hydroxylation is an exceedingly labile, if not transient species. Fortunately, the examples cited by Orf and Dolphin have been shown actually *not to be oxaziridines.* See Kaneko, C.; Yamada, S.; Yokoe, I.; Ishikawa, M. *Tetrahedron Lett.* **1967,** 1873.

(14) Using the technique of rapid-freeze ESR, Massey and co-workers were unable to detect radical species during the reoxidation of the reduced *p*-hydroybenzoate hydroxylase–substrate complex by molecular oxygen. See Howell, L. G.; Massey, V.; Strickland, S. *Wenner-Gren Cent. Int. Symp. Ser.* **1972,** *18,* 445–452. In our mechanism (Scheme III) formation of nitroxyl radical **4** is contingent upon the simultaneous and proximate formation of the substrate radical, Sub· (e.g., ArO·). The rapid freeze technique will stop second-order reactions which rely on diffusion to bring reactive species together in solution; rapid freezing may be of no avail in preventing reaction of the closely bound species **4** and Sub· (See Ballou, D. P.; Palmer, G. A. *Anal. Chem.* **1974,** *46,* 1248.)

(15) Massey et al., using stop-flow techniques, have demonstrated the intermediacy of at least two species, in addition to the putative 4a-hydroperoxide, during flavin cofactored hydroxylation of 2,4-dihydroxybenzoate and other activated aromatics; see ref. 2. Our scheme, or tautomeric equivalents, may be compatible with their observations. However, the spectral characteristics of our proposed intermediates (e.g., **14**) are difficult to estimate, and the spectral characteristics of their enzyme intermediates vary somewhat with substrate and reaction conditions. One appealing possibility is that substrate reacts with oxaziridine **13** as soon as **13** is formed from 4a-hydroperoxylflavin. Adduct **14** formed by radical coupling (cf. **6**) would be Massey's second, observable intermediate. Aromatization of the substrate moiety of **14** would produce the third intermediate which would fragment to products (Scheme III).

(16) For a review of the oxidation of phenols, see pp 326–345, especially pp

340 and 341 in "Free Radical Chemistry", Nonhebel, D. C., Walton, J. C., Eds., Cambridge University Press: Cambridge, 1974.
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(18) We cannot exclude at this time the possibility that brucine *N*-oxide might be a minor product formed in the reaction with the oxaziridine. The product isolated as described in ref 17, however, is shown to contain two atoms of chlorine by combustion analysis and displays ^{1}H NMR (270 MHz, D_2O) δ (HOD) 0.73 (2 H, AB q, J = 9.8 Hz, $^+NCH_2Cl$). Details of our study and a revised mechanism for the kinetic resolution of 2-*n*-propyl-3-methyl-3-isobutyloxaziridine by brucine will be published later.
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(20) The quantum yield (determined by ferrioxalate actinometry) for the photoreduction of **1** (436-nm narrow band-pass filter used) to flavin by tribenzylamine, $\phi \simeq 1.1$ (ϕ based on quantization of benzaldehyde formed from the *tert*-amine, at ~5% completion).
(21) See Bright, H. J.; Porter, D. J. T. *Enzymes*, *3rd Ed.* **1975**, *8*, 421–505.

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Aspects of Artificial Photosynthesis. Photoionization and Electron Transfer in Dihexadecylphosphate Vesicles

Sir:

Initial steps of solar energy conversion have been modeled by photoionizing aromatic hydrocarbons in aqueous micelles.[1-7] Experiments have been prompted by the recognized abilities of micelles to solubilize apolar molecules and to affect rates of reactions.[8] Micelles had two important functions. Firstly, solubilization in their hydrophobic environment was expected to decrease the ionization potential. Secondly, subsequent to photoejection, electron–cation radical recombination was considered to be prevented by Coulombic repulsions at the charged micellar surface. Photoionization of pyrene[2,3] has been investigated in aqueous micellar sodium dodecyl sulfate in detail. There was a relatively high yield of ionization and the anionic surface of the micelle decreased charge recombinations. Photoionization was, however, biphotonic and did not, consequently, result in a lowering of the ionization potential. One would also expect efficient photoionization in liposomes.[9] Experimental results did not, however, fulfill this expectation. Photoionization yields in liposomes were relatively low and the process for pyrene was biphotonic.[10-12]

This communication reports the efficient *monophotonic ionization* of pyrene, localized in the hydrophobic bilayers of completely synthetic dihexadecylphosphate, DHP, vesicles.[13] In this environment the ionization potential of pyrene is substantially lowered. Equally significantly, photoejected electrons are shown to exit the vesicle interior and to be transferred to an acceptor. DHP vesicles may well represent one of the simplest functional models[14] for mimicking photosynthesis.[15]

Figure 1 shows transient absorption spectra of argon-saturated DHP-solubilized pyrene[16] following excitation by a 8-ns nitrogen laser at 337.1 nm.[17] In the 400–500 nm region of the spectra, there are three bands whose maxima are centered at 410, 450, and 480 nm. These absorptions are attributable[1] to the triplet–triplet transition of pyrene (410 and 480 nm) and to pyrene cation radical (450 nm). Assignments were confirmed by the addition of base (pH 10). Only the decay rate of the 450 absorbing species increased.[18] The broad absorption band in the red is due to the hydrated electron, e^-_{aq}.[19] This absorption is removed by the addition of oxygen. The insert in Figure 1 shows the linear dependence of the e^-_{aq} on the laser beam intensity.[20] Evidently, absorption of only one 337.1-nm photon of 3.68-eV energy is required to ionize DHP-entrapped pyrene in the intensity range investigated. The ionization threshold of a solute, I_s, is given by[22]

$$I_s = I_g + P_+ + V_0 \qquad (1)$$

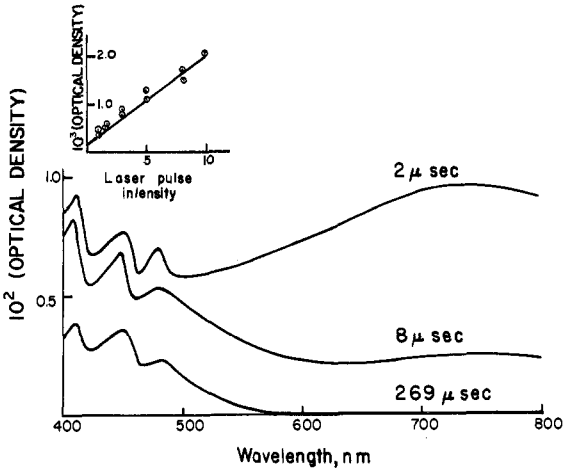

Figure 1. Absorption spectra of the transient formed on excitation of pyrene, localized in DHP vesicles. The peak laser output was 2.3 mJ per pulse. The insert shows the electron yield at 670 nm as a function of laser pulse intensity.

where I_g is the gas phase ionization potential of the solute (I_g (pyrene) = 7.55 eV),[2] P_+ is the polarization energy of the solute cation (P_+ (pyrene) = −1.6 eV),[2] and V_0 is the energy state of the electron in solution (V_0 (decane) = 0.22 eV).[23] Substituting these values to eq 1 results in I_s = 6.17 eV. Thus, the energy lowering of the ionization potential is 2.49 eV. The lowering of the ionization potential is a composite effect of alteration of the values of V_0 and P_+. Since the hydrated electron is in fact monitored in water, the value of V_0 in the vesicle can approach that in water (−1.5 eV).[24] Pyrene molecules are dynamically distributed in the vesicles; at a given time some of them may well be in close proximity to the charged polar head groups. A similar effect has been observed by Thomas and Piciulo.[7] Additional energy may be gained from the electrostatic stabilization of the pyrene cation radical by the negatively charged phosphate head group on the vesicles.

The photoexcited electron decays by two consecutive first-order processes at or near the ambient temperature (Figure 2). Half-life times for these decays are 0.72 and 2.48 μs at 21 °C and 0.95 and 2.19 μs at 26 °C. Increasing the temperature increased the contribution of the slow electron decay until the process became monoexponential (Figure 2). These results can be rationalized in terms of altered reaction sites of the electron as a function of temperature-induced morphological changes of the DHP vesicle. Above the phase temperature (46 °C, for example) the bilayers of the vesicle become fluid. All the electrons can, therefore, readily exit and decay in the bulk aqueous phase monoexponentially, by reacting with impurities (unremoved oxygen and titanium from sonication) and with each other. This monoexponential decay corresponds to the long-lived component (Figure 2). At lower temperatures, the surfactant vesicle is more rigid and their head groups are closer together. Under these circumstances, some of the electrons are scavenged by protons, concentrated at the surface of the negatively charged DHP vesicles. Using the observed half-life time for the fast electron decay ($t_{1/2} = 0.95 \times 10^{-6}$ s at 26 °C) and the rate constant ($k_{e^-_{aq}+H^+} = 2.0 \times 10^{10}$ M^{-1} s^{-1})[25] leads to an apparent proton concentration of 3.6×10^{-5} M. Such a degree of proton concentration has been demonstrated for aqueous anionic micellar sodium dodecyl sulfate[26] and is entirely expected for the much larger[27] DHP vesicles.

In separate experiments transfer of the photoejected electron to benzophenone has been demonstrated. External addition of benzophenone[28] to pyrene-containing DHP vesicles resulted in the exponential decrease of the half-life time of the hydrated electron (to a value of 0.4 μs) with the concurrent appearance

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