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Mechanism of the Benzophenone-Sensitized Photolysis of *O*-Benzoyl-*N*-(1-naphthoyl)-*N*-phenylhydroxylamine in Cationic Micellar Media

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The benzophenone-sensitized photolysis of the title hydroxylamine (**1**) in hexadecyltrimethylammonium chloride (HTAC) micelles was found to give benzoyloxy(**2**,**3**)- and phenyl(**4**,**5**)-migrated products, along with fragmentation products, 1-naphthanilide (**6**) and benzoic acid (**7**), which were obtained exclusively from the sensitized reaction in organic media. An analysis of the effects of added benzyl alcohol on the quantum yields for the reaction in HTAC micelles showed that the benzoyloxy-migrated products are derived from the amidyl-benzoyloxyl radical pair (that is present at the micellar surface), whereas the amidyl-phenyl radical pair (that is penetrated deeply into the micellar interior) is responsible for appearance of the phenyl-rearranged products. This effect of benzyl alcohol also confirmed that the hydrogen abstraction of the amidyl and benzoyloxyl radicals takes place in competition with the spin inversion of these triplet radicals. These interpretations were substantiated by the finding that the critical micelle concentration for HTAC is reduced in the presence of benzyl alcohol, but that the alcohol exerts only its very small effect on the aggregation number. On the other hand, the use of hexadecyltrimethylammonium bromide (HTAB) micelles instead of HTAC resulted in **2** and **3** in negligible quantum yields with increased quantum yields for the formation of **4**—**7**. This intriguing result was explained in terms of (1) much less efffective hydrogen-bonding solvation of the assumed hot triplet radical pair in the more hydrophobic HTAB micellar surface as well as (2) heavy-atom effects on the intersystem crossing from the singlet amidyl-benzoyloxyl radical pair to the triplet one. Based on the quantum yields for the triplet-sensitized photolysis of **1** in HTAC–HTAB mixed micelles, it was demonstrated that the hydrogen-bonding solvation described above plays a major role in suppressing the benzoyloxy photorearrangement reaction in the HTAB micelle cage.

The most important property of compartmentalized liquids, such as micelles, is that they have an ability to concentrate guest molecules into relatively small effective volumes and then to promote the re-encounter of such molecules.[1] This property also makes micelles a good device for inducing an efficient cage reaction of a hydrophobic triplet radical pair (which is produced photochemically) as the result of a significant decrease in the rate of escape of the radical pair from the micelle cage.[2] It is of great value to find out the factors that control the behavior and reactivity of a given reaction partner in micelles because such factors may enable us to prepare a reaction device of high selectivity and efficiency.

Since we published the first paper on the direct and triplet-sensitized photolyses of *N*,*O*-diacyl-*N*-phenylhydroxylamines,[3] we have continued to systematically investigate the mechanism of these photodecomposition reactions, including acyloxy photomigration.[4—9] One interesting and important finding is that the aroyloxyl radical generated by an energy-transfer mechanism undergoes extensive decarboxylation, giving aromatic hydrocarbon, (in competition with hydrogen abstraction forming aromatic carboxylic acid,) whereas there is negligible decarboxylation of the aroyloxyl radical obtained through an electron transfer from triplet sensitizers.[5] In addition, a quantitative analysis of the solvent effects on the intramolecular triplet-sensitized photolysis of *N*,*O*-diacylhydroxylamine having the benzophenone moiety shows that the benzoyl-substituted benzoyloxyl radical formed in aprotic solvent affords its decarboxylation product exclusively and then, in a solvent of great hydrogen-bonding solvation ability, both the hydrogen abstraction and decarboxylation of this radical occurs in comparable quantum yields.[9] A comparison of the quantum yields and rate constants for the hydrogen abstraction and decarboxylation of aroyloxyl radicals obtained by the direct photolysis in protic and aprotic solvents confirmed that there is a minor difference in reactivity toward the hydrogen abstraction between these two solvents,[3,7] and additionally that the relative rate for hydrogen abstraction is much greater than that for decarboxylation.[5] Thus, the occurrence of pronounced decarboxylation of the triplet-derived aroyloxyl radicals in aprotic solvents cannot be explained in terms of solvent effects on the rate of decarboxylation relative to hydrogen abstraction, leading us to propose the vibrationally excited (hot) triplet radical pair, the deactivation of which is markedly promoted (by forming hydrogen bonds to protic solvents) to eventually give the hydrogen-abstraction product.[9]

There has been only a limited study toward controlling the reactivities of radicals generated within the micelle supercage where polarity, viscosity, electrostatic, and hydrophobic interactions as well as hydrogen-bonding solvation may play critical roles in determining these reactivities.[2a,2b] In addition, the fact that we are able to generate both the triplet amidyl-aryl and amidyl-aroyloxyl radical pairs through the triplet-sensitized photolysis of the model *N,O*-diacylhydroxylamine in the micelle cage stimulated us to scrutinize cationic micellar effects on the behavior and reactivity of these two radical pairs.[10] *O*-Benzoyl-*N*-(1-naphthoyl)-*N*-phenylhydroxylamine (**1**, Chart 1) was chosen as the starting *N,O*-diacylhydroxylamine in the present study for the easy preparation of authentic samples for the aryl-rearranged products as well as for the high triplet energy-transfer efficiency between benzophenone (BP) and this type of hydroxylamine.[3b] In this paper we present results that demonstrate that the starting **1** in hexadecyltrimethylammonium chloride (HTAC) or hexadecyltrimethylammonium bromide (HTAB) containing BP undergoes a novel photorearrangement, and that both the product distribution and composition (derived from triplet **1** in homogeneous solutions) can be dramatically controlled by utilizing micelle supercages and their counter ions.

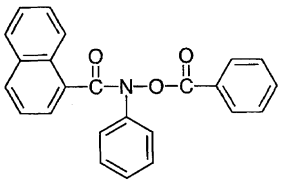

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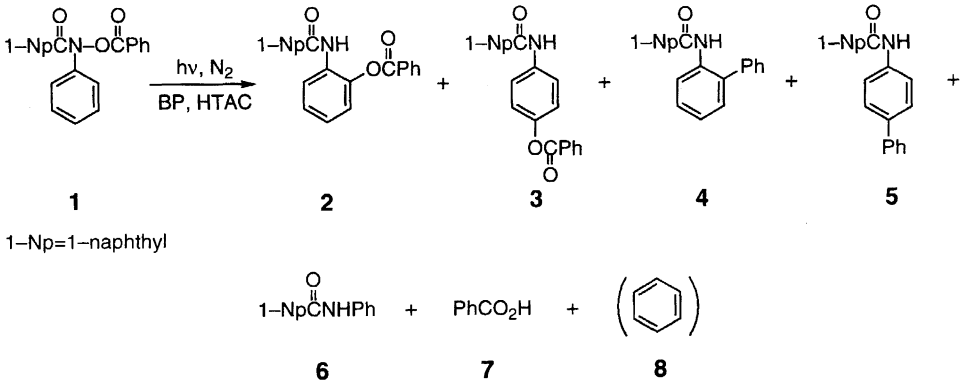
Chart 1.

Results and Discussion

BP-Sensitized and Direct Photolyses in HTAC Micelles. Upon the irradiation of a nitrogen-purged aqueous solution of **1** (1.0×10^{-3} M; 1 M = 1 mol dm^{-3}) with 366 nm light in the presence of BP (2.0×10^{-2} M) and HTAC (0.10 M) at room temperature, six new HPLC signals were detected on the chromatogram, while the signal area of BP remained constant during the irradiation. A comparison of the HPLC behavior for the products with that for independently prepared authentic samples under various analytical conditions revealed that the BP-sensitized reaction of **1** in HTAC micelles results in the formation of the benzoyloxy(**2** and **3**)- and the phenyl(**4** and **5**)-migrated products along with the fragmentation products **6** and **7** (Scheme 1). The fact that the irradiation of a 1,2-dichloroethane or a methanol solution of **1** containing BP with 366 nm light under nitrogen gives only **6** and **7** demonstrates that the micelle cage exerts a dramatic effect upon the product distribution. In Table 1 are collected the quantum yields (Φ) for the BP-sensitized reactions in HTAC micelles, 1,2-dichloroethane, and methanol as well as for the direct photolysis with 313 nm light in this micellar phase. The quantum yields for the sensitized photolysis were independent of the HTAC concentration in the range of 0.075



Scheme 1.

Table 1. Quantum Yields for Disappearance of **1** (Φ_{-1}) and for Appearance of **2**—**7** ($\Phi_{2—7}$) at 25±3°C

Solvent	Φ_{-1}	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7
HTAC/H_2O[a]	0.300 ±0.012	0.100 ±0.007	0.051 ±0.006	0.024 ±0.002	0.020 ±0.002	0.093 ±0.006	0.081 ±0.007
MeOH[a]	0.302 ±0.012	0[c]	0	0	0	0.300 ±0.012	0.262 ±0.015
CH_2ClCH_2Cl[a]	0.647 ±0.042	0	0	0	0	0.623 ±0.035	0.139 ±0.011
HTAC/H_2O[b]	0.376 ±0.012	0.207 ±0.009	0.129 ±0.007	0	0	0	0

a) BP-sensitized photolysis with 366 nm light. b) Direct photolysis with 313 nm light. c) Zero means $\Phi < 0.001$.

to 0.125 M (data not shown), but its lower concentration ($\leq$ 0.050 M) made it very difficult to accurately estimate the Φ value because of the appearance of turbidity. On the other hand, quenching of the room-temperature phosphorescence of BP by **1** approximately obeyed the Stern–Volmer equation to give a quenching constant of 0.6×10^3 M^{-1}, which is smaller than that (1.3×10^3 M^{-1}) in 1,2-dichloroethane (viscosity at 30 °C, η_{30} = 0.730 mPa s; relative permittivity at 25 °C, ϵ_{25} = 10.37)[11] by a factor of about 2 (Fig. 1). This substantiates the occurrence of a sensitized reaction from triplet **1** produced by triplet–triplet energy transfer also in the HTAC micellar phase. In a previous study,[3b] it was found that the phosphorescence quenching of BP proceeds more efficiently in acetonitrile (η_{30} = 0.324 mPa s; ϵ_{25} = 35.94)[11] than in 1,2-dichloroethane. Since the cationic micellar phase has a polarity near to that of ethanol (ϵ_{25} = 24.55),[11,2c] the lower quenching efficiency observed in the HTAC micellar phase may be due to the high intramicellar viscosity (η_{30} = 18 mPa s)[12] rather than the relatively high polarity of this phase.

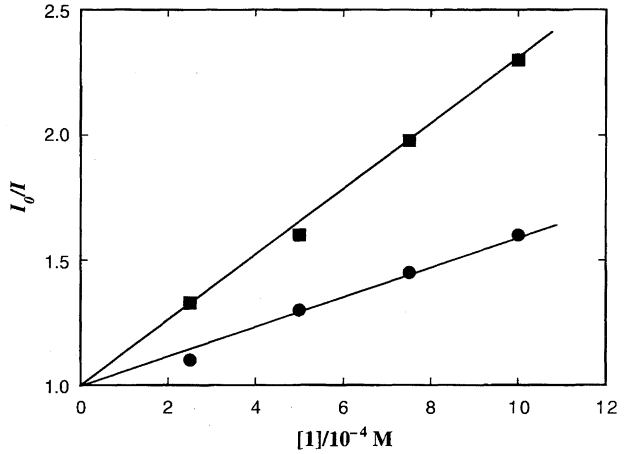


Fig. 1. Stern–Volmer plots for the phosphorescence quenching of BP (2.0×10^{-2} M) by **1** in nitrogen-saturated HTAC (0.10 M) micelles (●) and 1,2-dichloroethane (■) at room temperature. Excitation wavelength is 366 nm and I and I_0 refer to the phosphorescence intensities of BP with and without **1**, respectively.

As already described in the introduction, the previous study[9] allows us to assume that the decarboxylation of the triplet-derived benzoyloxyl radical occurs from the hot triplet radical pair ^{3}[1-NpC(=O)N(Ph)···OC(=O)Ph]‡, the hydrogen-bonding solvation of which promotes deactivation of this pair to eventually afford **6** and **7** in comparable quantum yields. The application of this assumption to the results obtained in 1,2-dichloroethane and methanol shows that the reaction in the former solvent takes place mainly via the decarboxylation [; benzene (**8**) could be detected by GLC] while in the latter solvent the vibrationally relaxed radical pair also participates in the reaction. Thus, the observation of a larger Φ value for the formation of the benzoyloxyl radical-derived products ($\Phi_2+\Phi_3+\Phi_7$ = 0.232) than that of the phenyl radical-derived products ($\Phi_4+\Phi_5+\Phi_6-\Phi_7$ = 0.056) in HTAC micelles is consistent with the occurrence of the hydrogen-bonding solvation described above. Because some water molecules may be entrapped by the micelle and exist mainly at the micellar surface,[1] both **1** and BP are deemed to be incorporated into the surface (Fig. 2).

It is very likely that the hot radical pair ^{3}[1-NpC(=O)-N(Ph)···OC(=O)Ph]‡ simultaneously generates the amidyl-benzoyloxyl and the amidyl-phenyl radical pairs also in the micelle cage. The hydrophobicity of these radicals as well as the high intramicellar viscosity markedly reduces the rate of escape of the radical pairs from the micelle cage relative to the rate of intersystem crossing to the singlet pairs, thereby causing efficient geminate recombination, which is responsible for the appearance of **2**—**5**. An inspection of Table 1 clearly indicates the exclusive formation of the 1,3-(**2**)- and the 1,5(**3**)-benzoyloxy migrated products on irradiation of a micellar solution of **1** with 313 nm light, being

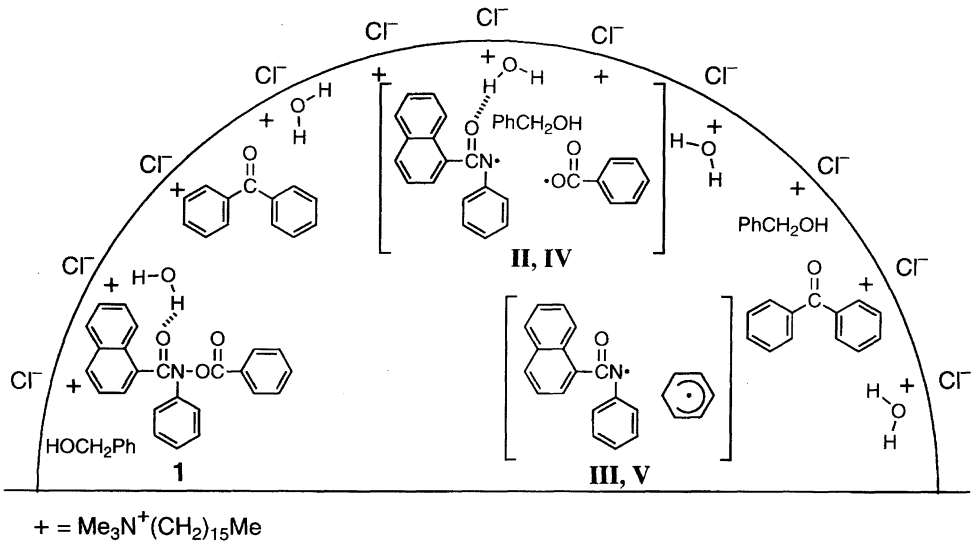


Fig. 2. Schematic illustration of the staring **1** and BP solubilized in the HTAC micellar surface and of the radical pairs **II**—**V** generated in HTAC micelles containing benzyl alcohol.

consistent with the previous finding that the direct photolysis of *N,O*-diacyl-*N*-phenylhydroxylamines occurs predominantly from the first excited singlet state and then affords only acyloxy-rearranged products in HTAC micelles.[3] Even trace amounts of the fragmentation products **6** and **7** could not be detected, showing the much slower rate of escape of the singlet amidyl–benzoyloxyl radical pair from the micelle cage relative to the rate of the geminate recombination forming **2** and **3**.

Effects of Added Alcohols on the Reaction Efficiency in HTAC Micelles. Since the triplet-sensitized reaction of **1** in the HTAC micelle cage was found to cause fragmentation of the initially-formed radical pair, in contrast to direct photolysis in this micelle cage, it is an important issue to elucidate the origin of **6** and **7**. In order to determine whether these two fragments are produced in the micellar phase or in the aqueous phase, we examined the effects of added alcohols on the quantum yields for the sensitized reaction (Table 2). Evidently, the enhanced hydrophobicity of the alcohol has a marked tendency to decrease the quantum yields for the acyloxy-rearranged products (Φ_2 and Φ_3) with an increase in those for the fragmentation (Φ_6 and Φ_7). In addition, quantum yields for the disappearance of the starting **1** (Φ_{-1}) and for the appearance of phenyl-migrated products (Φ_4 and Φ_5) are subject to the effects of hydrophobic alcohols, if any, to only a minor extent.

In Fig. 3 is typically shown the dependence of the quantum yields Φ_{-1} and Φ_{2-7} on the concentration of benzyl alcohol, which is the most hydrophobic of the alcohols examined. This alcohol must be largely accommodated into the micellar aggregate. Furthermore, the direct photolysis of **1** in HTAC micelles (which affords a singlet radical pair exclusively) gave only rearrangement products **2** and **3**.[3] Thus, the finding that an increase in the alcohol concentration enhances Φ_6 and Φ_7 accompanied by a decrease in Φ_2 and Φ_3 leads us to conclude that the hydrogen abstraction of the amidyl and benzoyloxyl radicals takes place in competition with a spin inversion of these triplet radicals in the micellar phase. Supporting evidence for this conclusion comes from

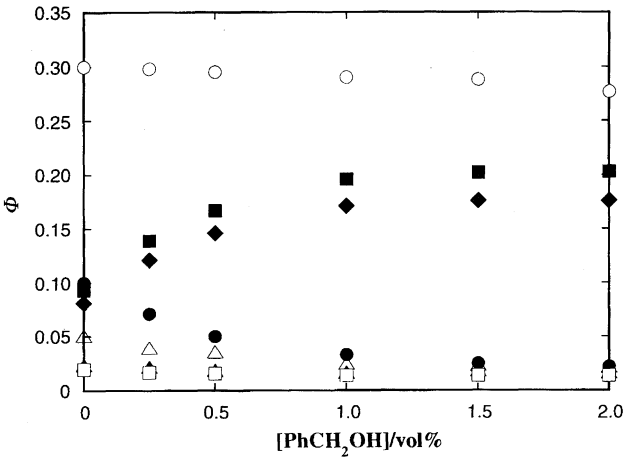


Fig. 3. Quantum yields for disappearance of **1** (○) and for appearance of **2** (●), **3** (△), **4** (▲), **5** (□), **6** (■), and **7** (◆) in the BP (2.0×10^{-2} M)-sensitized photolysis of **1** (1.0×10^{-3} M) in nitrogen-purged HTAC (0.10 M) micelles at 25±3 °C, as a function of the concentration of benzy alcohol. The HTAC micellar solution is irradiated with 366 nm light.

Table 2. Quantum Yields for the BP (2.0×10^{-2} M)-Sensitized Photolysis of **1** (Φ_{-1} and Φ_{2-7}; [**1**] = 1.0×10^{-3} M) in HTAC Micelles ([HTAC] = 0.10 M) Containing 2 vol% of Alcohl as Well as in HTAC–HTAB Mixed Micelles ([HTAC]+[HTAB] = 0.10 M) at 25±3 °C

Solvent	HTAC/HTAB (mol/mol)	cmc/10^{-3} M	Φ_{-1}	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7
H_2O	10/0	1.3	0.300 ±0.012	0.100 ±0.007	0.051 ±0.006	0.024 ±0.002	0.020 ±0.002	0.093 ±0.006	0.081 ±0.007
H_2O–2-PrOH[a]	10/0		0.272	0.067	0.041	0.023	0.017	0.115	0.100
H_2O–BuOH[a]	10/0		0.269	0.040	0.036	0.018	0.017	0.152	0.132
H_2O–$PhCH_2OH$[a]	10/0	0.3	0.277	0.022	0.022	0.017	0.014	0.203	0.176
H_2O	9/1		0.297 ±0.015	0.093 ±0.007	0.046 ±0.003	0.028 ±0.002	0.029 ±0.002	0.096 ±0.006	0.084 ±0.005
H_2O	7/3	1.1	0.291 ±0.013	0.071 ±0.004	0.037 ±0.003	0.034 ±0.003	0.046 ±0.004	0.100 ±0.008	0.088 ±0.007
H_2O	5/5		0.293 ±0.014	0.051 ±0.003	0.026 ±0.002	0.038 ±0.002	0.061 ±0.004	0.113 ±0.008	0.092 ±0.006
H_2O	3/7	0.8	0.291 ±0.016	0.028 ±0.002	0.012 ±0.002	0.042 ±0.003	0.081 ±0.006	0.118 ±0.008	0.099 ±0.006
H_2O	1/9		0.291 ±0.015	0.011 ±0.002	0.005 ±0.001	0.047 ±0.004	0.097 ±0.006	0.122 ±0.010	0.104 ±0.008
H_2O	0/10	0.6	0.290 ±0.017	0[b]	0[b]	0.050 ±0.004	0.102 ±0.005	0.126 ±0.010	0.110 ±0.008

a) Standard deviation of all the quantum yields is less than or nearly equal to 10%. b) Zero means $\Phi < 0.001$.

the detection of benzaldehyde (the concentration of which is comparable to that of the anilide **6** at a given irradiation time) as the alcohol-derived product. Taking into account the fact that spin correlation is lost for caged radical pairs formed by re-encounter of free radicals,[13] we were led to propose Scheme 2 based on these considerations. The existence of benzyl alcohol in the micellar phase may not only increase the proportion of the solvent-separated radical pair relative to that of the contact radical pair, but also accelerate the hydrogen abstraction within the former radical pair. We previously demonstrated that 1,5-acyloxy migration takes place preferentially within a solvent-separated radical pair.[3] Accordingly, the above interpretation is substantiated by our finding that the relative quantum yield of Φ_3 to Φ_2 is increased by a factor of about 2 in the presence of HTAC containing 2.0 vol% of benzyl alcohol (Table 2).

On the other hand, Φ_4 and Φ_5 are subject to the negligible effect of added benzyl alcohol (Fig. 3). Since the alcohol is considered to largely exist at the micellar surface, this implies that the triplet (**III**) and singlet (**V**) amidyl–phenyl radical pairs are more deeply buried in the micellar interior, as schematically depicted in Fig. 2. The less polar and more hydrophobic character of the amidyl–phenyl radical pair, compared with the amidyl–benzoyloxyl, might be responsible for the deeper penetration of the former radical pair.

Effects of Added Benzyl Alcohol on the HTAC Micellar Properties. We have so far discussed the effect of benzyl alcohol on the quantum yields for the BP-sensitized photolysis in HTAC micelles on the assumption that this alcohol exerts a negligible effect on the micellar size and shape, which may be estimated through an analysis of the critical micelle concentration (cmc) and aggregation number (N_A) for HTAC surfactant. First, we determined the cmc values for HTAC in the presence of benzyl alcohol by examining the dependence of the fluorescence intensity of 1,6-diphenyl-1,3,5-hexatriene as a probe on the HTAC concentration.[14] As shown in Fig. 4, there is a distinct decrease in the cmc value when the alcohol

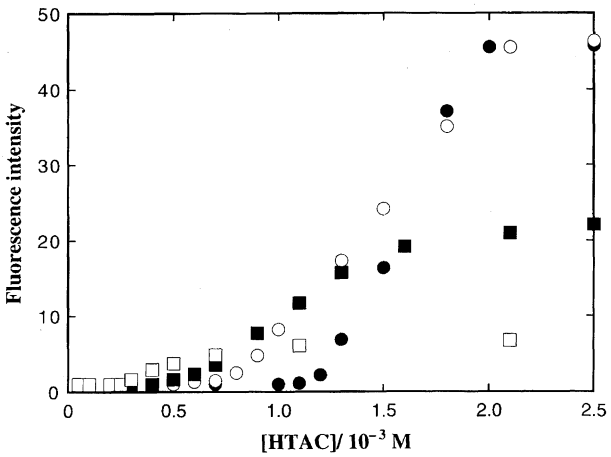
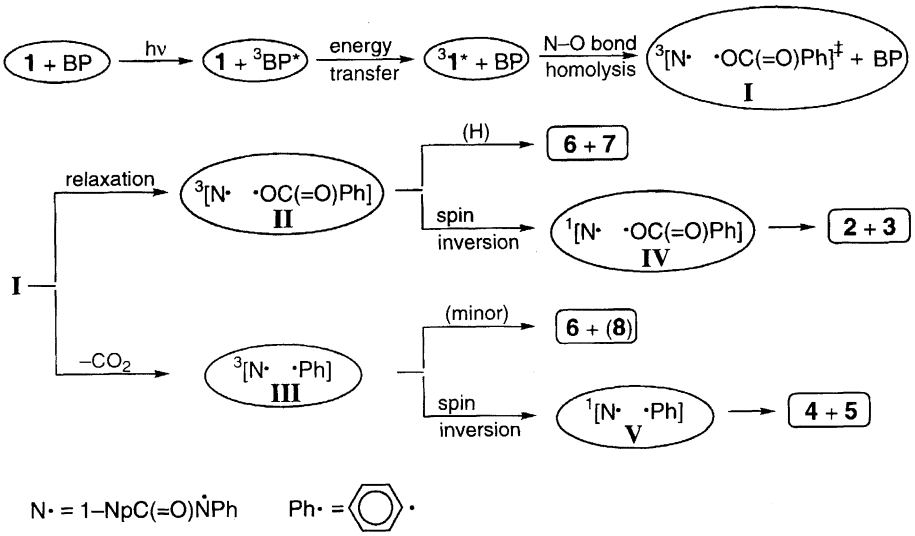


Fig. 4. Dependence of the fluorescence intensity of 1,6-diphenyl-1,3,5-hexatriene (4.0×10^{-6} M) on the HTAC concentration in the absence (●) and presence (○: 0.5; ■: 1.0; □: 2.0 vol%) of benzyl alcohol under nitrogen at 24±1 °C. Excitation wavelength is 360 nm.

concentration is increased [cmc = 1.3×10^{-3} (1.4×10^{-3}),[15] 0.8×10^{-3}, 0.6×10^{-3}, and 0.3×10^{-3} M at [$PhCH_2OH$] = 0, 0.5, 1.0, and 2.0 vol%, respectively], verifying that the increased alcohol concentration accelerates the HTAC micelle formation to a more extent and, hence, this hydrophobic alcohol is undoubtedly penetrated into the micellar interior. The observation that the fluorescence intensity of our probe is decreased with increasing the alcohol concentration may reflect an alteration in environment around the probe from hydrophobic to hydrophilic, being also consistent with the existence of added alcohol in HTAC micelles.

We now attempted to evaluate the N_A value for HTAC according to a method which employs the fluorescence quenching of pyrene by 5-doxylstearic acid in HTAC micelles containing 0—1 vol% of benzyl alcohol.[16] The application of Eq. 1[17] to the linear plots shown in Fig. 5 allowed us to estimate the N_A values as 110 (93±7,[16] 113;[18] [$PhCH_2OH$] = 0 vol%), 100 (0.5 vol%), and 92 (1.0 vol%):



Scheme 2.

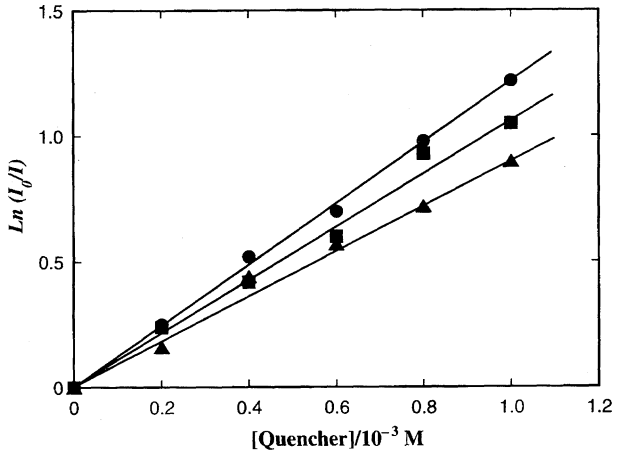


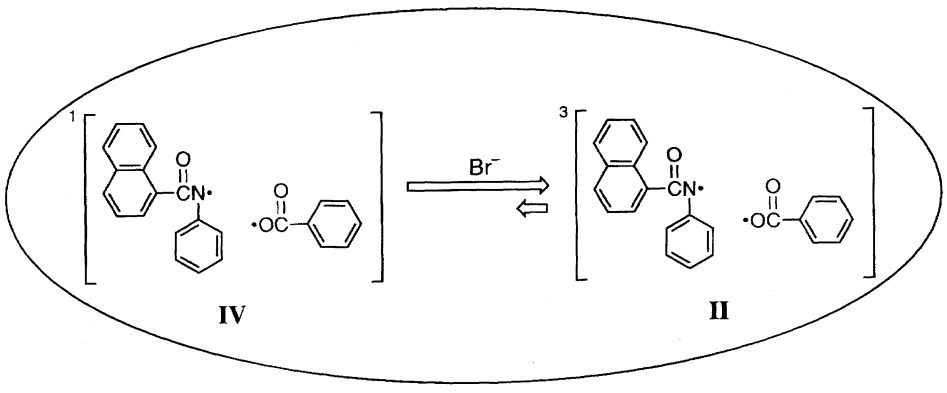
Fig. 5. Relationship between Ln (I_0/I) and the concentration of 5-doxylstearic acid (as a quencher) for the fluorescence quenching of pyrene (10^{-5} M) in nitrogen-saturated HTAC (0.10 M) micelles containing benzyl alcohol (●: 0; ■: 0.5; ▲: 1.0 vol%) at 24±1 °C. Excitation wavelength is 340 nm and I and I_0 refer to the fluorescence intensities of pyrene with and without the quencher, respectively.

$$N_A = ([HTAC] - cmc)/[M], \quad [M] = [Q]/Ln(I_0/I), \quad (1)$$

where [Q] is the concentration of 5-doxylstearic acid as a quencher and I and I_0 are the fluorescence intensities of pyrene with and without Q, respectively. Taking into account the experimental error of this method, we were led to conclude that added benzyl alcohol exerts only a minor effect on the HTAC micellar size, although there is a clear tendency for the size to be slightly reduced in the presence of the additive.

BP-Sensitized and Direct Photolyses in HTAB and HTAC–HTAB Mixed Micelles. It was recently found that the photochemically-generated triplet radical pair undergoes heavy-atom effects to promote intersystem crossing into the singlet radical pair.[6,13,19] Since the BP-sensitized photolysis of **1** in HTAB micelles is also very likely to occur at the micellar surface, it is expected that the bromide ion (Br^-) as a counter exerts its heavy-atom effect on the intersystem crossing process between triplet and singlet radical pairs.[20] Interestingly, the triplet-sensitized reaction of **1** (1.0×10^{-3} M) in HTAB (0.10 M) micelles with 366 nm light produced only **4**—**7** without forming the benzoyloxy-migrated products **2** and **3** ($\Phi_{-1} = 0.290\pm0.017$; $\Phi_4 = 0.050\pm0.004$; $\Phi_5 = 0.102\pm0.005$; $\Phi_6 = 0.126\pm0.010$; $\Phi_7 = 0.110\pm0.008$). The finding that more hydrophobic Br^- (compared with chloride ion) lowers the water concentration at the micellar interface to greatly suppress water penetration into micelles[21] provides a good explanation for the 2—5-fold increase in the Φ_4 and Φ_5 values for the reaction in HTAB micelles as compared to that in HTAC. In other words, less effective hydrogen-bonding solvation of the hot radical pair **I** in the HTAB micellar surface results in a more efficient decarboxylation within **I** to eventually give **4** and **5** in larger quantum yields, as observed (Scheme 2). On the other hand, no occurrence of an acyloxy photorearrangement in HTAB micelles reflects heavy-atom effects on the efficiency of intersystem crossing between spin-correlated radical pairs. If the intersystem crossing from **II** to **IV** undergoes heavy-atom effects, we should expect to observe increased Φ_2 and Φ_3 with decreased Φ_6 and Φ_7, upon sensitized photolysis in the HTAB micelle cage. The obtained result is not consistent with our expectation. Because hydrogen abstraction in **II** (that yields **6** and **7**) may compete with the intersystem crossing to **IV**, the benzoyloxy-migrated products should be formed in negligible quantum yields, provided that the opposite process **IV**→**II** is subject to pronounced heavy-atom effects. The presence of Br^- at the interface is, therefore, concluded to accelerate the intersystem crossing **IV**→**II** to a much larger extent than its reverse process (Scheme 3). A similar heavy-atom effect was not observed for either Φ_4 or Φ_5, substantiating a deeper penetration of the radical pairs **III** and **V** into the micellar interior as already described.

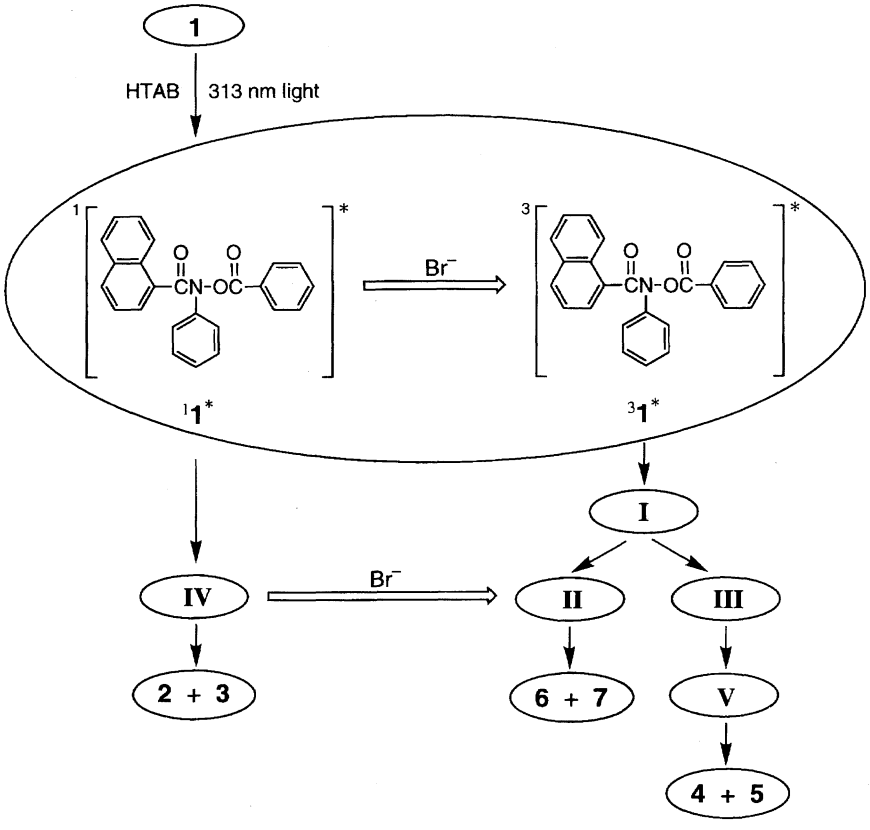
The fact that the direct photolysis of **1** and related *N,O*-diacylhydroxylamines generates exclusively singlet radical pairs in the HTAC micelle cage makes it possible to anticipate that the photoreaction of **1** in HTAB containing no sensitizer gives substantial amounts of the fragmentation products **6** and **7** in addition to the rearrangement products **2** and **3**, by enhancing the rate of intersystem crossing **IV**→**II** through the heavy-atom effect. Irradiation of a HTAB (0.10 M) micellar solution of **1** (1.0×10^{-3} M; $\Phi_{-1} = 0.277\pm0.008$) with 313 nm light afforded **6** and **7** ($\Phi_6 = 0.034\pm0.004$, $\Phi_7 = 0.030\pm0.004$) along with **2** and **3** ($\Phi_2 = 0.126\pm0.005$,



Scheme 3.

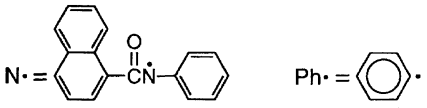
$\Phi_3 = 0.060 \pm 0.003$) as expected, but the phenyl-rearranged products **4** and **5** ($\Phi_4 = 0.015 \pm 0.001$, $\Phi_5 = 0.012 \pm 0.001$) were also obtained at the same time. While we failed in producing exclusively the singlet amidyl-benzoyloxyl radical pair in HTAB micelles, the detectable formation of **4** and **5** strongly suggests that both the excited singlet-state **1** and the singlet radical pair (which is formed by the direct photolysis) are subject to heavy-atom effects, as depicted in Scheme 4.

It is worthwhile to explore the effects of HTAC–HTAB mixed micelles on the product distribution and composition obtained by the BP-sensitized reaction of the starting hydroxylamine **1**, since these two micelles possess comparable cmc [1.4×10^{-3} M (HTAC);[15] 0.8×10^{-3} M (HTAB)[22]] and N_A [93 (HTAC);[16] 92 (HTAB)[22]] values and, hence, are of similar size. In Table 2 are collected quantum yields (for the sensitized reaction in the mixed micelle cage) and cmc values as a function of the HTAB concentration. The linear relationship between the cmc and the mole fraction of HTAB (data not shown) indicates the formation of nearly ideal mixed micelles without abruptly changing their structure, being reflected in a smooth increase in $\Phi_{4\text{—}7}$ and a decrease in Φ_2 and Φ_3 with the HTAB concentration, of which Φ_{-1} is independent. Interestingly, the replacement of the HTAC micelle cage by the HTAB reduces quantum yield ($\Phi_2 + \Phi_3$) for the benzoyloxy migration by 0.151, the value of which is approximately equal to the sum of increments of the quantum yields for the phenyl migration ($\Phi_4 + \Phi_5$: +0.108) and the fragmentation (Φ_6: +0.033). As already described, the former increment should be attributed to the appreciably weakened hydrogen-bonding solvation of the hot radical pair **I** (Scheme 2) in the HTAB micellar surface, while heavy-atom (Br^-) effects on the spin inversion process **IV**→**II** must contribute to the latter increment. Thus, much less effective hydrogen-bonding solvation of the assumed intermediate **I** in the HTAB micellar surface than in the HTAC plays a major role in causing benzoyloxy photomigration in negligible quantum yields in the former micelles (Fig. 6). A careful inspection of Table 2 shows that the quantum-yield ratio Φ_3/Φ_2 is maintained nearly constant irrespective of the HTAB mole fraction, suggesting the great similarity of the amidyl–benzoyloxyl radical pair structure in HTAC micelles to that in HTAB. In contrast, the ratio Φ_5/Φ_4 is increased by



I= ^{3}[N· ·OC(=O)Ph]‡ **II**= ^{3}[N· ·OC(=O)Ph]

III= ^{3}[N· ·Ph] **IV**= ^{1}[N· ·OC(=O)Ph] **V**= ^{1}[N· ·Ph]



Scheme 4.

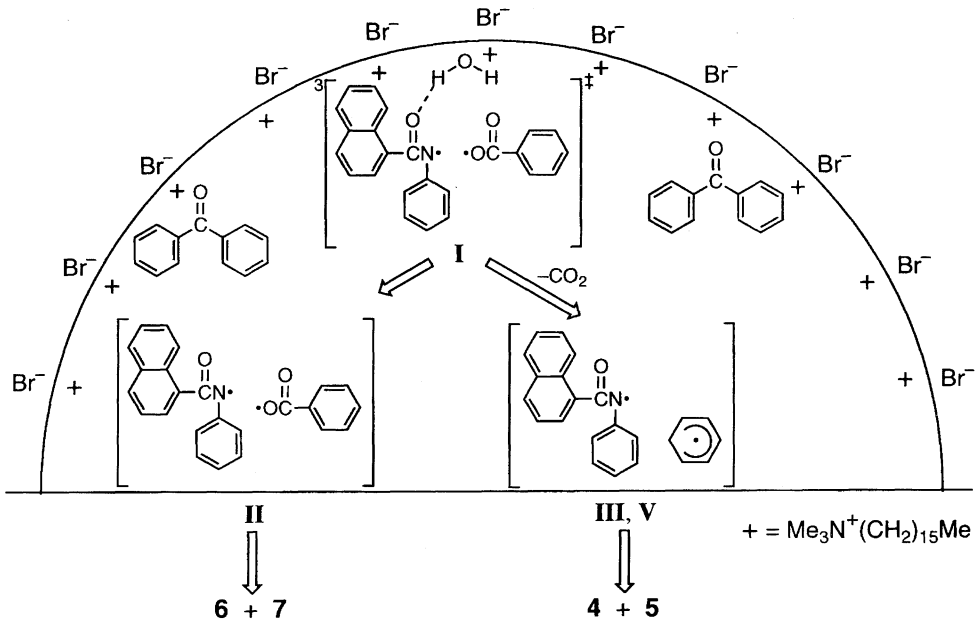


Fig. 6. Schematic illustration for the decarboxylation and relaxation processes of the hot amidyl–benzoyloxyl radical pair **I** [that eventually lead to the phenyl-migrated (**4** and **5**) and fragmentation (**6** and **7**) products] formed in the HTAB micellar surface.

a factor of 2—3 with an increase in the HTAB mole fraction. In a previous study,[3] we obtained a piece of evidence in support of the recombination of the amidyl-aroyloxyl radical pair that gives the starting hydroxylamine in addition to aroyloxy-rearranged products. No observation of the recombination product, *N*-(1-naphthoyl)diphenylamine, derived from the amidyl–phenyl radical pair, therefore, implies a great difference in structure between these two radical pairs. Taking into account that the amidyl–phenyl radical pairs **III** and **V** are more deeply penetrated into the micellar interior as compared to the radical pairs **II** and **IV** (Fig. 2), we were led to presume that HTAB micelles of more hydrophobic surface alters a microscopic environment around the former radical pairs in the micellar interior so as to enhance the relative quantum yield of Φ_5 to Φ_4.

Experimental

General Methods. HPLC analyses of the photoproducts were performed on a Shimadzu Model LC-6A high-performance liquid chromatography system equipped with a 4.6×250-mm ODS (Zorbax) column and a Shimadzu Model SPD-2A UV detector (detection wavelength = 240 nm; mobile phase, MeCN : H_2O = 65 : 35 v/v). Fluorescence and phosphorescence spectra at room temperature were measured under nitrogen with a Shimadzu Model RF-5000 spectrofluorimeter. A GLC analysis was carried out on a Shimadzu Model GC-8AP gas chromatograph using 10% Silicone SE-30 on Uniport B (60—80 mesh, Gasukuro Kogyo). UV and IR spectra were taken at room temperature with a Shimadzu Model UV-2200 spectrophotometer and a Hitachi Model 270-30 infrared spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were recorded using tetramethylsilane as an internal standard on a JEOL Model JNM-500 or a JEOL Model EX-270 spectrometer. Elemental analyses were performed on a Perkin–Elmer PE2400 series II CHNS/O analyzer.

Materials and Solvents. *N*-Phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc dust in water containing ammonium chloride.[23] The crude hydroxylamine was used without further purification. The reaction of 1-naphthoyl chloride with two molar amounts of *N*-phenylhydroxylamine in ice-cold ether-dichloromethane gave *N*-(1-naphthoyl)-*N*-phenylhydroxylamine which was recrystallized from ethyl acetate-hexane, mp 128.0—129.5 °C (lit, 129.0—130.0 °C).[3] *O*-Benzoyl-*N*-(1-naphthoyl)-*N*-phenylhydroxylamine (**1**) as the starting material was obtained by *O*-acylation of *N*-(1-naphthoyl)-*N*-phenylhydroxylamine with benzoyl chloride in dichloromethane containing pyridine. Recrystallization of the crude **1** from ethanol afforded colorless crystals of analytical grade. Similar *N*- and *O*-acylation procedures were applied to the preparation of authentic samples for the benzoyloxy- and phenyl-migrated products, starting with the corresponding aminophenol and aminobiphenyl, respectively. These authentic samples were purified by repeated recrystallization from ethanol. The reaction between diphenylamine and 1-naphthoyl chloride in dimethyl sulfoxide containing 1,8-diazabicyclo[5.4.0]undec-7-ene at room temperature allowed us to obtain an authentic sample, *N*-(1-naphthoyl)diphenylamine, which was recrystallized from hexane–ethyl acetate as one of the recombination products of the amidyl–phenyl radical pair. The physical and spectroscopic properties of the starting **1** and each authentic sample are as follows.

***O*-Benzoyl-*N*-(1-naphthoyl)-*N*-phenylhydroxylamine (1).** Mp 135.0—136.5 °C; IR (KBr) 1750 and 1680 cm^{-1}; ^{1}H NMR (270 MHz; $CDCl_3$) δ = 7.15—7.66 (12H, m), 7.79 (2H, dd, J = 8.4, 8.4 Hz), 8.03 (2H, d, J = 8.4 Hz), and 8.39 (1H, d, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 124.49, 125.35, 126.22, 126.41, 126.84, 127.31, 128.25, 128.41, 128.61, 128.98, 130.08, 130.19, 130.33, 131.89, 133.33, 134.10, 139.75, 164.18, and 166.39. Found: C, 78.36; H, 4.36; N, 3.91%. Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81%.

2-(1-Naphthoylamino)phenol. Mp 181.0—182.0 °C; IR (KBr) 3410, 3110, and 1640 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) δ = 6.94 (1H, dd, J = 7.3, 7.9 Hz), 7.12 (1H, d, J = 7.3 Hz), 7.16 (1H, d, J = 7.9 Hz), 7.21 (1H, dd, J = 7.3, 8.2 Hz), 7.53—7.64 (3H, m), 7.82 (1H, d, J = 7.3 Hz), 7.93 (1H, d, J = 7.9 Hz), 7.97 (1H, s), 8.02 (1H, d, J = 8.2 Hz), 8.38 (1H, d, J = 8.2 Hz), and 8.70 (1H, s). Found: C, 77.35; H, 5.28; N, 5.13%. Calcd for $C_{17}H_{13}NO_2$: C,

77.55; H, 4.98; N, 5.32%.

4-(1-Naphthoylamino)phenol. Mp 200.5—201.0 °C; IR (KBr) 3210 and 1610 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) δ = 6.88 (2H, d, J = 8.2 Hz), 7.47—7.59 (7H, m), 7.74 (1H, d, J = 7.3 Hz), 7.90 (1H, d, J = 7.3 Hz), 7.97 (1H, d, J = 8.2 Hz), and 8.38 (1H, d, J = 8.2 Hz). Found: C, 77.45; H, 5.12; N, 5.02%. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32%.

2-(1-Naphthoylamino)phenyl Benzoate (2). Mp 150.0—151.5 °C; IR (KBr) 3220, 1740, and 1650 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) δ = 7.28 (1H, d, J = 8.2 Hz), 7.32 (1H, d, J = 7.3 Hz), 7.40—7.50 (6H, m), 7.63 (1H, dd, J = 7.3, 7.6 Hz), 7.68 (1H, d, J = 8.2 Hz), 7.85 (2H, d, J = 7.6 Hz), 7.92 (1H, d, J = 8.2 Hz), 8.15 (2H, d, J = 7.3 Hz), 8.36 (1H, d, J = 8.2 Hz), and 8.46 (1H, br s). Found: C, 78.28; H, 4.73; N, 3.53%. Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81%.

4-(1-Naphthoylamino)phenyl Benzoate (3). Mp 170.0—172.0 °C; IR (KBr) 3310, 1735, and 1650 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) δ = 7.27 (2H, d, J = 8.2 Hz), 7.51—7.67 (6H, m), 7.75—7.78 (4H, m), 7.92 (1H, d, J = 8.2 Hz), 7.99 (1H, d, J = 8.2 Hz), 8.22 (2H, d, J = 8.2 Hz), and 8.38 (1H, d, J = 8.2 Hz). Found: C, 78.34; H, 4.77; N, 3.60%. Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81%.

***N*-(1-Naphthoyl)-2-biphenylamine (4).** Mp 140.0—141.0 °C; IR (KBr) 3200 and 1640 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) δ = 7.25—7.54 (12H, m), 7.74 (1H, br s), 7.84 (1H, d, J = 8.2 Hz), 7.88 (1H, d, J = 8.2 Hz), 8.33 (1H, d, J = 8.2 Hz), and 8.57 (1H, d, J = 8.2 Hz). Found: C, 85.60; H, 5.41; N, 4.08%. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33%.

***N*-(1-Naphthoyl)-4-biphenylamine (5).** Mp 105.5—107.0 °C; IR (KBr) 3400 and 1680 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) δ = 7.26—7.73 (12H, m), 7.78 (1H, br s), 7.95 (1H, d, J = 8.2 Hz), 8.15 (1H, d, J = 8.2 Hz), 8.44 (1H, d, J = 8.2 Hz), and 9.14 (1H, d, J = 8.2 Hz). Found: C, 85.16; H, 5.04; N, 4.40%. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33%.

***N*-(1-Naphthoyl)diphenylamine.** Mp 80.0—81.0 °C; IR (KBr) 1665 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ = 7.51—7.70 (9H, m), 7.91 (2H, d, J = 7.9 Hz), 8.09 (2H, d, J = 8.2 Hz), 8.42 (2H, d, J = 8.2 Hz), and 9.10 (2H, d, J = 8.2 Hz). Found: C, 85.28; H, 5.50; N, 4.44%. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33%.

1-Naphthanilide (**6**) was used after the previously-prepared **6** was recrystallized from ethyl acetate.[3] Purified benzoic acid (**7**) and benzophenone (BP) were obtained by repeated recrystallization from aqueous ethanol. Benzene (**8**), dichloromethane, and 1, 2-dichloroethane were of spectroscopic grade and were used as received. Methanol was purified according to a standard method.[11] Hexadecyltrimethylammonium chloride (HTAC) and hexadecyltrimethylammonium bromide (HTAB) were repeatedly recrystallized from acetone–methanol. Distilled acetonitrile and water were employed as a mobile phase for the HPLC analysis. All other chemicals used were obtained from commercial sources and were of the highest grade available.

Measurements. A potassium tris(oxalato)ferrate(III) actinometer was employed to determine the quantum yields for the direct and BP-sensitized photolyses of **1** at its low conversion (<20%).[24] A 450 W high-pressure Hg lamp was used as the light source from which 313 nm light for the direct photolysis was isolated by means of a potassium chromate (2.0×10^{-3} M) in a 1.0 wt% aqueous solution of potassium carbonate and Corning 7-54 filters. The 366 nm light for the sensitized photolysis was selected from the same Hg lamp with Corning 0-52, Corning 7-60, and Toshiba IRA-25S glass filters. Given amounts of **1**, BP, and surfactant (HTAC or HTAB) were at first dissolved in dichloromethane (10 mL) and then the resulting solution was concentrated to dryness on a rotary evaporator. After the solvent was completely removed in vacuo, distilled water was added to the residual solid to solubilize **1** and BP into micelles by ultrasonic dispersal. Before irradiation of a nitrogen-purged micellar solution of **1** containing BP with 366 nm light, the solution was allowed to stand for 1—2 h at room temperature. Linear calibration curves for each compound, made under the same analytical conditions, were utilized to quantify both the disappearance of **1** and the appearance of **2**—**7**. Quantum yields for the BP-sensitized reaction in alcohol-containing micelles and for the direct photolysis were measured similarly. All of the quantum yields are an average of more than six determinations.

Critical micelle concentrations for HTAC and HTAB surfactants with and without benzyl alcohol were determined according to the method of De, Aswal, Goyal, and Bhattacharya, which employs the dependence of the fluorescence intensity of 1,6-diphenyl-1,3,5-hexatriene on the surfactant concentration.[14] The steady-state method of Szajdzinska-Pietek and Wolszczak (utilizing the quenching of pyrene fluorescence by the amphiphilic aminyl oxide radical, 5-doxylstearic acid,) was applied to an estimation of the HTAC micellar aggregation number in the presence and absence of benzyl alcohol.[16]

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