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Anionic Micellar Effects on the Benzophenone-sensitized Photolysis of *N*-(1-Naphthoyl)-*N*-phenyl-*O*-benzoylhydroxylamine

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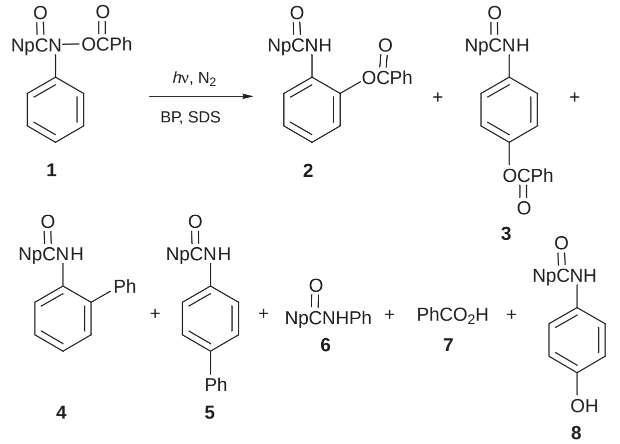
The title hydroxylamine in sodium dodecyl sulfate micelles containing benzophenone is subjected to photorearrangements giving benzoyloxy- and phenyl-migrated products along with fragmentation products; subsequent photohydrolysis of the 1,5-benzoyloxy-rearranged product proceeds selectively.

It is of great value to discover factors which control the behaviour and reactivity of a given reaction partner in micelles because such factors may enable the preparation of a reaction pathway of high selectivity and efficiency. Since we published the first paper on the direct and triplet-sensitized photolyses of *N,O*-diacyl-*N*-phenylhydroxylamines,[4] we have continued to systematically investigate the mechanism of these photodecomposition reactions including photoacyloxy migration.[5–10] One interesting and important finding is that the aroyloxyl radical generated by an energy-transfer mechanism undergoes extensive decarboxylation giving aromatic hydrocarbons (in competition with hydrogen abstraction forming aromatic carboxylic acids) whereas there is negligible decarboxylation of the aroyloxyl radical obtained *via* electron transfer from triplet sensitizers.[6] In addition, quantitative analysis of solvent effects on the direct and sensitized photolyses of *N,O*-diacylhydroxylamines led us to propose a vibrationally excited (hot) triplet radical pair, deactivation of which is markedly promoted (by forming hydrogen bonds to protic solvents) to eventually give the hydrogen abstraction product.[4,6,8,10] The finding that we are able to generate both the triplet amidyl–aryl and amidyl–aroyloxyl radical pairs through the triplet-sensitized photolysis of *N*-(1-naphthoyl)-*N*-phenyl-*O*-benzoylhydroxylamine **1** in a hexadecyltrimethylammonium chloride (HTAC) micelle cage stimulated us to scrutinize anionic micellar effects on the behaviour and reactivity of these two radical pairs.[11]

On irradiation of a nitrogen-purged aqueous solution of **1** with 366 nm light in the presence of benzophenone (BP) and sodium dodecyl sulfate (SDS) at room temperature, seven new HPLC signals were detected on the chromatogram, while the signal area of BP remained constant during the irradiation. Comparison of the HPLC behaviour for the products with that for independently prepared authentic samples under standard analytical conditions revealed that the BP-sensitized reaction of **1** in SDS micelles results in the formation of the benzoyloxy **2** and **3** and phenyl **4** and **5** migrated products along with fragmentation products **6** and **7** and *N*-(1-naphthoyl)-4-aminophenol **8** (Scheme 1). Quantum yields (Φ_{-1} and Φ_{2-8}) for the sensitized photolyses in SDS and HTAC micelles (Table 1, see full text) show that the reaction in the former micelle gives a detectable amount of *N*-acylaminophenol **8**, formation of which is not observed in the latter micelle. Because **8** was not obtained by allowing a SDS micellar solution **3** and BP to stand at room temperature, the fact that (on irradiation under the same conditions) **3** undergoes hydrolysis in this micelle cage forming **8** and benzoic acid **7** in quantum yields of 0.036 ± 0.003 and 0.037 ± 0.004, respectively allows us to conclude that the aminophenol derivative **8** arises from the BP-sensitized photohydrolysis of the initially formed rearrangement product **3** in the SDS micelle cage which contains entrapped water molecules.



Scheme 1 Np = 1-naphthyl.

Consideration of the presence of a hot triplet pair, ${}^3[1\text{-NpC}(=O)N(Ph)\cdot\cdot OC(=O)Ph]^{\ddagger}$ {larger Φ value for the formation of the benzoyloxyl radical-derived products ($\Phi_2 + \Phi_3 + \Phi_7 = 0.150$) than that of the phenyl radical-derived products [$\Phi_4 + \Phi_5 + \Phi_6 - (\Phi_7 - \Phi_8) = 0.038$]} obtained in SDS micelles indicates the occurrence of hydrogen-bonding solvation in this micelle cage. Water molecules taking part in the photohydrolysis of **3** are considered to form a hydrogen bond with the amide carbonyl oxygen in the postulated radical pair intermediate. The hydrophobicity of amidyl, benzoyloxyl and phenyl radicals as well as the relatively high intramicellar viscosity[13] 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**. This interpretation is consistent with the exclusive formation of the 1,3 (**2**) and the 1,5-benzoyloxy (**3**) migrated products on irradiation of a SDS micellar solution of **1** containing no BP with 313 nm light (Table 1, see full text).

As is evident from Table 2 (see full text), the increased concentration of hydrophobic benzyl alcohols significantly decreases the quantum yields for the benzoyloxy- and the phenyl-rearranged products (Φ_{2-5}) with an increase in those for the fragmentation products (Φ_6 and Φ_7). In addition, the quantum yield for the disappearance of the starting **1** (Φ_{-1}) is scarcely, if at all, dependent on the alcohol, confirming

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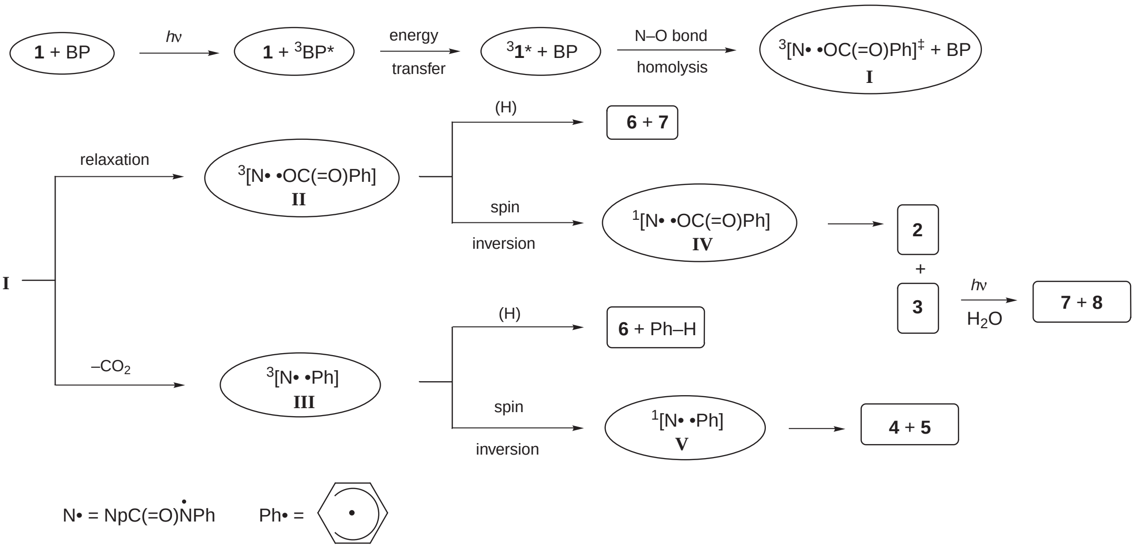

Scheme 2

that hydrogen abstraction of amidyl, benzoyloxyl and phenyl radicals takes place in competition with spin inversion of the triplet amidyl–benzoyloxyl and amidyl–phenyl radical pairs in the micellar phase. Supporting evidence for this conclusion comes from the detection of benzaldehyde (the concentration of which is comparable to that of anilide **6** at a given irradiation time), as the alcohol-derived product (Fig. 2, see full text), thus leading us to propose Scheme 2. The existence of benzyl alcohol in the micellar phase should accelerate hydrogen abstraction within the two triplet radical pairs. On the other hand, the quantum yield for the photohydrolysis of **3** forming **8** (Φ_8) is slightly reduced upon increasing the concentration of benzyl alcohol (Table 2). Since the alcohol is believed to be at the micellar surface, this implies that a fraction of water molecules in the SDS micelle cage are replaced by the added alcohol resulting in a lowering of reactivity with water in the cage.

As shown in Fig. 4 (see full text), there is a distinct decrease in critical micelle concentration $\overline{\text{CMC}}$ when the benzyl alcohol concentration is increased [$\overline{\text{CMC}} = 7.5 \times 10^{-3}$, 6.3×10^{-3} and 5.2×10^{-3} mol dm^{-3} at [$PhCH_2OH$] = 0, 0.25 and 0.50% (v/v), respectively], verifying that the increased alcohol concentration accelerates SDS micelle formation to a certain extent and, hence, this hydrophobic alcohol undoubtedly penetrates into the interior of the micelle. Fluorescence quenching of pyrene by cetylpyridinium chloride in SDS micelles made it possible to estimate the aggregation number for the SDS surfactant as 61 in the absence of benzyl alcohol,[15] *cf.* 64 {[$PhCH_2CH$] = 0.25% (v/v)} and 69 {[$PhCH_2OH$] = 0.50% (v/v)} [Fig. 5 and eqn. (1), see full text].[15] Accordingly, we conclude that added benzyl alcohol exerts only a minor effect on the SDS micellar size.

Techniques used: HPLC, UV–VIS, fluorescence and actinometry

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Fig. 1: Structure of **1**.

Fig. 2: Relationship between the concentration of benzyl alcohol as an additive and benzaldehyde as the alcohol-derived product.

Fig. 3: Schematic illustration of the amidyl–benzoyloxy and amidyl–phenyl radical pairs generated in SDS micelles containing benzyl alcohol.

Fig. 4: Dependence of the fluorescence intensity of 1,6-diphenyl-1,3,5-hexatriene on the SDS concentration in the absence and presence of benzyl alcohol.

Fig. 5: Relationship between $\ln(I_0/I)$ and the quencher concentration for the fluorescence quenching of pyrene in SDS micelles containing benzyl alcohol.

Table 1: Quantum yields for disappearance of **1** and for appearance of **2**–**8**.

Table 2: Effects of benzyl alcohol on the quantum yields for the BP-sensitized photolysis of **1** in SDS micelles.

Table 3: Quantum yields for the BP-sensitized photolysis of **1** in anionic [$Me(CH_2)_nOSO_3Na$; $n = 9$, 11, 13] micelles.

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