Photocontrol of Micellar Catalyses

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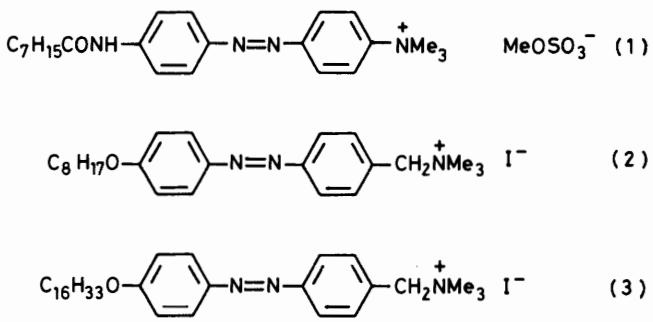
Three photoresponsive surfactants, $C_7H_{15}CONHC_6H_4N{=}NC_6H_4N^+Me_3MeOSO_3^-$ (1), $C_8H_{17}OC_6H_4N{=}NC_6H_4CH_2N^+Me_3I^-$ (2), and $C_{16}H_{33}OC_6H_4N{=}NC_6H_4CH_2N^+Me_3I^-$ (3), have been synthesised. The absorption spectrum of 2,6-dichlorophenolindophenol † as a probe for micelle formation indicated that the aggregation mode of these photoresponsive surfactants is affected by photoinduced *trans–cis* isomerisation of the azobenzene head groups. The catalytic activities of these surfactant aggregates in base-catalysed proton abstraction from benzoin and alkaline hydrolysis of *p*-nitrophenyl cyclohexanecarboxylate were estimated in the dark and under photoirradiation. It was found that the rate constants in the micellar systems change sensitively in response to photoirradiation. The results imply that photoinduced isomerisation of the head groups leads to a change in the catalytic activity. This is the first example of photocontrol of micellar catalysis.

PHOTORESPONSIVE systems are ubiquitous in Nature, and light is used as a trigger in many systems to cause the subsequent life processes. It is noteworthy that such physiological processes are frequently linked with photoinduced structural changes of photoantennas. We have been interested in the application of the photoresponsive phenomena to biomimetic systems. For example, we have combined crown ethers as a functional group with azobenzene as a photoantenna and have attempted the photocontrol of solvent extraction and ion transport of alkali metal cations.[1-5] Similarly, several groups have been attempting the photocontrol of chemical and physical functions of membranes,[6] microemulsions,[7] polypeptide chains,[8] synthetic polymers,[9] cyclodextrins,[10] and an anthracene-containing crown ether.[11]

In this paper, we report the photocontrol of micellar catalyses which frequently imitate the fundamental functions of enzymic catalyses.[12,13] We synthesised three cationic surfactants, 4-octanoylamino-4′-(trimethylammonio)azobenzene methosulphate (1), 4-octyloxy-4′-(trimethylammoniomethyl)azobenzene iodide (2), and 4-hexadecyloxy-4′-(trimethylammoniomethyl)azobenzene iodide (3), which have azobenzene heads as photoisomerisable groups. It is known that symmetrical *trans*-azobenzene is a nonpolar molecule, while bent *cis*-azobenzene is a polar molecule due to the large dipole moment across the azo-linkage.[14,15] According to Piszkiewicz,[16,17] micelle formation occurs in an allosteric manner. If so, the changes in the structure and the hydrophilicity of the surfactant head groups would induce a shift of the critical micelle concentration (c.m.c.). We thus considered that the micellar catalysis may be readily photocontrolled by utilising the shift of the c.m.c. which occurs in response to photoirradiation. We tested the possibility through an investigation of the micellar effects on base-catalysed proton abstraction from benzoin (carbon acid) and hydrolysis of *p*-nitrophenyl cyclohexanecarboxylate (PNPC).

RESULTS AND DISCUSSION

Photoisomerisation of Surfactants.—In aqueous solution, the absorption bands of the surfactants at *ca.* 350 nm decreased rapidly upon photoirradiation by u.v. light



through a glass filter (330 nm $< \lambda <$ 380 nm) and reached equilibrium intensities within 4 min. The percentages of *cis*-isomer in the photostationary state are summarised in Table 1. The azobenzene head groups of (1) and (2) which have shorter hydrocarbon chains were isomerised to the *cis*-forms to the extent of 62—71%, whereas that of (3) which has a hexadecyl hydrocarbon chain was

TABLE 1

Percentage of *cis*-surfactants in the photostationary state in aqueous solution (6.25 vol% DMF) [a]

Surfactant	$\lambda_{max.}$/nm	ϵ	*cis*% at 10^4[surfactant]/M 0.20 [b]	0.30 [c]	1.0 [c]	5.0 [c]
(1)	360	21 500	71			55
(2)	350	15 500	62	88	74	54
(3)	342	18 300	31	77	52	30

[a] 4 min irradiation through a UV-D35 filter (330 nm $< \lambda <$ 380 nm). [b] 1 cm quartz cell. [c] 1 mm layer between glass plates.

isomerised only to the extent of 31%. The difference is probably characteristic of the aggregative nature of (3) in aqueous solution. When an aqueous solution was placed between two glass plates (*ca.* 1 mm apart) and photoirradiated, the percentage of *cis*-isomer was significantly enhanced. We found, however, that the percentage of *cis*-isomer [particularly, that of (3)] decreases with increasing surfactant concentrations. In order to prepare the surfactant solutions which contain almost identical percentages of *cis*-surfactants, we dissolved the surfactants in *NN*-dimethylformamide (DMF) and photoirradiated a thin layer of the solution

† 4-[(3,5-Dichloro-4-hydroxyphenyl)imino]cyclohexa-2,5-dienone.

between two glass plates. We could thus obtain DMF solutions containing the following percentages of *cis*-surfactants: (1) 56—60, (2) 58—65, (3) 55—66%. Kinetic measurements were carried out by mixing the DMF solutions with buffered aqueous solutions.

Thermal *cis–trans*-isomerisation of these surfactants was relatively slow at 30 °C: for example, 37% of (3) still remained as the *cis*-form after one day. Thus, thermal *cis–trans*-isomerisation during the kinetic measurements (usually *ca.* 30 min) is negligible. On the other hand, irradiation by visible light with a 200 W tungsten lamp markedly facilitated the regeneration of the *trans*-forms: for example, 97% of *trans*-(3) was recovered after 10 min irradiation. The result implies that photoisomerisation is almost reversible.

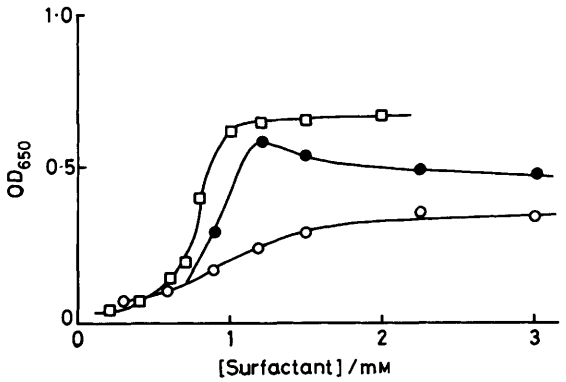


FIGURE 1 OD_{650} *versus* surfactant [HDPB and HDPB + (1) (in a molar ratio of 2 : 1)] concentration: 30 °C, [DCPI] 9.38×10^{-5}M, [HCl] 1.41×10^{-4}M, EtOH 6.25 vol%. □, HDPB; ○, HDPB + (1); ●, HDPB + photoirradiated (1)

Influence of Photoirradiation on Micelle Formation.— 2,6-Dichlorophenolindophenol (DCPI) is often used for the measurement of the c.m.c. of cationic micelles,[18] for it is red (neutral species, $\lambda_{max.}$ 500—520 nm) in dilute hydrochloric acid but turns blue (anionic species, $\lambda_{max.}$ 600—650 nm) by the addition of cationic micelles. Thus, one can easily estimate the formation of micelles in aqueous solution. As shown in Figure 1, the blue colour of DCPI appeared with increasing *N*-hexadecylpyridinium bromide (HDPB) concentration and became saturated at higher HDPB concentrations. The c.m.c. is thus estimated to be *ca.* 0.8mM from the OD_{650}–[surfactant] plot. On the other hand, neither *trans*-(1) nor photoirradiated (1) could form a micelle: the distinct blue colour did not appear at [(1)] <2.0mM and there was a precipitate at [(1)] >2.0mM. We thus dissolved (1) in the HDPB micelle and estimated the influence of photoirradiation on the HDPB–(1) mixed micelle. When *trans*-(1) was added to the solution of HDPB above the c.m.c., the blue colour of DCPI decreased considerably. Figure 1 shows the plot of OD_{650} against concentration of HDPB + (1) {in a molar ratio of 2 : 1, [surfactant] = [HDPB] + [(1)]}. Even at higher surfactant concentrations, the OD_{650} of the mixed system was about half of the HDPB micelle. The result suggests that *trans*-(1) disorders the micellar structure of HDPB. When HDPB was mixed with photoirradiated (1), the intensity of the blue colour was significantly increased with respect to that of *trans*-(1) (87% of the HDPB micelle at [surfactant] 1.20mM). One can thus presume that photoirradiated (1) disorders the micellar structure of HDPB to a smaller extent.

trans-(2) was soluble in dilute hydrochloric solution up to 1.0mM, but the distinct blue colour of DCPI was not observed. On the other hand, the blue colour of DCPI appeared in the presence of [*trans*-(3)] >0.5mM. The results indicate that *trans*-(3) in aqueous solution forms the cationic aggregate.* In Figure 2, the OD_{650} of

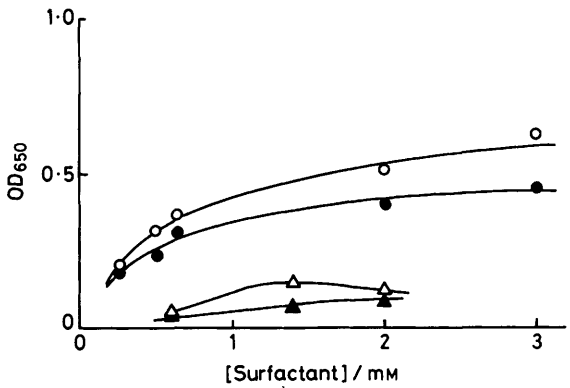


FIGURE 2 OD_{650} *versus* surfactant [HDPB + {(2) or (3)} (in a molar ratio of 1 : 1)] concentration: 30 °C, [DCPI] 1.38×10^{-4}M, [HCl] 4.13×10^{-4}M, EtOH 12.5 vol%. △, HDPB + (2); ▲, HDPB + photoirradiated (2); ○, HDPB + (3); ●, HDPB + photoirradiated (3)

DCPI is plotted against the concentration of HDPB + {(2) or (3)} {in a molar ratio of 1 : 1, [surfactant] = [HDPB] + [(2) or (3)]}. It is clear from Figure 2 that (i) (2) is capable of strongly disordering the HDPB micelle, whereas the OD_{650} value of HDPB is affected to a smaller extent by the addition of (3), indicating that (3) and HDPB form a comicelle, (ii) addition of (3) increases the OD_{650} at the concentration range lower than the c.m.c. of HDPB (0.8mM), but the comicelle does not provide an abrupt, sigmoid-type increase in the c.m.c. region, and (iii) the micelle structure of HDPB is significantly disordered by photoirradiation and the effect appears more distinctly in (3) than in (2). The trend that the OD_{650} of DCPI is decreased by photoirradiation in the concentration range 0.25—3.0mM is in contrast to the case of the HDPB + (1) system in which the OD_{650} of DCPI is increased by photoirradiation. As described in the Introduction, symmetrical *trans*-azobenzene is classified as a nonpolar molecule, while *cis*-azobenzene is a polar molecule due to the large dipole moment across the azo-linkage.[14,15] One may thus visualise that

* We noticed, however, that a new, broad absorption band appears in the 650—880 nm spectral region at higher *trans*-(3) concentrations. Supposedly, the new absorption band stems from the association of DCPI molecules on the surface of *trans*-(3) aggregates. Thus, DCPI is not a suitable probe for the aggregation of (3). We did not specify further the aggregate formation of *trans*-(3) by using DCPI: for a related system, see N. Nakashima, H. Fukushima, and T. Kunitake, *Chem. Lett.*, 1981, 1555.

trans-(1) is efficiently bound to the HDPB micelle and disorders the micellar structure, whereas the less hydrophobic *cis*-(1) is partitioned to a greater extent to the bulk water phase and has little negative influence on the micelle structure. This would also accommodate the fact that the photoirradiation of the HDPB–(1) system causes the recovery of the OD_{650}. On the other hand, *trans*- and *cis*-(3) are both bound to the HDPB micelle because of the hydrophobic hexadecyl group. If so, *cis*-(3) which has a bent head group would disorder the micellar structure more effectively than *trans*-(3) which has an almost linear molecular shape. The intermediate case is (2). Probably, (2) behaves like (3) and partitions favourably in the micelle phase with the resulting decrease in the absorbance upon photoirradiation.

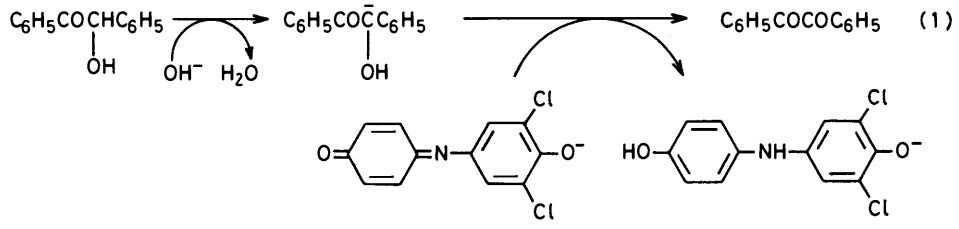
Catalysis of Proton Abstraction from Benzoin.—Proton abstraction from benzoin [equation (1)] is a base-catalysed reaction. The deprotonation step being rate-determining, the oxidation by DCPI of the carbanion intermediate is a rapid, trapping step.[19,20] Hence, the disappearance of the absorption band of DCPI, $\lambda_{max.}$ 606 nm ($\varepsilon_{max.}$ 15 900), is zero-order in DCPI. The reaction rate (v_{obs}) is thus expressed by equation (2). We have

$$v_{obs} = (k_{OH}[OH^-] + k_{buffer}[buffer])[benzoin] = k_1'[benzoin] \quad (2)$$

determined the reaction rates at constant pH (10.29 ± 0.02) with a constant buffer concentration (0.01M-carbonate), so that the catalytic activities were compared in terms of the apparent first-order rate constant (k_1').

The HDPB micelle effectively catalysed the reaction (Figure 3 and Table 2). As is usually observed for conventional micellar catalysis, a plot of k_1' against [HDPB] increased along a sigmoid curve and then decreased gradually. The maximum rate augmentation was 86-fold compared with the non-micellar system. The HDPB + *trans*-(1) mixed system gave smaller rate constants than the HDPB micelle, but the catalytic activity of the mixed system was significantly improved by photoirradiation. At [surfactant] 1.2mM, the rate difference between the dark and the photoirradiated system was 3.2-fold (Table 2). It is noteworthy that the plots of k_1' against [surfactant] (Figure 3) are well correlated with those of OD_{650} against [surfactant] (Figure 1). Thus, the binding of *trans*-(1) to the micellar phase causes the suppression of micellar catalysis, but the catalytic activity recovers upon photoirradiation which excludes to some extent the azo-surfactants as more hydrophilic *cis*-forms out of the micelle phase.

The influence of HDPB + {(2) or (3)} on the rate of proton abstraction is illustrated in Figure 4. As opposed to the influence of (1) on micellar catalysis, micelles containing photoirradiated (2) or (3) exhibited lower catalytic activity, and the difference became more conspicuous at high [surfactant]. We speculate on the basis of the OD_{650}–[surfactant] plots that photoirradiated (2) or (3) remain in the micelle phase because of their high hydrophobicity and produce disorder in the neat micellar structure. Figure 4 provides support for our hypothesis. A comparison of Figure 4 with Figure 2 establishes that photoirradiated (2) or (3) brings forth a negative influence on micelle formation. Strangely, the HDPB + (2) mixed micelle, in which a clear increase in OD_{650} was not observed (Figure 2), exhibited relatively high catalytic activity. The result cannot be explained at present. One plausible explanation would be that in the HDPB + (2) mixture, small amounts of HDPB may form a micelle on their own without mixing with (2). If so, the remaining HDPB micelle would contribute efficiently to the rate enhancement but only to a small extent to the increase in the OD_{650} (compare the augmentation of the rate constants with that of OD_{650}).



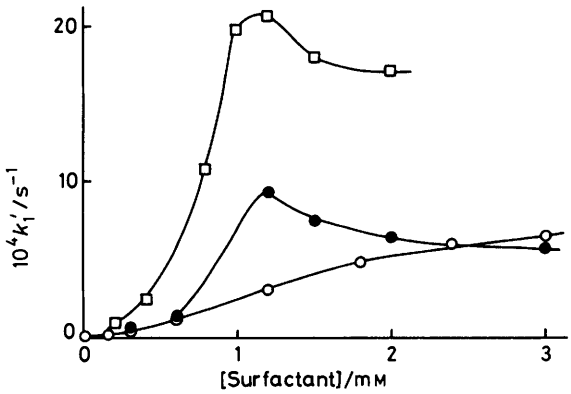


FIGURE 3 Apparent first-order rate constants (k_1') for proton abstraction from benzoin *versus* surfactant [HDPB and HDPB + (1) (in a molar ratio of 2 : 1)] concentration: 30 °C, pH 10.3 with 0.01M-carbonate, 6.25 vol% DMF, [DCPI] 4.00 × 10^{-5}M, [benzoin] 2.00 × 10^{-4}M. □, HDPB; ○, HDPB + (1); ●, HDPB + photoirradiated (1)

Typical first-order rate constants are recorded in Table 2. Examination of Table 2 reveals that micellar catalysis of proton abstraction from benzoin can be photocontrolled by factors of 2—3.

Catalysis of Alkaline Hydrolysis of p-*Nitrophenyl Cyclohexanecarboxylate* (*PNPC*).—It has been reported that the hydrolysis of phenyl esters is catalysed by cationic micelles in the basic pH region.[12,13] We have

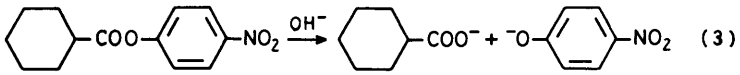
TABLE 2

Influence of photoirradiation on OD_{650} of DCPI and apparent first-order rate constants (k_1') for proton abstraction from benzoin [a]

Surfactant (concentration in mM)	OD_{650} dark	OD_{650} light	$10^4 k_1'/s^{-1}$ dark	$10^4 k_1'/s^{-1}$ light	k_{light}/k_{dark}
None			0.236		
HDPB (0.80)	0.402 [b]		10.6		
HDPB (1.20)	0.664 [b]		20.4		
HDPB (0.80) + (1) (0.4)	0.245 [b]	0.575 [b]	2.94	9.35	3.2
HDPB (1.0) + (2) (1.0)	0.166 [c]	0.085 [c]	7.60	4.46	0.59
HDPB (1.0) + (3) (1.0)	0.508 [c]	0·394 [c]	5.45	5.05	0.93
HDPB (1.5) + (3) (1.5)	0.628 [c]	0.454 [c]	9.30	4.59	0.49

[a] The detailed reaction conditions are recorded in the captions for corresponding Figures. [b] [DCPI] 9.38×10^{-5}M. [c] [DCPI] 1.38×10^{-4}M.

examined the influence of photoresponsive surfactants (2) and (3) on the hydrolysis of PNPC [equation (3)].



(3)

PNPC

In this experiment, we did not use HDPB. The reaction was first-order for up to four half-lives. The first-order rate constants thus obtained are plotted as a function of surfactants in Figure 5, and typical rate constants are summarised in Table 3.

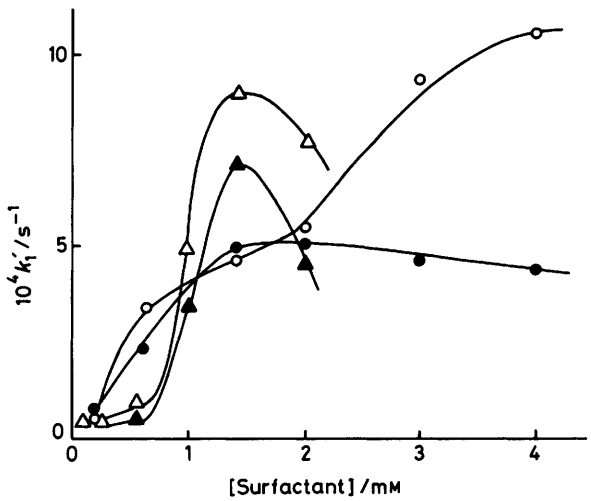


FIGURE 4 Apparent first-order rate constants (k_1') for proton abstraction from benzoin *versus* surfactant [HDPB + {(2) or (3)} (in a molar ratio of 1 : 1)] concentration. The reaction conditions are identical to those in Figure 3. △, HDPB + (2); ▲, HDPB + photoirradiated (2); ○, HDPB + (3); ●, HDPB + photoirradiated (3)

Photoirradiation again caused the suppression of the hydrolytic rate constants. In particular, a large irradiation effect was observed for (3). The rate constants for *trans*-(3) markedly increased at [(3)] 0.3mM, indicating that the formation of the aggregate occurs at this concentration.* The rate increased with increasing concentration of (3), but the solution became turbid above 1.0mM. On the other hand, a solution of photoirradiated (3) was clear up to 4.0mM, but an appreciable rate was not observed. The phenomenon observed for photoirradiated (3) is rationalised in terms of either increased hydrophilicity which would enhance the c.m.c. or a bent structure which would be disadvantageous to aggregate formation. In any case, *cis*-(3) is much less effective as a hydrolytic catalyst than *trans*-(3). The magnitude of the photocontrol attained in the hydrolysis is *ca.* 3-fold (Table 3).

TABLE 3

Influence of photoirradiation on first-order rate constants (k_1) for the hydrolysis of *p*-nitrophenyl cyclohexanecarboxylate [a]

Surfactant (concentration in mM)	$10^4 k_1/s^{-1}$ dark	$10^4 k_1/s^{-1}$ light	k_{light}/k_{dark}
None	0.201		
HDPB (2.0)	1.43		
(2) (1.0)	0.254	0.197	0.77
HDPB (1.0) + (3) (1.0)	2.16	1.59	0.74
(3) (1.0)	1.68	0.521	0.31

[a] The detailed reaction conditions are recorded in the caption for Figure 5.

Conclusions.—The present system demonstrated that the micellar catalysis can be controlled, in principle, by photoinduced *trans–cis*-interconversion of the azobenzene head groups of the surfactants. The novel phenomenon is attained because the surfactants with the *cis*-head groups are more hydrophilic and disorders the micellar structure more effectively. Efforts to seek more efficient photoresponsive surfactants and to apply this concept to other micelle-catalysed reactions are continuing.

* (3) may form a membranous aggregate in aqueous solution. At [DCPI] 5.00×10^{-5}M, [benzoin] 1.00×10^{-3}M, and [(3)] 1.0mM, v_{obs} is 4.82×10^{7} mol l^{-1} s^{-1}. When the solution of (3) [or (3) + DCPI] was sonicated for 5 min with a Bransonic sonifier (type 185), the reaction rate was reduced to 2.28×10^{-7} (or 3.44×10^{-7}, respectively) mol l^{-1} s^{-1}. Since such a sonication effect was not observed for the HDPB micelle, (3) probably formed a ' stable ' aggregate structure in aqueous solution. The formation of membranous aggregates by similar azobenzene-containing surfactants has been reported, M. Shimomura and T. Kunitake, *Chem. Lett.*, 1981, 1001.

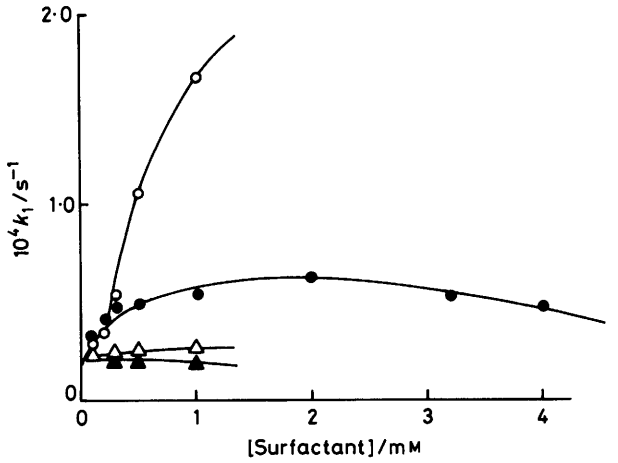


FIGURE 5 First-order rate constants (k_1) for the hydrolysis of *p*-nitrophenyl cyclohexanecarboxylate (PNPC) *versus* surfactant (2) or (3) concentration. The reaction conditions are 30 °C, pH 8.30 with 0.01M-borate, 6.25 vol% DMF, and 5.0 vol% acetonitrile, [PNPC] 3.0×10^{-4}M. △, (2); ▲, photo-irradiated (2); ○, (3); ●, photoirradiated (3)

EXPERIMENTAL

Materials.—*4-Octanoylamino-4'-(dimethylamino)azobenzene* was prepared in toluene (30 ml) from octanoyl chloride (1.6 g, 0.01 mol) and 4-amino-4'-(dimethylamino)-azobenzene (2.4 g, 0.01 mol) in the presence of pyridine (4 ml) and recrystallised from ethanol, m.p. 186—188 °C (Found: C, 71.95; H, 8.3; N, 15.25. $C_{22}H_{30}N_4O$ requires C, 72.1; H, 8.25; N, 15.3%). The *salt* (1) was obtained by the treatment of this compound with dimethyl sulphate (excess) at 75 °C for 3 h in dioxan. The precipitate was collected by suction and washed with benzene, m.p. 186 °C (decomp.) (Found: C, 57.4; H, 7.3; N, 11.35. $C_{24}H_{36}N_4O_5S$ requires C, 58.5; H, 7.35; N, 11.35%). When recrystallised from ethanol, a significant fraction of (1) decomposed to 4-octanoylamino-4'-(dimethylamino)azobenzene. Hence, we used this sample without further purification.

4-Hexadecyloxy-4'-(dimethylaminomethyl)azobenzene was prepared in *NN*-dimethylformamide by mixing the sodium salt of 4-hydroxy-4'-(dimethylaminomethyl)azobenzene (1.5 g, 5.8 mmol) with hexadecyl iodide (2.07 g, 5.87 mmol) in an NaOH-containing methanol solution and was recrystallised from ethanol, m.p. 71—73 °C (Found: C, 77.25; H, 10.3; N, 8.55. $C_{31}H_{49}N_3O$ requires C, 77.6; H, 10.3; N, 8.75%). The *salt* (3) was obtained by the treatment of this compound with methyl iodide (excess) in refluxing methanol for 2 h, m.p. 195—202 °C (Found: C, 61.85; H, 8.6; N, 6.7. $C_{32}H_{52}IN_3O$ requires C, 61.8; N, 8.45; N, 6.75%), δ($CDCl_3$) 0.88 (3 H, CH_3C), 1.28 (28 H, $[CH_2]_{14}$), 3.50 [9 H, $N(CH_3)_3$], 4.06 (2 H, OCH_2), 5.28 (2 H, NCH_2), and 7.02 and 7.94 (8 H aromatic protons).

The *salt* (2) was synthesised from 4-hydroxy-4'-(dimethylaminomethyl)azobenzene and octyl bromide *via* 4-octyloxy-4'-(dimethylaminomethyl)azobenzene according to the similar method as (3). 4-Octyloxy-4'-(dimethylaminomethyl)azobenzene had m.p. 48—50 °C. The salt (2) had m.p. 214—216 °C (Found: C, 56.15; H, 7.1; N, 8.1. $C_{24}H_{36}IN_3O$ requires C, 56.6; H, 7.1; N, 8.25%).

Kinetic Measurements.—The rate measurements were carried out spectrophotometrically at 30 °C by using a thermostatted cell-holder. Hydrolysis of PNPC was measured in aqueous solution containing 6.25 vol% DMF and 5.0 vol% acetonitrile buffered at pH 8.30 with 0.01M-borate. The progress of the reaction was followed by monitoring the appearance of the absorption band of *p*-nitrophenolate at 410 nm.

Proton abstraction from benzoin was carried out under anaerobic (N_2) conditions by using a Thunberg cuvette at pH 10.29 ± 0.02 with 0.01M-carbonate. The progress of the reaction was followed by monitoring the disappearance of the absorption band of DCPI at 606 nm. The reaction was zero-order in DCPI for up to 95% reaction, the reaction rate being calculated from the initial slope.

Photoisomerisation.—The sample solutions were irradiated at room temperature with a 500 W high-pressure mercury lamp. The distance from the lamp to the sample solutions was 12.5 cm. A Toshiba UV-D35 glass filter was employed (330 nm $< \lambda <$ 380 nm).

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