Tetrahedron Letters, Vol. 22, No. 15, pp 1409 - 1412 ,1981 0040-4039/81/151409-04$02.00/0
Printed in Great Britain

PHOTOCONTROL OF MICELLAR CATALYSIS

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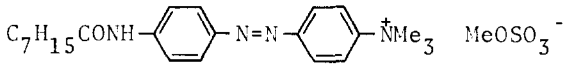
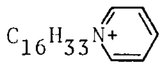
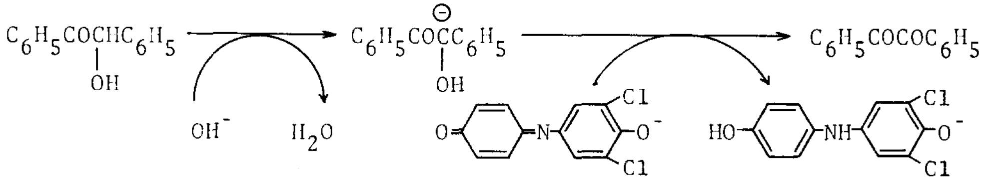
A photoresponsive surfactant with a cationic azobenzene head group (I) was synthesized. It was demonstrated that by mixing (I) with a conventional cationic micelle the rate of the micelle-catalyzed reaction (base-catalyzed proton abstraction from benzoin) can be controlled by light. The origin of the photocontrol was accounted for by the difference in the partitioning of trans-(I) and cis-(I) in the micelle phase.

Photoresponsive systems are ubiquitously seen in nature, and light is used as a trigger to cause the subsequent life processes. In these systems, the physiological changes are frequently linked with photo-induced structural changes. Hence, one has to combine a photo-antenna to cause some structural change with a functional group to mediate some subsequent event in order to mimic the fundamental functions of the photoresponsive systems. We have been interested in the application of the phenomena to biomimetic systems. In this paper, we report the first example of photocontrol of micellar catalysis which frequently imitates the fundamental functions of enzymatic catalysis.[1)]

We used (I) as a photoresponsive surfactant and hexadecylpyridinium bromide (HDPB) as a micelle-forming surfactant. As a reaction, we chose the proton abstraction from benzoin (Eq. 1) which is catalyzed by cationic micelles and is conveniently monitored by following the disappearance of the absorption band of 2,6-dichlorophenolindophenol(DCPI).[2,3)]


: (I)


Br⁻ : HDPB


(1)

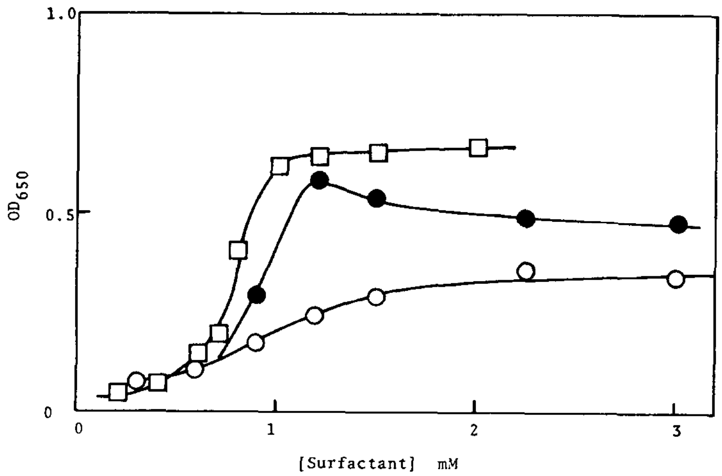


Fig. 1. OD_{650} vs. surfactant concentration. 30°C, [DCPI]=9.38×10^{-5} M, [HCl]=1.41×10^{-4} M. □ HDPB; ○ HDPB+(I)(2:1 in mol); ● HDPB+photo-irradiated (I)(2:1 in mol).

The absorption band of trans-(I)(λ_{max} 360 nm in water) decreased rapidly with photo(uv)-irradiation and reached an equilibrium intensity within 3 min. The cis% was calculated to be 71% from the equilibrium absorbance assuming that the absorbance of cis-(I) at this wavelength is negligible in comparison to that of trans-(I). The regeneration of trans-(I) in the dark was relatively slow, 80% of the initial spectrum being recovered after one day at 30°C.

DCPI is often used for the measurement of the cmc of cationic micelles,[4] for it is red (neutral species, λ_{max} 500-520 nm) in dilute hydrochloric acid, but turns blue (anionic species, λ_{max} 600-650 nm) by addition of cationic micelles. Thus, one can easily detect the formation of micelles in aqueous solution. For example, the blue color of DCPI appears with increasing HDPB concentrations, and the cmc is estimated to be ca. 0.8 mM from the OD_{650} vs. [surfactant] plot (Fig. 1). On the other hand, neither trans-(I) nor photo-irradiated (I) could not form the micelle: the blue color did not appear at [(I)] < 2.0 mM and they precipitated at [I]>2.0 mM. When (I) was added to the solution of HDPB above the cmc, the blue color of DCPI almost disappeared. In Fig. 1, OD_{650} was plotted against the concentration of HDPB+(I) mixture (2:1 in mol, [surfactant]=[HDPB]+[(I)]). Even at the higher concentrations, the OD_{650} value of the mixed system was about half of the HDPB micelle. These results suggest that (I) rather acts as a micell-destroying reagent. Interestingly, when HDPB was mixed with photo-irradiated (I)[5], the intensity of the blue color was significantly strengthened (87% of the HDPB micelle: Table 1 and Fig. 1). One can thus presume that cis-(I) destroys the HDPB micelle to a smaller extent than trans-(I). The difference may be reflected by the micellar catalysis.

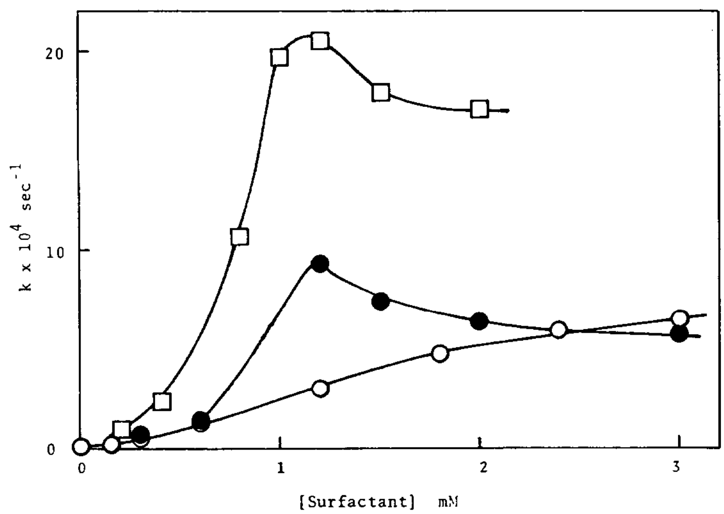


Fig. 2. Apparent first-order rate constants (k) for proton abstraction from benzoin vs. surfactant concentration. □HDPB; ○ HDPB+(I); ● HDPB+photo-irradiated (I). The detailed conditions are recorded in Table 1.

Table 1. Apparent first-order rate constants(k) for proton abstraction from benzoin[a)]

Additive (mM)	Treatment	OD_{650}	k × 10^4 sec^{-1}
None	dark		0.236
HDPB (1.20)	dark	0.664	20.4
HDPB (0.80)	dark	0.402	10.6
HDPB (0.80) + (I)(0.40)	dark	0.245	2.94
HDPB (0.80) + (I)(0.40)	light	0.575	9.35

a) 30°C, pH 10.29 with 0.01 M carbonate, 6.25 vol% DMF, $[DCPI]=4.00\times10^{-5}$ M, $[benzoin]=2.00\times10^{-4}$ M.

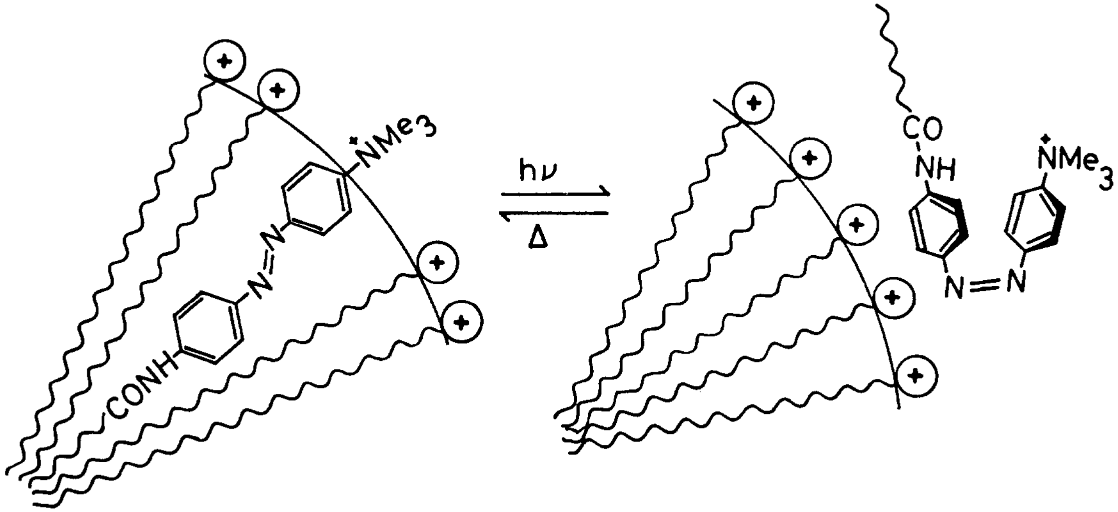
Proton abstraction from benzoin is a base-catalyzed reaction. The deprotonation being rate determining, the disappearance of the absorption band of DCPI (λ_{max} 606 nm, ε=15900) is zero-order.[2,3] The reaction rate is expressed by Eq. 2.

$$v = (k_{OH}[OH^-] + k_b[buffer])[benzoin] = k[benzoin] \qquad (2)$$

In this paper, we evaluated the micellar catalysis by the apparent first-order rate constant, k. The results are summarized in Table 1 and Fig. 2. Obviously, the plots of k vs. [surfactant] are well correlative to those of OD_{650} vs.

[surfactant] in Fig. 1: the mixed system gives the smaller rate constants than the HDPB micelle and the photo-irradiated rate constants are significantly greater than the dark rate constants. At [surfactant]=1.2 mM, the rate difference between the dark and the photo-irradiated system is 3.2-fold. This indicates that the micellar catalysis can be controlled, in principle, by switching the light source on and off.

It is interesting to consider why cis-(I) destroys the micelle less effectively. It is known that symmetrical trans-azobenzene is calssified as a non-polar molecule, while cis-azobenzene belongs to a polar molecule due to large dipole moment across the azo-linkage.⁶⁾ One may thus presume that less hydrophobic cis-(I) is partitioned to a greater extent to bulk water. This would elucidate the recovery of the HDPB micellar catalysis by photo-irradiation.



The effort to seek more efficient photoresponsive surfactants is now continued in this laboratory.

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3) S. Shinkai and T. Kunitake, J. Chem. Soc., Perkin 2, 1976, 980.
4) M. C. Corrin and W. D. Hawkins, J. Am. Chem. Soc., 69, 679 (1947).
5) When the solution of ~10^{-3} M (I) was photo-irradiated, the cis% at the photostationary state was 56%. This solution was used for the spectral and kinetic measurements.
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(Received in Japan 30 December 1980)