

MICELLAR STRUCTURE AND MICELLAR CONTROL OF PHOTOCHEMICAL REACTIONS

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Summary

In view of the vast potential of micellar systems as media in which reactions may be conducted, a clear understanding of the structure of micelles is essential. The unique features of micelles and how these have been utilized to catalyse and control photochemical reactivity are briefly surveyed here. Micellar media, when used for chemical reactions, exhibit features that are completely different from those of ordinary non-aqueous solvents. A thermal or photochemical reaction conducted in micellar media is influenced by the effects of the micellar environment which result in control and/or modification of reactivity. The salient features of micelles that influence the photochemical reactivity are cage and microviscosity effects, localization and compartmentalization effects, pre-orientational, polarity and counterion effects.

1. Introduction

The study of photophysical processes and photochemical reactions in ordered molecular assemblies such as micelles, microemulsions, vesicles, monolayer films, supported multilayer assemblies and constrained phases such as liquid crystals and molecular crystals has added a new dimension to photochemical research [1 - 5]. Amongst the various ordered molecular assemblies, micellar systems have been thoroughly investigated [1 - 3, 6]. The sensitivity of photophysical processes and photochemical reactions to environmental perturbations has been utilized to probe the nature of micellar aggregates. An understanding of the architecture of micelles has promoted their use as reaction media. The potential of employing micellar effects to bring about catalysis and specificity in photochemical and thermal reactions has been demonstrated [1 - 3]. The unique features of micelles, and how these have been exploited to catalyse and control photochemical reactivity, are highlighted through a brief survey of reports on photochemical reactions in micellar media.

A surfactant (surface-active material) or detergent is a molecule that possesses both polar (or ionic) and non-polar moieties, *i.e.* it is an "amphiphilic" or "amphiphatic" species. This property causes aqueous

solutions of detergents to exhibit a number of unusual and important properties. The structure of a detergent may be written as RX where R is a hydrocarbon chain containing 8 - 18 carbon atoms or some other hydrophobic residue, and X is a hydrophilic group. Depending on the nature of X , detergents can be classified as (a) non-ionic, *e.g.* polyoxyethylene(9,5)-*p*-1,1,3,3-tetramethylbutylphenol (Triton X-100), (b) cationic, *e.g.* cetyltrimethylammonium bromide, $n\text{-C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ (CTAB), or (c) anionic, *e.g.* sodium dodecylsulphate (SDS), $n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$.

In aqueous solutions the polar portion of the detergent is hydrophilic and the non-polar portion is hydrophobic. The result of these conflicting chemical features is a tendency for co-operative self-association of detergent monomers to form aggregates. So-called hydrophobic effects [7, 8] are the driving force behind the formation of such aggregates; these result from a tendency for interactions of low entropy and/or contact between molecules of markedly different polarity, *e.g.* hydrocarbons and water, to be minimized. The term micelle refers to the aggregates of colloidal dimensions that are formed upon the addition of detergent to water, and implies that these aggregates are in dynamic equilibrium with the detergent monomers.

It is commonly observed that there is a relatively small range of concentration below which micelles are absent (or present in very low concentrations) and above which virtually all detergent molecules exist as micellar aggregates. This range defines a "critical micelle concentration" (CMC), which may be determined from an experimental plot of some observable property *versus* detergent concentration. It has been found that the critical micelle concentration depends on the hydrocarbon chain length, chain structure, valence and nature of the counterion, temperature, added electrolytes and non-electrolytes [6]. The solubility of a detergent is low at low temperatures but increases dramatically above a certain temperature referred to as the "critical micelle temperature" (CMT) or "Kraft point". The number of detergent monomers forming a micellar aggregate is the "aggregation number" denoted AN or \bar{n} . Depending on the temperature, concentration and other experimental variables, micelles may be roughly spherical, ellipsoidal,

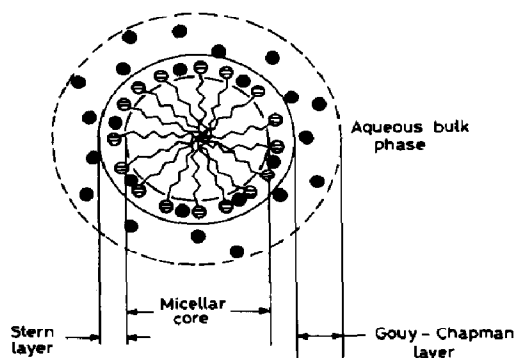


Fig. 1. Conventional representation of a micelle (the Hartley model): \oplus , ionic head group; \ominus , counterions; \sim , hydrocarbon chain.

disc-like or rod-shaped [9, 10]. A conventional representation of a micelle is shown in Fig. 1.

2. Cage and microviscosity effects

Cage effects arise from the ability of micelles to hold two reactive intermediates together long enough for reaction to occur. For example, photochemical fragmentation reactions often produce a geminate radical pair which can either recombine or diffuse apart. Relative to homogeneous solvents, in micelles large cage effects are observed whose magnitude cannot be explained by the microviscosity inside the micelle. The main reason for this is that the hydrophobicity of the solvents inhibits diffusion into the aqueous phase, thereby increasing the time spent by the radical intermediates in the restricted space of the micelle.

Microviscosity effects inside a micelle result from its viscosity being unusually high compared with the overall viscosity of the solution. The microviscosity is a measure of the fluidity of the environment of a probe molecule that is incorporated into the micelle. This phenomenon leads to the modification of photochemical reactions which are sensitive to viscosity. Table 1 is a survey of the microviscosities of the commonly-known micelles, *viz.* SDS, CTAB, potassium dodecanoate (KDC) and Triton X-100.

The photodecarbonylation of unsymmetrical dibenzyl ketones A—CO—B in homogeneous solutions occur via free radicals to produce A—B, A—A and B—B in the statistical distribution 50:25:25 [18]. In contrast,

TABLE 1
Microviscosity of micellar interiors of commonly known surfactants

Surfactant	η (cP)
<i>Cationic</i>	
CTAB	17 (27) ^a , 22 (30) ^b , 34 (24) ^c
<i>Anionic</i>	
SDS	19 (25) ^d , 6 (30) ^b , 8 (25) ^e
KDC	19 (27) ^f , 23 (24) ^e
<i>Non-ionic</i>	
Triton X-100	35 ^g , 28 (24) ^c

The numerals in parentheses give the temperature in degrees Celsius.

^aFrom ref. 11.

^bFrom ref. 12.

^cFrom ref. 13.

^dFrom ref. 14.

^eFrom ref. 15.

^fFrom ref. 16.

^gFrom ref. 17.

when the reactions are conducted in CTAC micelles, a non-statistical distribution of approximately 98:1:1 is obtained [19] (Fig. 2). Also, the yield is a function of CTAC concentration and thus there is a significant enhancement of radical cage reactions of hydrophobic radical pairs relative to those in homogeneous solutions. The dramatic increase in the cage effect with the increase in the surfactant concentration is attributed to an important property of the micelle, *i.e.* the ability to sequester small organic molecules in the hydrophobic core for a period of time ranging from microseconds to milliseconds. Thus for radical reactions, the probability of spin-correlated events is increased because the diffusional separation of the radical fragments and the formation of spin-uncorrelated free radicals is inhibited. The micellar environment inhibits the diffusion of radicals to the bulk aqueous phase, the maximum separation distance of the radical pair being maintained at a few tens of ångströms or less. Since fewer radicals escape, these can undergo more efficient intersystem crossing and recombination.

In the α cleavage of ketones, when radical pairs are produced and the loss of CO is prevented on energetic grounds, fragments from the reactions of the primary radical pair become important. Deoxybenzoin provides one such example [20]. The photochemistry of this compound in acetonitrile or benzene yields benzaldehyde and dicumyl as the major products with α -methylstyrene and benzil being minor products, while in CTAC micelles α -methylstyrene and benzaldehyde are the major products. This indicates that the micelle sequesters the initial radical pair so that disproportionation is strongly favoured, *i.e.* the micelle keeps the initially formed spin-correlated triplet radical pair together long enough for intersystem crossing to the singlet to occur. Similar observations have been made with other carbonyl systems [21].

An interesting aspect of this cage effect of micelles is the observed carbon-13 enrichment of reactants involved in free-radical reactions [22]. The photolysis of dibenzyl ketone (DBK) (Fig. 3) proceeds via an initial

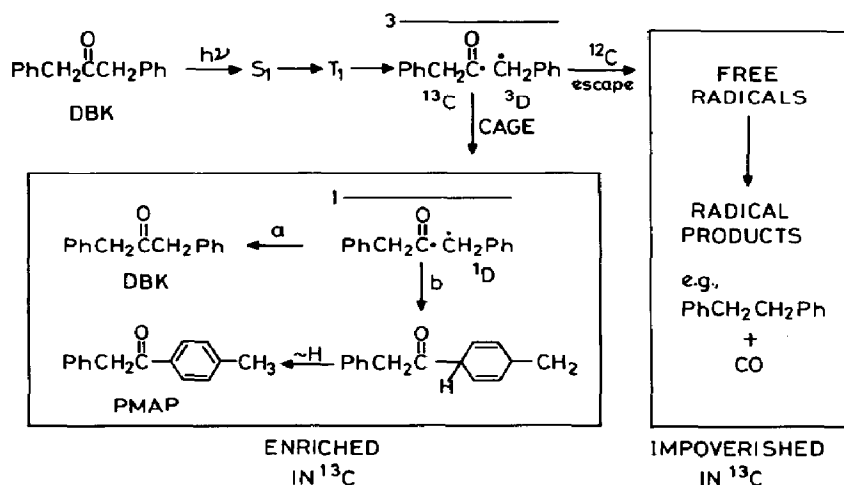
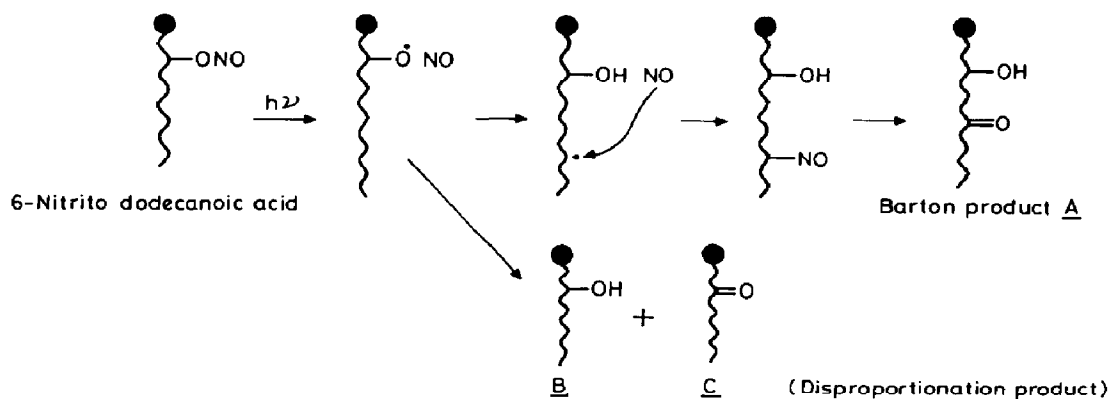


Fig. 3. Photolysis of DBK.

triplet radical pair (3D). Intersystem crossing of a radical pair such as 3D occurs via a nuclear-hyperfine-induced mechanism. Since carbon-12 does not possess a nuclear moment, hyperfine radical pairs with carbon-13 will undergo more rapid intersystem crossing than radical pairs with carbon-12. Figure 3 shows the various possible processes. Since 1D and $^1D'$ radical pairs can undergo recombination and 3D and $^3D'$ cannot, the 1D and $^1D'$ radicals formed are enriched in carbon-13. As the photoreaction proceeds, therefore, the starting material is found to be enriched in carbon-13. The degree of enrichment is relatively small for homogeneous solutions but increases by over an order of magnitude for micelles. This difference has been attributed to the "super cage" environment that allows a spin-correlated radical pair to diffuse sufficiently far apart to allow hyperfine interaction to develop but not so far apart that spin-uncorrelated free radicals are produced.

Law and de Mayo [23] ascribe the difference in the ratio of Barton products (A and C, Fig. 4), obtained during the photolysis of alkyl nitrites in micellar media and hexane respectively, to an internal viscosity which inhibits the diffusion of the cage radicals. Irradiation in KDC resulted in products A, B and C (Fig. 4), C being the main product (A was the main product in hexane). The formation of ketone (C) has been attributed to the disproportionation of the alkoxy radical formed by nitrite photolysis as a result of which its rate of formation is controlled by diffusion. The formation of A is viscosity dependent since the nitric oxide must diffuse to the radical centre.



	A	B	C	A/C
n - hexane	40 %	12%	4.8 %	8.3
hexadecane	13	17	15	0.87
KDC micelle	5.4	16	39	0.14

- A Methyl 6-hydroxy-9-oxo-dodecanoate
B Methyl 6-hydroxy dodecanoate
C Methyl 6-oxo-dodecanoate

Fig. 4. Photolysis of alkyl nitrites.

Yet another reaction which is subjected to the micellar cage effect is the photoreduction of carbonyl compounds [24]. When benzophenone itself is dissolved in detergent solutions, the photochemical processes are affected by the structure of the micelle. The micelle sequesters the radical pair (ketyl radical and hydrogen donor radical) so that efficient intersystem crossing may occur. In most cases, the hydrogen donor is the detergent itself so that when intersystem crossing occurs, the benzophenone attaches itself to the micellar backbone. The magnetic isotope effect on the lifetime of the observed transients as well as on the degree of cage recombination has been studied by various groups [24].

The photolysis of diphenylmercury is also known to be influenced by the micellar effect [25]. When nitrogen-saturated solutions of diphenylmercury are irradiated benzene is found to be the main product. No trace of biphenyl (the radical recombination product) was detected either in hexane or in methanol. However, in CTAB and SDS micellar solutions a significant amount of biphenyl was detected. This indicates that the hydrophobic effect prevents non-polar radicals such as phenyl from diffusing out of the micelle and enhances the re-encounter probability.

The increase in the quantum yield of fluorescence of stilbenes and cyanine dyes in micelles (with respect to organic solvents) is attributed to the higher microviscosity of the micelle [26]. A surfactant stilbene has been synthesized for use as a viscosity probe of micellar systems. The surfactant stilbene undergoes photochemical trans-cis isomerization with quantum yields very similar to stilbenes. Like stilbene, the quantum yield ($\Phi_{t \rightarrow c}$) of surfactant stilbene decreases with viscosity while the quantum yield of fluorescence increases. For example, $\Phi_{t \rightarrow c}$ decreases from 0.5 in CH_2Cl_2 to 0.39 in CTAB while Φ_{f1} increases from 0.04 in CH_2Cl_2 to 0.18 in CTAB. A similar increase in fluorescence quantum yield for cyanine dyes in SDS has also been reported.

3. Localization and compartmentalization effects

The most striking feature of micelles is their ability to solubilize a variety of compounds. The dynamics of solute partitioning has been studied using luminescence probes [27]. Such studies have revealed that in the time scale 1 - 100 ns micelles form physically discrete cells among which the solute molecules distribute themselves. Poisson statistics have been found appropriate for this distribution:

$$P(n) = \frac{\langle S \rangle^n}{n!} \exp(-\langle S \rangle)$$

where $P(n)$ is the probability of finding a micelle with n solute molecules and $\langle S \rangle$ is the "mean occupancy number" or ratio of the bulk concentration of solute molecules to the bulk concentration of micelles. It is evident that two situations are possible: (a) the substrate concentration is such that the

probability of multiple occupancy of a micelle is large ($\langle S \rangle = 3$). This leads to localization of the reactant and hence the production of extremely high local concentrations favourable to bimolecular reactions; (b) the substrate concentration is such that most of the micelles are "empty" at any given instant, *i.e.* less than 10% of the micelles contain one or more solute molecules ($\langle S \rangle = 0.1$). (b) leads to the compartmentalization of the favourable reactants for unimolecular processes. Both these situations have been exploited to control photochemical processes.

Increasing the occupancy number of a micelle and thereby the local concentration of reactant causes an increase in the efficiency of bimolecular photochemical reactions relative to that in non-aqueous or aqueous systems. This is the "micellar catalysis" effect and has been observed in many bimolecular photochemical reactions. Estimated rate enhancements of up to 10^3 compared with homogeneous rates are expected, so reactions that are relatively inefficient in homogeneous solutions may become quite efficient in the presence of micelles. The photodimerization of acenaphthylene [28] and coumarin [29], the photocycloaddition of acenaphthylene to acrylonitrile and methylacrylate [30] and the photocycloaddition of isobutylene to cyclohexenone [31] are a few examples that illustrate the local concentration or micellar catalysis effect (Figs. 5 and 6).

The compartmentalization of reactants is a feature unique to micellar systems, leading to the "protection" of the excited singlet and triplet states of the molecules by the suppression of bimolecular quenching processes. The potential of this property of micelles to control unimolecular photochemical processes has been demonstrated by Turro and coworkers

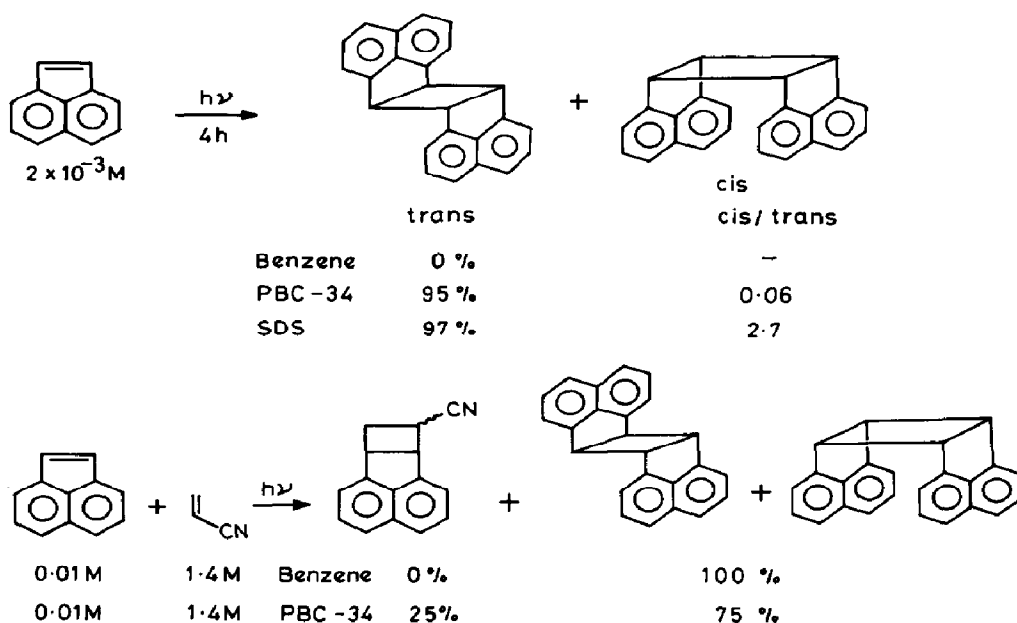
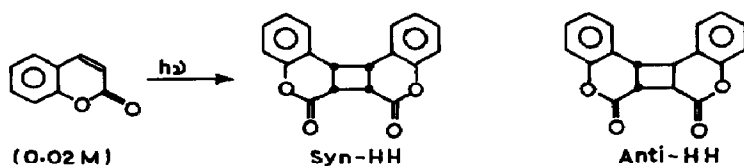


Fig. 5. Micellar catalysis effect (see text).



<u>Solvent</u>	<u>Product</u>	<u>Quantum yield</u>
Methanol	Anti-HH	$< 10^{-5}$
Benzene	Anti-HH	$< 10^{-5}$
Water	Syn-HH	2×10^{-3}
S D S	Syn-HH	2×10^{-3}
C T A B	Syn-HH	0.3×10^{-3}
Triton X-100	Syn-HH	1×10^{-3}

Fig. 6. Micellar catalysis effect (see text).

[32]. Phosphorescence was clearly observed on solubilization of 1-bromonaphthalene, naphthalene, pyrene and triphenylene in micelles (SDS, CTAC and CTAB) under conditions where the multiple occupancy of the micelles was low. Phosphorescence, though weak, was observable even in aerated micellar media; under similar conditions, no phosphorescence emission was detected in organic solvents. This observation has been attributed to the protection of the triplet states from oxygen quenching and other bimolecular quenching processes such as triplet-triplet annihilation and self-quenching. This technique of micellar compartmentalization has been used by Ramesh and Ramamurthy [33] to inhibit the diffusion-controlled self-quenching process in thioketones. Avoiding multiple occupancy of micelles, they observed an enhanced phosphorescence intensity in nitrogen-purged micellar solutions compared with that in acetonitrile, indicating that thioketone triplet was indeed protected from deactivation by ground state thioketone.

4. Pre-orientational effects

UV studies have led to the conclusion that aromatic probe molecules are mildly surface active and reside at the micellar surface. Alkyl-substituted benzenes and naphthalene show an increasing tendency to reside in the hydrocarbon core on increasing the length of the substituent chains on the aryl ring [34, 35]. The same general results were found using nuclear magnetic resonance (NMR) probes [35]. Similar conclusions were drawn for benzophenone, anthracene [36], acridine and methyl indole [37]. In general, it has been shown that benzene and higher arenes are mildly surface

active and are located at the interface of ionic micelles near the head group [37]. Also, molecules with polar substituents such as $-\text{CN}$, $-\text{NH}_2$, $-\text{OH}$ and $-\text{C}=\text{O}$ tend to accumulate at the surface of the micelle [38]. However, simple alkanes, *e.g.* hexane, are expected to solubilize in the micellar core owing to their similarity to the surfactant chains.

Organic compounds with a hydrophilic functional group have thus been demonstrated to reside primarily at the micellar interface. These hydrophilic groups tend to interact with the aqueous exterior and this should cause the solubilized molecules to reside at the interface in a specific orientation. The probability of such a process is enhanced when the solubilized molecules have suitably placed hydrocarbon chains (by virtue of their hydrophobicity) that force them into the micellar core. This tendency of solubilized molecules to become specifically oriented in the ordered micelle environment is known as the "pre-orientational effect".

By combining both hydrophobic and hydrophilic moieties in the solubilized molecules, the alignment of the latter into a specific geometry should be facilitated. The alignment of the substrate in the micellar media may affect the regiochemistry of the product in the case of photoannulation reactions, by restricting the possible approaches of the reactants. Recent reports describe the potential of micellar pre-orientation in achieving regioselectivity for dimerizations.

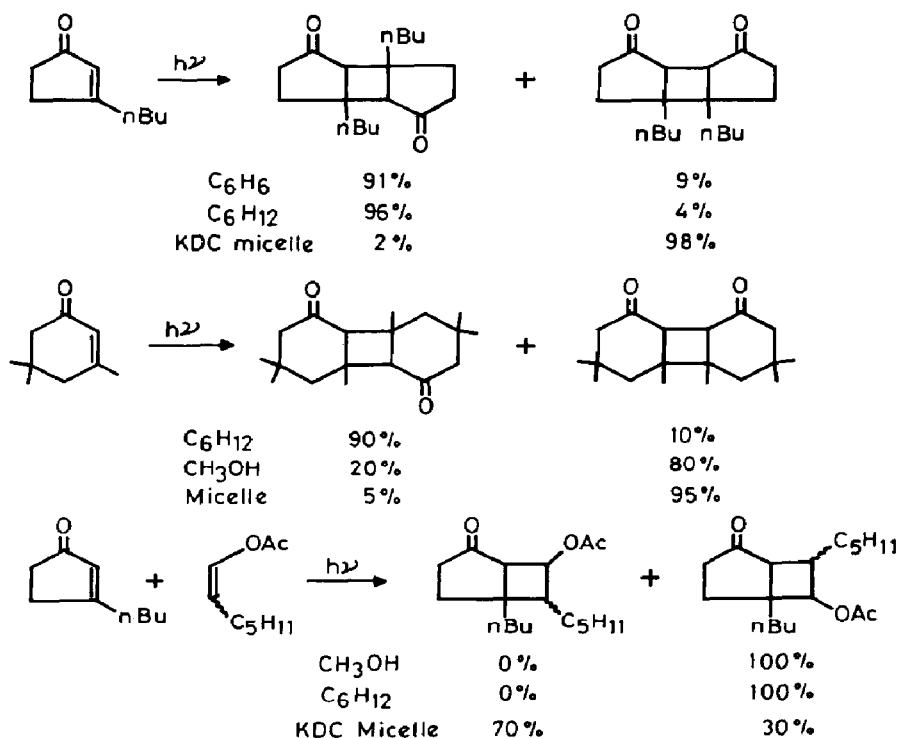


Fig. 7. Irradiation of cycloalkenones in KDC micelles.

de Mayo and coworkers [39,40] have reported that irradiation of 3-alkylcyclopentenones in KDC micelles leads to a greatly increased efficiency for dimerization compared with that in homogeneous solution. Irradiation of 3-*n*-butyl- and 3-*n*-decylcyclopentenone in KDC micelles leads to a complete reversal in regioselectivity with the formation of the corresponding head-head dimer in about 98% yield (Fig. 7). These compounds dimerize in organic solvents to the corresponding head-tail dimer in preference to the head-head dimer although the ratio of head-tail to head-head approaches 1:1 in methanol and acetonitrile (Fig. 7). However, the complete reversal in micelles has been ascribed to a specific micellar effect and it is suggested that this is not due to polarity of the medium. Pre-orientation is expected to result from the enones being oriented with the carbonyl group in the Stern layer and the alkyl group in the core. These results have been successfully extended to mixed cycloadditions between 3-alkylcyclopentenones and olefins with a reversal in regioselectivity compared with that in organic solvents [40]. The expected orientation of enones and olefins in micelles is shown in Fig. 8.

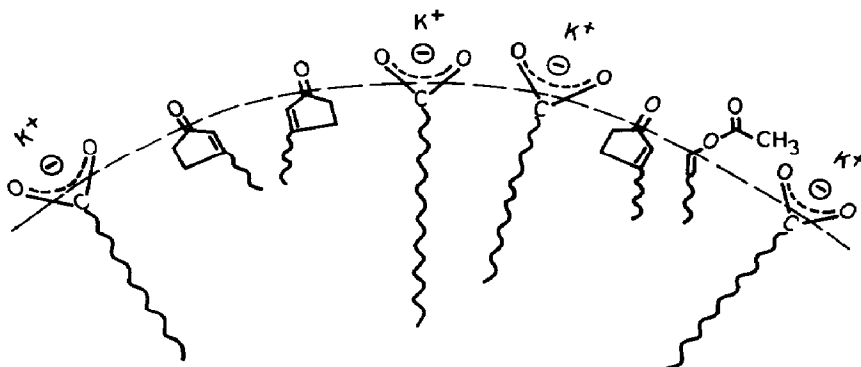


Fig. 8. Expected orientation of enones and olefins in micelles (see Section 4).

The dimerization of isophorone has been shown to be enhanced in micellar systems and microemulsions [31]. The formation of dimers in organic solvents depends, as in the previous case, on the polarity of the medium. Head-tail dimers are formed as major products in non-polar solvents while polar solvents enhance head-head dimerization. In micellar media head-head dimers are formed in high yields, presumably owing to the micellar alignment effect.

Nakamura *et al.* [41] have obtained a similar reversal in regioselectivity in the [4 + 4]-dimerization of 2-pyridones. These dimerize in ethanol to give the corresponding trans dimers as the major product. In CTAB, appropriate substitution of 2-pyridones by long chains leads to a reversal in regioselectivity (Fig. 9). Similarly, in the case of [4 + 4]-photodimerization of 9-(hydroxymethyl)anthracene [42], the formation of head-head dimers is promoted by micellar media (Fig. 10).

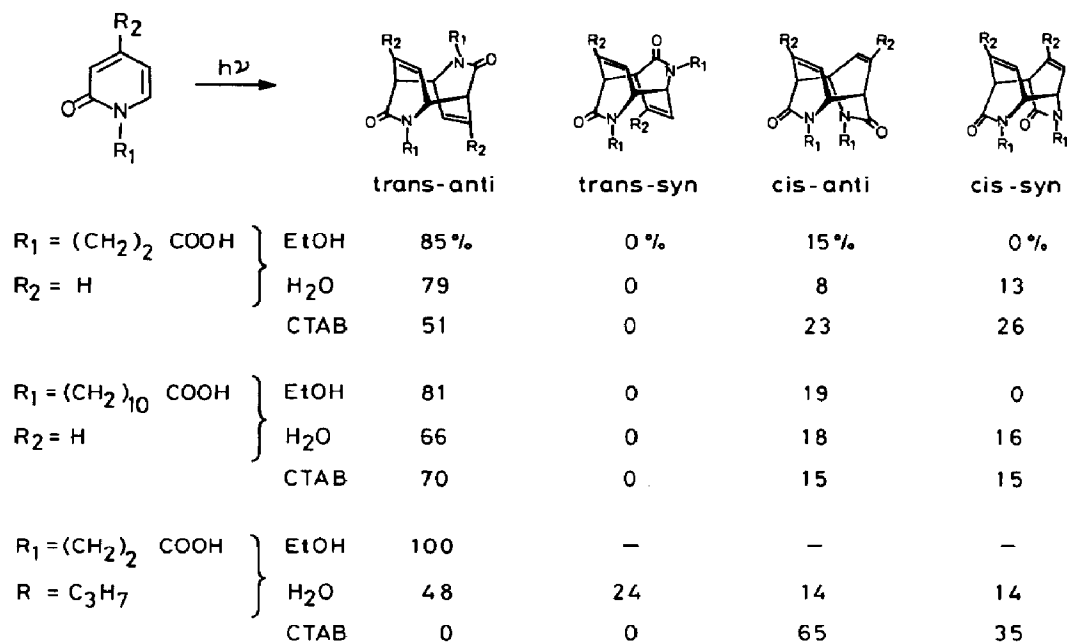
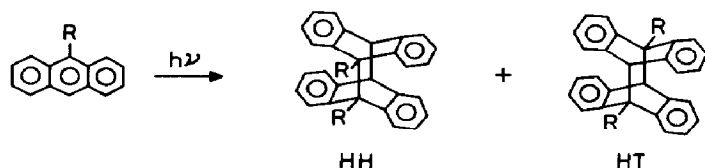


Fig. 9. Photodimerization of 2-pyridones in CTAB.



	Ratio of HT vs. HH			
	Benzene	Ether	Methanol	SDS Micelle
$R = \text{CH}_2\text{OH}$	2.9	1.2	3.2	0.67
$= \text{CH}_2\text{CH}_2\text{COOH}$	—	3.5	8.9	0.91
$= \text{COOH}$	—	4.9	6.5	2.30

Fig. 10. [4 + 4]-photodimerization of substituted anthracenes.

The pre-orientational effect of micelles in controlling the regiochemistry of photodimerization of 2-substituted naphthalenes has also been reported [43]. In organic solvents the trans dimer is the major product (Fig. 11). When the photolysis of 2-substituted naphthalenes solubilized in micellar media was carried out the ketones and the cage products were the only products isolated. The exclusive formation of the cis dimer or products derived therefrom has been attributed to the ability of micelles to pre-orient the 2-substituted naphthalenes at the micellar interface in such a manner that the hydrophilic groups ($-\text{OR}$, $-\text{COOR}$ or $-\text{CN}$) are directed towards the polar exterior and the aromatic naphthyl moiety is directed towards the micellar interior.

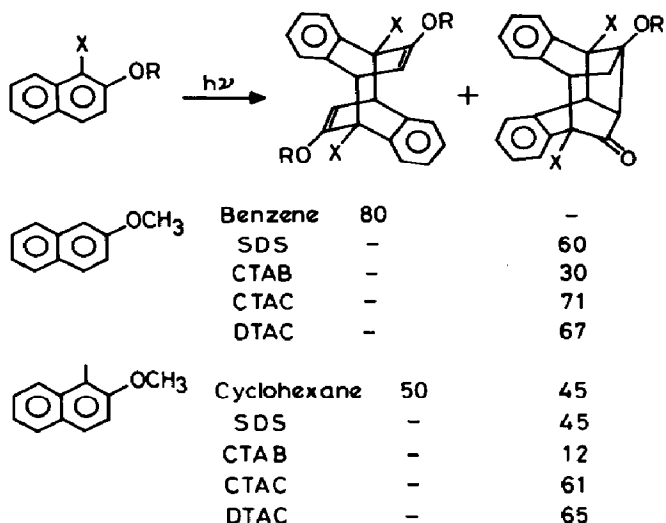
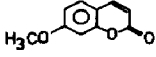
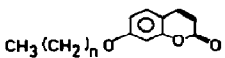


Fig. 11. Photodimerization of 2-substituted naphthalenes.

It has been suggested that the micellar alignment effect is responsible for the regioselectivity so far observed. However, the Stern region is quite polar and since the cyclopentenone systems studied exhibit a polarity-dependent product distribution, the contributions due to the polarity cannot be ruled out. Thus in order to identify the extent of the pre-orientational effect due to micellar alignment and its influence on the regioselectivity of photocycloadditions, such polarity effects should be excluded. 7-Alkoxy coumarins which dimerize in organic solvents to give the corresponding syn head-tail dimer irrespective of the solvent polarity have been used as models in order to eliminate any polarity effects in the polar Stern region [44]. Micellar solubilized 7-alkoxy- and 4-methyl-7-alkoxy coumarin molecules are expected to be arranged so that the carbonyl groups are directed towards the polar exterior while the aromatic parts lie towards the hydrocarbon-like interior of the micelles (Fig. 12). Irradiation of the shorter chain coumarins ($n = 0 - 5$) (Table 2) in micellar media did not lead to the expected reversal in regioselectivity during photodimerization in contrast to the efficient reversal observed by previous workers using similar chain lengths but different systems. The chain lengths were increased beyond C_5 up to C_{18} and it was expected that the accompanying increase in hydrophobicity of the reactant molecules would lead to a more effective micellar alignment. However, contrary to these expectations, no reversal in regioselectivity was obtained. This led to the conclusion that the micellar orientational effect is most effective in those systems where the forces that control the regiochemistry are weaker than the hydrophobic association energies induced by the associated alkyl chains.

TABLE 2
Irradiation of coumarins in micellar media

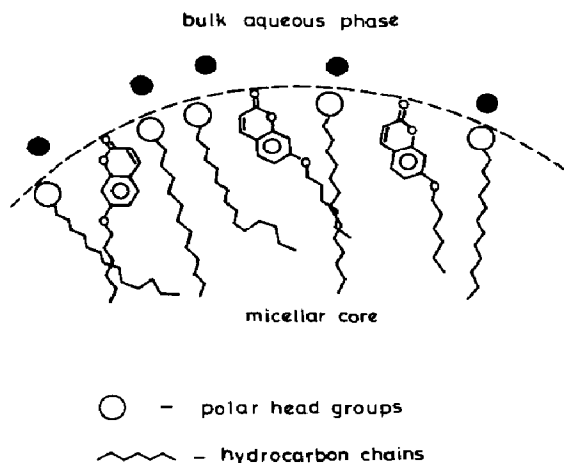
Coumarin	Nature of dimer				
	Solvent			Micelle	
	Chloroform ^a	Benzene ^a	Water ^b	SDS ^c	CTAB ^c
	SHT	No reaction	SHT	SHT	SHT
					
$n = 3$ (butyl)	SHT	No reaction	Insoluble	SHT	SHT
$n = 5$ (hexyl)	SHT	No reaction	Insoluble	SHT	SHT
$n = 6$ (heptyl)	SHT	No reaction	Insoluble	SHT	SHT
$n = 7$ (octyl)	SHT	No reaction	Insoluble	SHT	SHT
$n = 11$ (dodecyl)	SHT	No reaction	Insoluble	SHT	SHT
$n = 15$ (hexadecyl)	SHT	No reaction	Insoluble	SHT	SHT
$n = 17$ (octadecyl)	SHT	No reaction	Insoluble	SHT	SHT
				AHT	}
				(1:2)	

SHT, syn head-tail; AHT, anti head-tail.

^a[Coumarin] = 0.2 M.

^b[Coumarin] = 0.002 M.

^c[Coumarin] = 0.006 M.



Expected orientation of long chain
coumarin molecules in micelles.

Fig. 12. Expected orientation of long-chain coumarin molecules in micelles.

5. Polarity effects

Polarity effects exist because the interior of a micelle is less polar than the aqueous phase but more polar than the hydrocarbon solvent. Therefore reactions affected by polarity will have different reactivities in micelles compared with those in aqueous solution or organic solvents. The actual polarity experienced by a solute molecule will be a time-averaged value of that of the various environments through which the molecule passes. There is a bewildering array of opinions regarding the penetration of water into the micelle, which is a factor contributing to its polarity. Almost any conceivable model of hydration finds support somewhere in the literature. At one extreme lies the "reef" model (water does not penetrate beyond the ionic head group) and at the other extreme is the "fjord" model in which water percolates almost to the centre of the micelle. Intermediate schemes are also available.

It has been established that aromatic molecules and substrates bearing hydrophilic groups are solubilized at the micelle-water interface, which is a region of high polarity. Solvent-sensitive photochemical reactions of substrates located in such regions would result in products corresponding to those produced in solvents of high polarity. Conversely, such reactions also serve as sensors of the polarity of the microenvironment. The type II reaction of phenylheptyl ketone illustrates this feature (Fig. 13) [45]. The quantum yield of the reaction is 0.7 in CTAC and $[\text{cis-cyclobutanol}]/[\text{trans-cyclobutanol}] = 1.2$. These values are much closer to those for the type II reaction in *t*-BuOH (Bu \equiv butyl) ($\Phi = 1.0$, $[\text{cis}]/[\text{trans}] = 1.5$) than those in benzene ($\Phi = 0.33$, $[\text{cis}]/[\text{trans}] = 4.7$) suggesting that the environment around the site of solubilization of the ketone is polar. Recently, Whitten and coworkers drew similar conclusions [46].

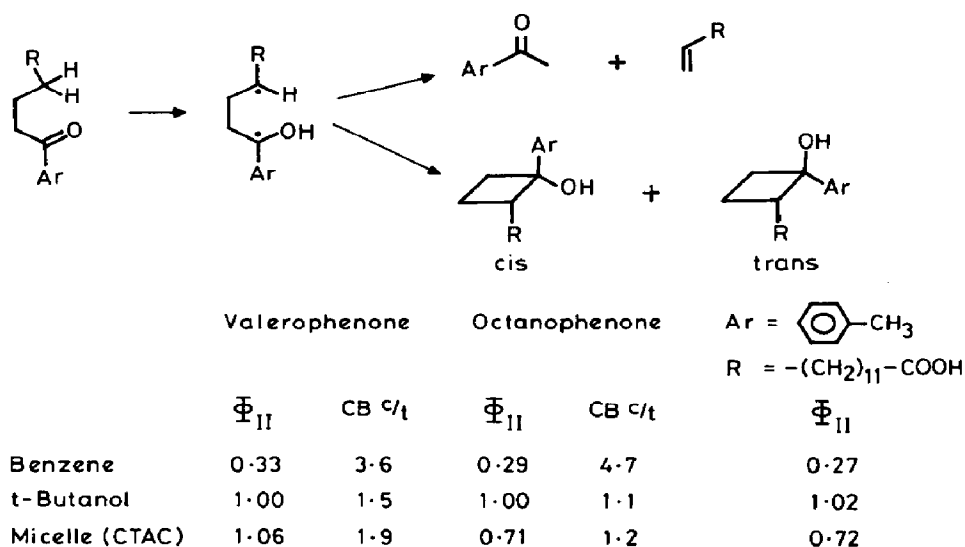


Fig. 13. Type II reaction of phenylalkyl ketones.

Coumarin dimerizes in solution to give four different dimers. The syn head-head and head-tail dimers are generally predominant in polar solvents. Muthuramu and Ramamurthy [29] observed that in micellar media such as SDS and CTAB the reactivity and emission intensity of coumarin are enhanced significantly. Also, the syn head-head dimer is the sole product in these micelles. The selectivity in the formation of the dimer and the enhanced reactivity are attributed to the polar environment in which coumarin undergoes dimerization.

It has been reported that the chemiluminescence of hydrophobic 9-methyleneacridans is increased dramatically in micelles compared with aqueous solution owing to the decreased polarity in the interior of the micelles [47]. From the results reported it appears that the reactant is solubilized in the interior of the micelle.

6. Counterion effects

Ionic micelles have the property of being able to bind oppositely charged ions. Together with their ability to solubilize hydrophobic molecules this property has been utilized in reactions involving organic substrates and metal ions.

For example, it has been shown that adsorbed metal ions on anionic micelles can act as efficient electron acceptors from excited micelle-solubilized donors [48]. The replacement of the Na^+ ions in sodium dodecylsulphate by Cu^{2+} yields assemblies in which Cu^{2+} ions constitute the counterion of the micelle. When donor (D) molecules such as *N,N'*-dimethyl-5,11-dihydro-indolo[3,2-*b*]carbazole are incorporated into such micelles and irradiated, extremely rapid electron transfer occurs from the excited singlet state of D to the Cu^{2+} counterion. The Cu^+ ion formed in the aqueous phase can be used for a second redox process such as the reduction of $\text{Fe}(\text{CN})_6^{3-}$. The back reaction of the $\text{Fe}(\text{CN})_6^{4-}$ with the oxidized donor D is prevented by the negatively charged micellar surface. Such a system, therefore, has been successful in storing light energy originally converted into chemical energy during a photoredox process.

Yet another feature of counterions is that they function as heavy atoms. Love and Skrilec and Thomas *et al.* [48] have shown that by replacing the Na^+ ions of SDS by Tl^+ ions the rate of phosphorescence of aromatic hydrocarbons such as naphthalene and pyrene which have been solubilized in such micelles can be enhanced at room temperature. This observation has been attributed to the heavy-atom-counterion-induced intersystem crossing of aromatic excited singlet states to triplet states. The above observations suggest that by using micelles with different counterions it may be possible to attain state selectivity in the reactive state of a photochemical reaction or photophysical processes. Wolff [49] observed that the quantum yields of fluorescence of excited aromatic molecules such as substituted anthracenes, indenes and *N,N*-diphenylamine show an increase in CTAC compared with

CTAB and, conversely, a lower quantum yield of triplet formation is exhibited in CTAC compared with CTAB. An interesting observation is the enhancement in triplet-state derived products from the photodimerization of acenaphthylene. The irradiation of acenaphthylene in solution has been studied extensively. It has been established that the excited singlet yields exclusively the cis dimer (Fig. 14) while the triplet state yields a mixture of trans and cis dimers in the ratio 9:1 (Fig. 14). Ramesh and Ramamurthy [50] and Mayer and Sauer [51] independently found that the [cis]/[trans] value in CTAB is about half that in CTAC and SDS under identical conditions (Fig. 14). At a lower bulk concentration of the reactant (1.3 mM compared with 8 mM in the above case) the photodimerization is almost exclusively via the triplet channel in CTAB, whereas in CTAC, DTAC and SDS micelles the singlet-state derived cis dimer still predominates. The low [cis]/[trans] value has been attributed to the "external heavy-atom effect" of the bromide counterions, it being suggested that these enhance the $S_1 \rightarrow T_1$ intersystem crossing via intermolecular spin-orbit coupling, and the yield of the triplet-derived trans dimer is increased. Similar observations have been made in the case of 5,6-dichloroacenaphthylene. These results on the photodimerization of acenaphthylenes in micellar media suggest that for photochemical reactions that proceed via competing singlet states and triplet states, state selectivity can be achieved by utilizing heavy-atom counterions for triplet-state products and light-atom counterions for predominantly singlet-state products. However, this technique has its limitations. Firstly,

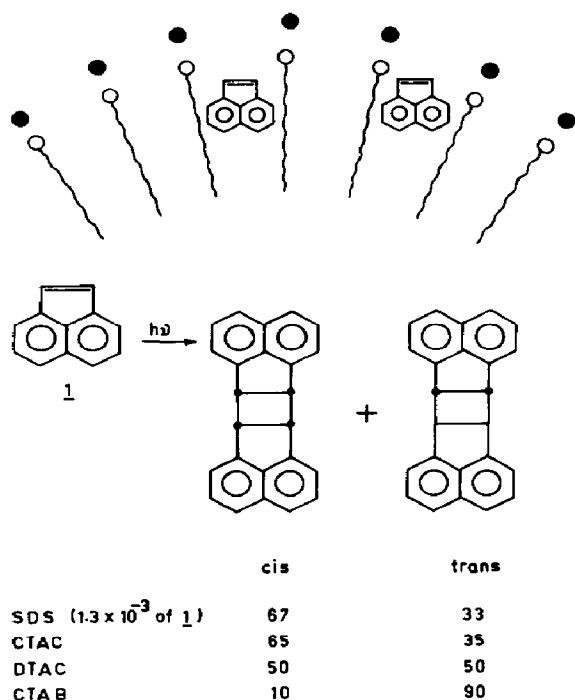


Fig. 14. Irradiation of acenaphthylene.

the photochemical reaction should be sensitive to the heavy-atom effect. Secondly, the $S_1 \rightarrow T_1$ intersystem crossing should be more sensitive to heavy-atom perturbation than $T_1 \rightarrow S_0$. If the latter is more sensitive, then the use of micelles having heavy-atom counterions will result in a reduction in the yield of triplet-derived products.

7. Charged micelle-water interfaces

The aggregation of ionic amphiphiles leads to a distribution of ionic head groups and counterions which produces a charged micelle-water interface. The electrically charged interface has been utilized to accelerate or retard reaction rates between a micelle-solubilized substrate and an ionic reactant in the aqueous exterior. Depending on whether the charge of the detergent causes repulsion of an attacking nucleophile or organization through attraction, a retardation or acceleration of the reaction results. Such effects have been utilized in the photoinduced substitution reactions of aromatic compounds. The photoinduced conversion of 4-methoxy-1-nitronaphthalene to 4-methoxy-1-naphthalenecarbonitrile and the photorearrangement of 4-nitrobenzaldehyde (Fig. 15) illustrate the influence of this effect [52, 53].

4-Methoxy-1-nitronaphthalene and 1-nitronaphthalene undergo photochemical aromatic substitution reactions with cyanide. SDS micelles decrease the quantum yield compared with aqueous solution. However, a 6800-fold increase in quantum yield was observed for 4-methoxy-1-nitronaphthalene in CTAC micelles. The higher local concentration of CN^- ion near the CTAC micelles can at least partially explain the increase in quantum yield [52].

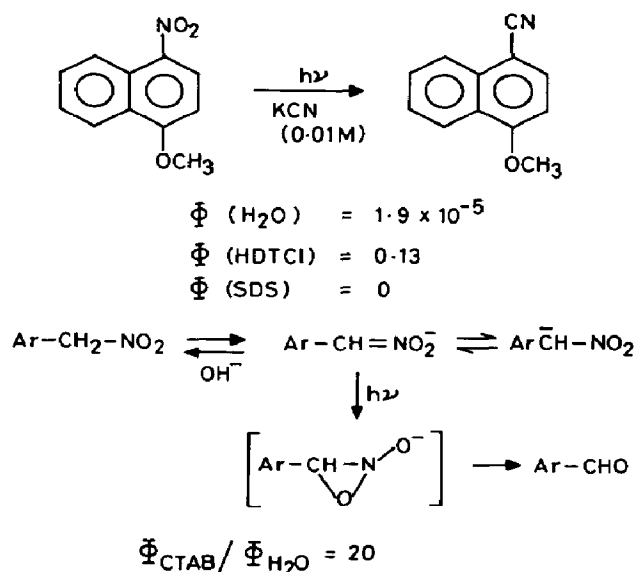


Fig. 15. Photoreactions of nitroaromatics.

The photoconversion of 4-nitrophenylnitromethane to 4-nitrobenzaldehyde in an ethanol-water system was found to proceed by an intramolecular rearrangement of oxygen to the adjacent nitro group. A cationic surfactant increased the quantum yield of this photorearrangement by a factor of 20. This is thought to result from the electrostatic interaction of the cationic head groups of CTAB with the anionic form [53].

The charged micelle-water interface plays an important role in photoreactions for the storage of light energy. However, since these reactions typically do not produce permanent products and since they have been reviewed regularly they are not presented here.

An intimate knowledge of the precise molecular structure of micelles would certainly promote a more intelligent exploitation of micelle-mediated processes. We foresee a lot of activity in the coming years based on the control of reactivity using micelle and micelle-like systems.

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