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Micellar control of photochemical reactions

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Abstract. Micelles as media for chemical reactions exhibit features that are unique in comparison to ordinary non-aqueous or aqueous solvent media. A thermal or photochemical reaction conducted in micellar media is influenced by the micellar environmental effects resulting in control and/or modification of reactivity. The salient features of micelles and their influence on photochemical reactivity are briefly discussed in this paper.

Keywords. Micelles; cage effect; pre-orientational effect; polarity effect; counterion effect; photochemical reactions.

1. Introduction

The study of photophysical processes and photochemical reactions in ordered molecular assemblies like micelles, microemulsions, vesicles, monolayer films, supported multilayer assemblies and constrained phases like liquid and molecular crystals has added a new dimension to photochemistry (Fendler 1984). Amongst the various ordered molecular assemblies micellar systems have been well investigated. Sensitivity of photophysical processes and photochemical reactions to environmental perturbations have been utilized to probe the nature of micellar aggregates. Understanding the architecture of micelles has helped in its utility as a reaction medium. The potential of micellar effects to bring about catalysis and specificity in photochemical and thermal reactions has been demonstrated. The unique feature of micelles, and how these have been utilized to catalyse and control photochemical reactivity are highlighted in this paper through a brief survey of reports on photochemical reactions in micellar media.

2. Localization, compartmentalization and cage effect

The most striking feature of micelles is the ability to solubilize a variety of compounds. The dynamics of solute partitioning has been studied using luminescence probes. Such studies have revealed that in the time scale 1–100 n sec micelles form physically discrete cells among which the solute molecules distribute themselves. Poisson statistics has been found to be appropriate for this distribution. Poisson statistics leading to solute distribution is given by

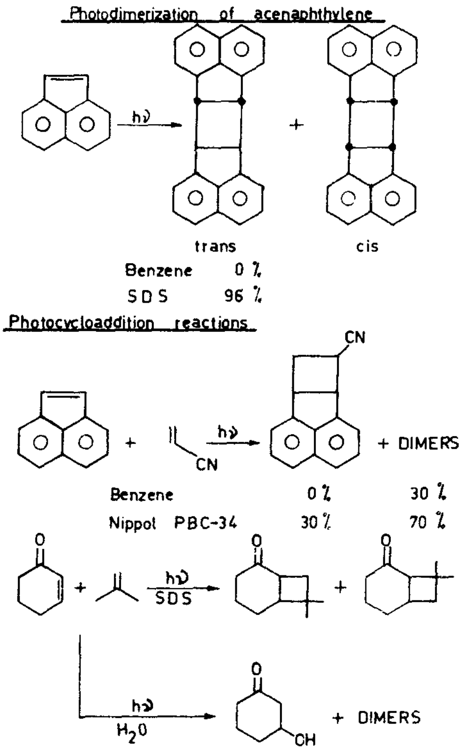
$$P(n) = \frac{S^n}{n!}\exp(-S),$$

where $P(n)$ is the probability of finding a micelle with n solute molecules and S is the "mean occupancy number" or ratio of the bulk concentration of solute molecules to a bulk concentration of micelles. It is evident that two situations are possible: (i) The substrate concentration is such that the probability of multiple occupancy of a micelle is large ($S = 2, 3$). This leads to localization of the reactant and hence extremely high local concentrations favourable for bimolecular reactions. (ii) The substrates 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 ($S = 0{\cdot}1$). This situation leads to the compartmentalization of the reactants favourable 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. The photodimerization of acenaphthylene (Nakamura *et al* 1977), photocycloaddition of acenaphthylene to acrylonitrile (Nakamura *et al* 1978) and methylacrylate and photocycloaddition of isobutylene to cyclohexenone (Fargues *et al* 1979) (scheme 1) are a few examples which illustrate the local concentration or micellar catalysis effect.

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 suppressing bimolecular quenching processes. The potential of this feature of micelles to selectively effect unimolecular photochemical processes has been demonstrated by Turro *et al* (1978). Solubilization of 1-bromonaphthalene, naphthalene, pyrene and triphenylene in micelles (SDS, CTAC and CTAB) under conditions where multiple occupancy of a micelle was low resulted in the ready observation of phosphorescence from these compounds. Phosphorescence though weak was observable even in aerated micellar media

Scheme 1



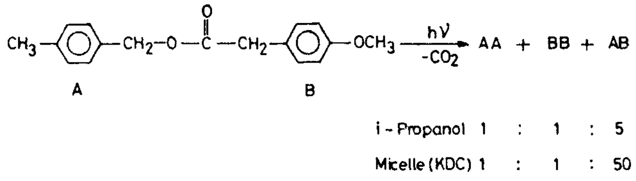
although, under similar conditions, no phosphorescence emission was detectable in organic solvents media. This observation has been attributed to the 'protection' of the triplet states from oxygen quenching and other bimolecular quenching processes like triplet-triplet annihilation and self-quenching. This technique of micellar compartmentalization has been used by Ramesh and Ramamurthy (1982) to inhibit the diffusion-controlled self-quenching process in thioketones. Avoiding multiple occupancy of the micelles, they observed 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.

Micellar cage-effect is observed when a hydrophobic radical pair is generated in a micelle. In such a situation the probability of cage reaction between spin correlated radical pairs increases relative to reaction of free radicals without spin correlation.

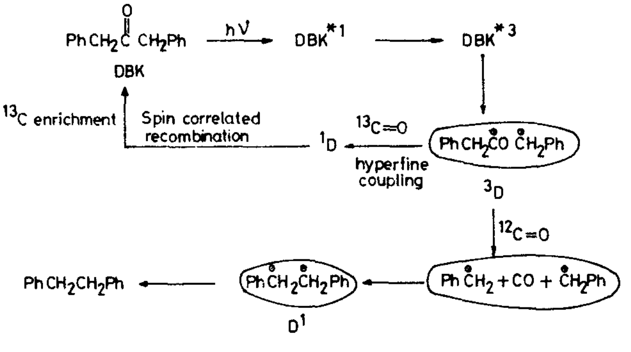
The photodecarbonylation of unsymmetrical dibenzyl ketones A-CO-B in homogeneous solutions occurs *via* free radicals to produce A-B, A-A and B-B in the statistical distribution of 50 : 25 : 25. In contrast when the reaction is conducted in CTAC micelles, a non-statistical distribution of approximately 98 : 1 : 1 is obtained (Turro 1983) (scheme 2). Also the yield is a function of CTAC concentration thus exhibiting a significant enhancement of radical cage reactions of hydrophobic radical pairs relative to homogeneous solutions. An interesting aspect of this 'cage effect' of micelles is the observed ^{13}C enrichment of reactants involved in free radical reactions.

The photolysis of dibenzyl ketone (DBK) (scheme 3) proceeds *via* an initial triplet radical pair (^3D). Inter-system crossing of a radical pair such as ^3D occurs *via* a nuclear hyperfine induced mechanism. Since ^{12}C does not possess a nuclear moment, hyperfine radical pairs with ^{13}C will undergo more rapid inter-system crossing than radical pairs with ^{12}C. Scheme 3 shows the various processes possible. Since ^1D and $^1D'$ radical pairs

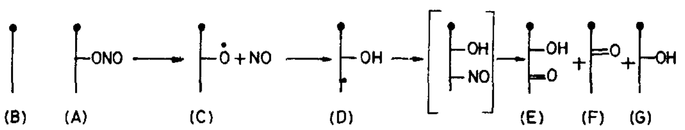
Scheme 2



Scheme 3



Scheme 4



	(E)	(F)	(G)
Micelle (KDC)	5·4%	39%	16%
Hexane	40%	4·8%	12%

can undergo recombination and $^3D/^3D'$ cannot, ^1D and $^1D'$ radicals are formed enriched in ^{13}C. As the photoreaction proceeds, therefore, the starting material is found to be enriched in ^{13}C (Flutton *et al* 1979). The magnitude of enrichment is relatively small for homogeneous solution but increases by over an order of magnitude in 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 result. Similar observations with other carbonyl systems have been made (Turro and Krauetler 1980).

Law and de Mayo (1978) ascribe the difference in the ratio of Barton products (E, F, scheme 4), obtained during the photolysis of alkyl nitrites in micellar media and hexane respectively, to internal viscosity which inhibits diffusion of the cage radicals. Irradiation (A) in potassium dodecanoate (B) resulted in products E, F and G (scheme 4). The yield of F was maximum compared to that of E in hexane. The formation of ketone (F) has been attributed to the disproportionation of the alkoxyl radical formed by nitrite photolysis as a result of which its rate of formation is controlled by diffusion process. The formation of E is viscosity-dependent since the nitric oxide must diffuse to radical centre at D.

3. Preorientational effect

Organic compounds with a hydrophilic functional group have been demonstrated to reside primarily at the micellar interface. These hydrophilic groups interact favourably with the aqueous exterior which is expected to cause the solubilizates to reside at the interface in a specific orientation. Such a condition is enhanced when the solubilizates have suitably placed hydrocarbon chains by virtue of their hydrophobicity that forces it into the micellar core. This predisposition of the solubilizates to get oriented into a specific fashion in the ordered environment of micelles is known as the "preorientational effect".

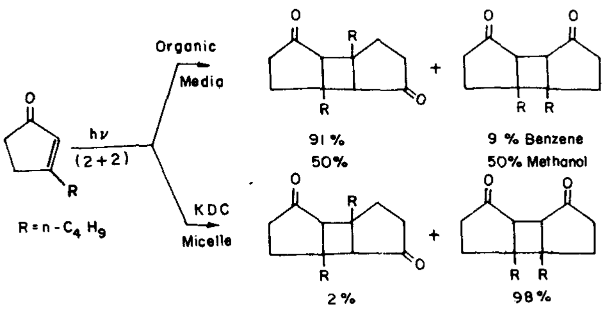
A combination of hydrophobic and hydrophilic moeities on the solubilizate is expected to lead to better alignment of the solubilizates into a specific geometry. Alignment of the substrate in micellar media may affect the regiochemistry of the product, in the case of photoannulation reactions, by restricting the possible approaches of the reactants. Recent reports describe the potential of micellar preorientation in achieving regioselectivity of dimerizations.

Mayo and coworkers (Lee and de Mayo 1979; de Mayo and Sydnes 1980; Berenjian *et al* 1982) have reported that irradiation of 3-alkylcyclopentenones in potassium dodeconoate (KDC) micelles leads to greatly increased efficiency of dimerization over that in homogeneous solution. Irradiation of 3-*n*-butyl and 3-*n*-decylcyclopentenone in KDC micelle leads to complete reversal in regioselectivity with the formation of the compounds corresponding to head-head dimer 98 % (scheme 5). These 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 methanol and acetonitrile (scheme 5). However the complete reversal in micelles has been ascribed to a specific micellar effect and is suggested that it is not due to the polarity of the medium. Preorientation is expected to be the result of 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 as compared to that in organic solvents (Berenjian *et al* 1982).

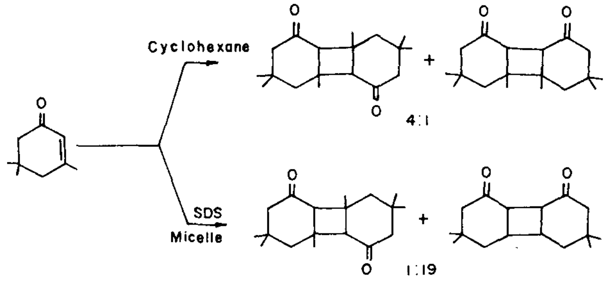
Dimerization of isophorone (scheme 6) has been shown to be enhanced in micellar and microemulsion systems (Fargues *et al* 1979, 1982). Formation of dimers in organic solvents depends, as in the previous case, on the polarity of the medium. Head-tail dimers are formed as major products in nonpolar solvents while polar solvents enhance head-head dimerization. In micellar media head-head dimers are formed in high yields, presumably due to the micellar alignment effect.

Nakamura *et al* (1981) have obtained a similar reversal in regioselectivity of 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 (scheme 7). Similarly in the case of

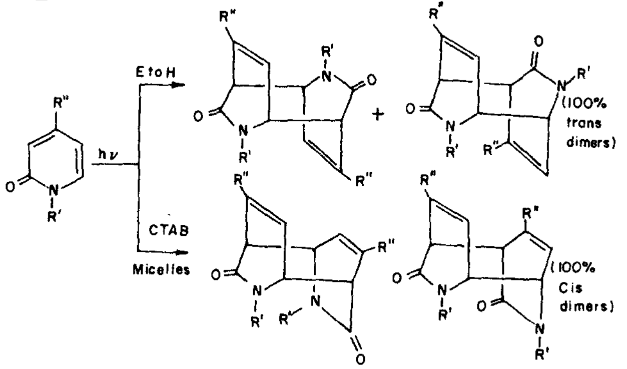
Scheme 5



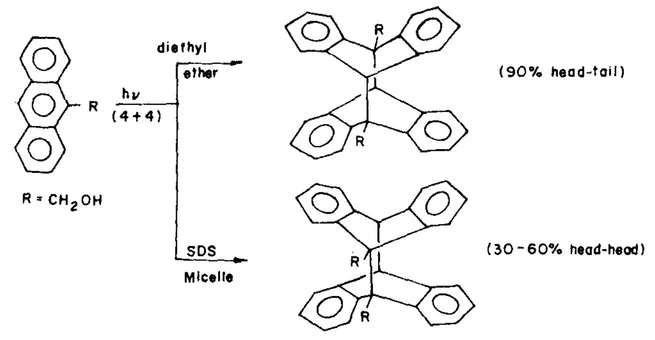
Scheme 6



Scheme 7

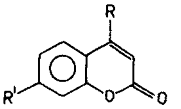


Scheme 8



4 + 4 photodimerization of (hydroxymethyl) anthracene (Wolf 1981), formation of head-head dimer is promoted in micellar media (scheme 8).

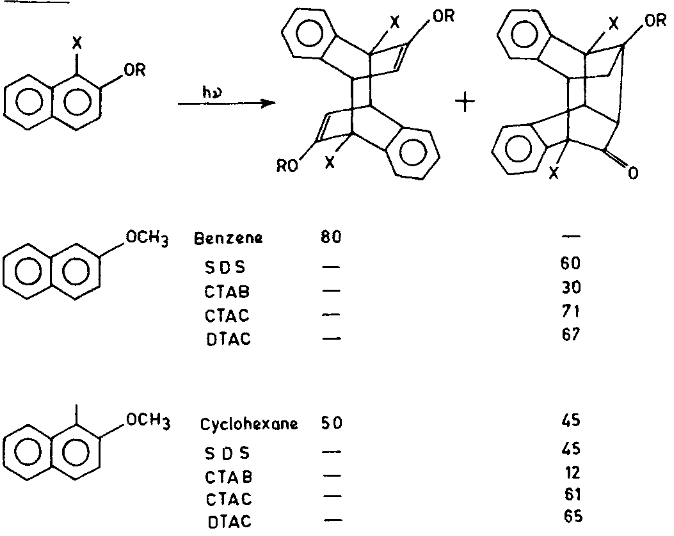
The above examples demonstrate the general usefulness of the micellar alignment effect to achieve regioselectivity. However, Muthuramu *et al* (1983) have shown that micellar alignment effect has limitations. 7-Alkoxy-coumarins which dimerize in organic solvents to give the corresponding syn head-tail dimer, irrespective of solvent polarity, were used as models to eliminate any polarity effects due to the polar Stern region. Irradiation of the shorter chain coumarins (n = 0–5) (figure 1) in micellar media did not lead to the expected reversal in regioselectivity during photodimerization in contrast to the effective reversal observed by the previous workers with chain lengths of similar lengths with other systems. The chain lengths were increased beyond five upto C_{18} with the expectation that the accompanying increase in hydrophobicity of the reactant molecules would lead to more effective micellar alignment. However, contrary to expectations no reversal in regioselectivity was obtained. This led to the conclusion that micellar orientational effect is most effective only in those systems where the forces that control regiochemistry are weaker than the hydrophobic association energies induced by the associated alkyl chains. This conclusion, viewed in the background of the weak dipole forces involved during the photodimerization of 3-alkylcyclopentenones, is strengthened by the observation in the case of 2-alkoxy-naphthalenes where it is known that the forces controlling the regioselectivity of the 4 + 4 dimerization are weak.



1 R = H; R' = OCH_3
2 R = H; R' = $O(CH_2)_3CH_3$
3 R = H; R' = $O(CH_2)_5CH_3$
4 R = H; R' = $O(CH_2)_6CH_3$
5 R = H; R' = $O(CH_2)_7CH_3$
6 R = H; R' = $O(CH_2)_{11}CH_3$
7 R = H; R' = $O(CH_2)_{13}CH_3$
8 R = H; R' = $O(CH_2)_{15}CH_3$
9 R = H; R' = $O(CH_2)_{17}CH_3$
10 R = CH_3; R' = OCH_3
11 R = CH_3; R' = $O(CH_2)_3CH_3$
12 R = CH_3; R' = $O(CH_2)_5CH_3$
13 R = CH_3; R' = $O(CH_2)_6CH_3$
14 R = CH_3; R' = $O(CH_2)_7CH_3$
15 R = CH_3; R' = $O(CH_2)_{11}CH_3$
16 R = CH_3; R' = $O(CH_2)_{17}CH_3$

Figure 1. Methoxycoumarins investigated in micelles.

Scheme 9



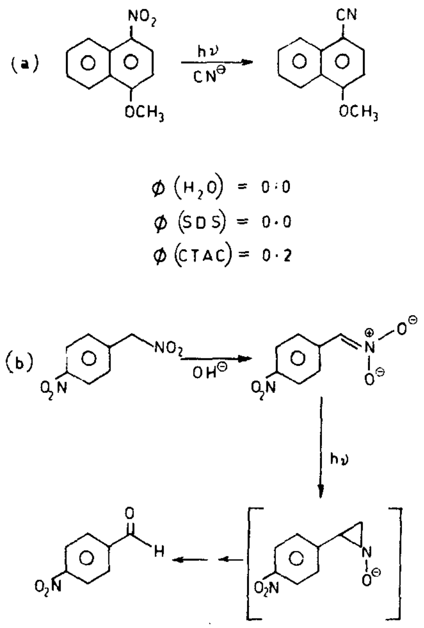
OCH_3	Benzene	80	—
	SDS	—	60
	CTAB	—	30
	CTAC	—	71
	DTAC	—	67
OCH_3	Cyclohexane	50	45
	SDS	—	45
	CTAB	—	12
	CTAC	—	61
	DTAC	—	65

dipole forces (Teitei *et al* 1978). Photodimerization in micellar media lead to *cis* dimer derived products, although the major product in homogeneous media is the corresponding *trans* dimer (scheme 9) (Ramesh and Ramamurthy 1984).

4. Charged micelle-water interface

The aggregation of ionic amphiphiles leads to the distribution of ionic head groups and counter-ions such that a charged micelle-water interface results. The electrically-charged interface has been utilized to accelerate or retard reaction rates between micelle-solubilized substrate and an ionic reactant in the aqueous exterior. Depending on whether the charge of the detergent causes repulsion of attacking nucleophile or organization through attraction, a retardation or acceleration of the reaction results.

Scheme 10



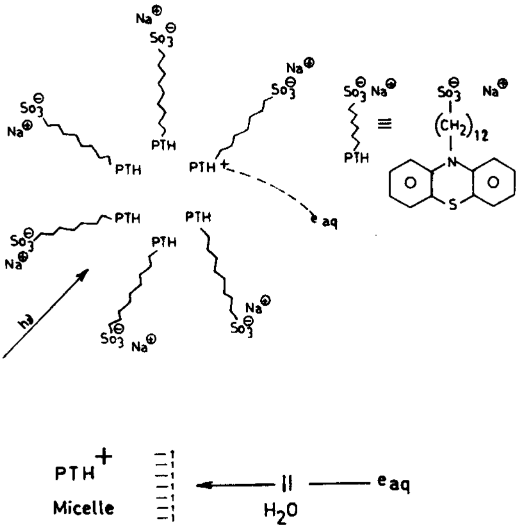
Such effects have been utilized in the photoinduced substitution reactions of aromatic compounds. Photoinduced conversion of 4-methoxy-1-nitronaphthalene to 4-methoxy-1-napthalene-carbonitrile (Hautala and Letsinger 1971); and photorearrangement of 4-nitrobenzaldehyde (Yamada *et al* 1978) (scheme 10) illustrate the influence of this effect.

The charged micelle water interface plays an important role in light energy storing photoreactions (Alkaitis and Gratzel 1976). It has been demonstrated that when functional micelles with attached redox chromophore (*e.g.* sodium 12-(10′-phenethiazinyl)dodecylsulphenate) are irradiated hydrated electrons and cations are produced monophotonically in high yield. This effect has been explained in terms of photoejection of electrons from the micellar into the aqueous phase and subsequent stabilization of the radical ions by the charged micelle water interface. The latter acts as a Schottky barrier, preventing the approach of hydrated electrons and parent ions. Schematic illustration of the process is given in scheme 11.

5. Polarity effect

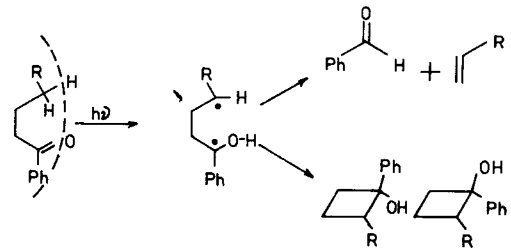
It has been established that aromatic molecules and substrates bearing hydrophilic groups are solubilized at the micelle-water interface which is a region of high polarity. Solvent-sensitive photochemical reactions of substrates located in such regions would result in products corresponding to those produced in solvents of high polarity. Conversely such reactions serve as sensors of the polarity of the microenvironment also. The type II reaction of phenyl ketone illustrates this feature (scheme 12) (Turro *et al* 1977). The quantum yield of the reaction is 0·7 in CTAC and the ratio of cyclobutanols

Scheme 11


Na⊕
SO3⊖
PTH
PTH+
e aq
hν
≡
(CH2)12
N
S
PTH+
Micelle
H2O
e aq

$e_{aq} + e_{aq} \xrightarrow{H_2O} H + 2OH^-$

Scheme 12


R
H
hν
O
Ph
O-H
Ph
H
+
R
Ph
OH
R
OH
Ph
R

(1) (2) (3)

R = n - C_4H_9

Phenyl heptyl ketone		Cyclobutanols
Medium	Ø	Ratio (2)/(3)
t -BuoH	1·0	1·5
C_6H_6	0·33	4·7
CTAC	0·7	1·2

5/6 is 1·2. These values are much closer to those for type II reaction in *t*-BuOH (ϕ = 1·0, 5/6 = 1·5) than those in benzene (ϕ = 0·33, 5/6 = 4·7) thus suggesting that the environment around the site of solubilization of the ketone is polar. Recently, Winkle *et al* (1983) arrived at similar conclusions.

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 (1982) observed that in micellar media 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. Selectivity in the formation of the dimer and enhanced reactivity are attributed to the polar environment in which coumarin undergoes dimerization.

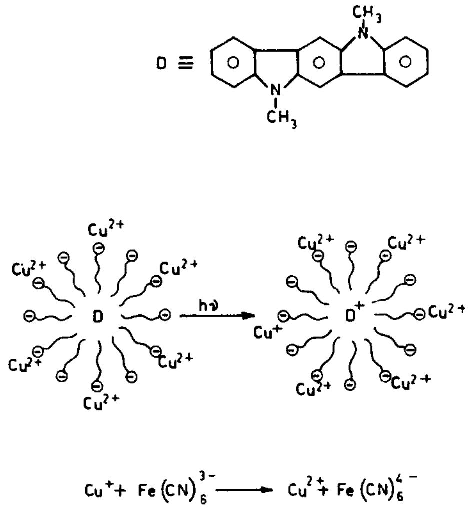
6. Counterion effects

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

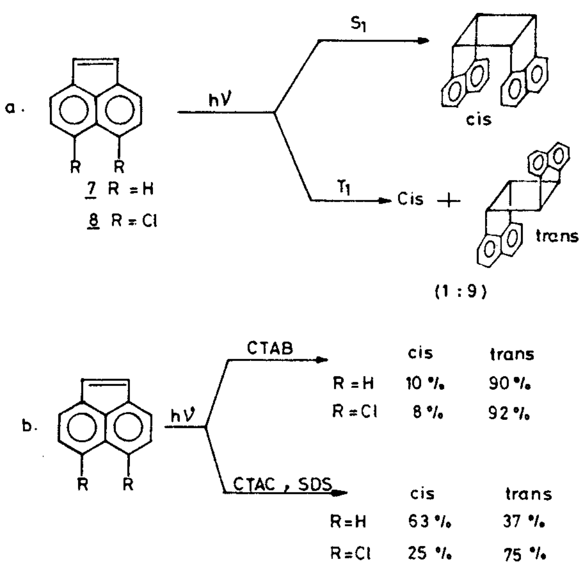
For example, it has been shown that adsorbed metal ions on anionic micelles can act as efficient electron acceptors from excited micelle solubilized donors (Mori *et al* 1979). The replacement of the Na ions in sodium dodecyl sulphate by Cu^{2+} yields assemblies in which Cu^{2+} ions constitute the counterion of the micelle. Donor molecules like N,N'-dimethyl-5,11-dihydroindole [3,2-b] carbazole (D) when incorporated into such micelles and irradiated leads to extremely rapid electron transfer from excited singlet state of D to Cu^{2+} counterion. The Cu^{+} formed in the aqueous phase can be used for a second redox process such as reduction of $Fe(CN)_6^{3-}$. The back reaction of the $Fe(CN)_6^{4-}$ 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. Schematic representation of the counterion effect in this process is depicted in scheme 13.

Yet another feature of counterions is that they function as heavy atoms. Kalyanasundaram *et al* (1977) have shown that by replacing Na ions of SDS by Tl ions the rate of phosphorescene of aromatic hydrocarbons like a naphthalene and pyrene 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 differing counter ions it may be possible to attain state selectivity in the reactive state of a photochemical reaction or photophysical processes. Wolff (1982) observed that the quantum yield of fluorescence of excited aromatic molecules such as substituted anthracenes, indenes and N,N-diphenylamine show an increase in CTAC as compared to CTAB and conversely, exhibit lower quantum yield of triplet formation in CTAC as compared to CTAB. An interesting observation is the enhancement in triplet state derived products from the photodimerization of acenaphthylene. Irradiation of acenaphthylene in solution has been studied extensively. It has been established that the excited singlet yields exclusively the *cis* dimer (scheme 14) while the triplet state yields a mixture of *trans* and *cis* dimers in the ratio 9 : 1 (scheme 14). Ramesh and Ramamurthy (1984) and Mayer and Sauer (1983) independently found that the *cis*/*trans* ratio in CTAB is about half that in CTAC and SDS under identical conditions (scheme 14). At lower bulk

Scheme 13


D ≡
CH₃
N
N
CH₃
Cu²⁺
D
hν
D⁺
Cu⁺
Cu⁺ + Fe(CN)₆³⁻ → Cu²⁺ + Fe(CN)₆⁴⁻

Scheme 14


a.
R R
7 R = H
8 R = Cl
hν
S₁
cis
T₁
Cis +
trans
(1 : 9)
b.
R R
hν
CTAB
cis trans
R = H 10 % 90 %
R = Cl 8 % 92 %
CTAC, SDS
cis trans
R=H 63 % 37 %
R=Cl 25 % 75 %

concentration of the reactant (1·3 mM as compared to 8 mM in the above case) the photodimerization is almost exclusively *via* the triplet channel in CTAB, whereas in CTAC, DTAC and SDS micelles singlet state derived *cis* dimer still predominates. The low *cis*/*trans* ratio has been attributed to the "external heavy atom effect" of the bromide counter ions which are suggested to enhance the $S_1 \rightarrow T_1$ intersystem crossing *via* intermolecular spin-orbit coupling and the triplet-derived *trans* dimer yield is increased. Similar observations have been made in the case of 5,6-dichloroacenaphthylene. These results on the photodimerization of acenapthylenes in micellar media suggest that for photochemical reactions that proceed *via* competing singlet and triplet states, state selectivity can be achieved by utilizing heavy atom counter ions for triplet state product and light atom counter ions for predominantly singlet state products. However, this technique has its limitations. Firstly, the photochemical reaction should be sensitive to 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 using micelles having heavy atom counter ions will result in a reduction in the yield of triplet derived products.

In view of the great potential of micellar systems as media for conducting reactions a clear understanding of the structure of micelles is very essential. An intimate knowledge of the precise molecular structure of micelles certainly would help the more intelligent exploitation of micelle-mediated processes. One can foresee much activity in the coming years on control of reactivity using micelle and micelle-like systems.

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References

Alkaitis S A and Gratzel 1976 *J. Am. Chem. Soc.* **98** 3549

Berenjian N, de Mayo P, Sturgeon M, Sydnes L K and Weedon A C 1982 *Can. J. Chem.* **60** 426

de Mayo P and Sydnes 1980 *J. Chem. Soc. Chem. Commun.* 994

Fargues R, Mauretta M T, Oliveros E, Riviere M and Lattes A 1979 *Nov. J. Chim.* **3** 487

Fargues R, Maunetta M T, Oliveros E, Riviere M and Lattes A 1982 *J. Photochem.* **18** 101

Fendler J 1984 *Chem. Eng. News* 25 (Jan. 2)

Flutton R S, Roth H D, Kroeutler B, Cherry W R and Turro N J 1979 *J. Am. Chem. Soc.* **101** 2227

Hautala R R and Letsinger R L 1971 *J. Org. Chem.* **36** 3762

Kalyanasundaram K, Greiser F and Thomas J K 1977 *Chem. Phys. Lett.* **51** 501

Law K Y and de Mayo P 1978 *J. Chem. Soc. Chem. Commun.* 1110

Lee K H and de Mayo P 1979 *J. Chem. Soc. Chem. Commun.* 493

Mayer H and Sauer J 1983 *Tetrahedron Lett.* 4091

Muthuramu K and Ramamurthy V 1982 *J. Org. Chem.* **47** 3976

Muthuramu K, Ramnath N and Ramamurthy V 1983 *J. Org. Chem.* **48** 1872

Mori Y, Braun A M and Gratzel 1979 *J. Am. Chem. Soc.* **101** 567

Nakamura Y, Imakura Y, Kato T and Morita Y 1977 *J. Chem. Soc. Chem. Commun.* 887

Nakamura Y, Imakura Y and Morita Y 1978 *Chem. Lett.* 965

Nakamura Y, Kato T and Morita Y 1981 *Tetrahedron Lett.* **22** 1025

Ramesh V and Ramamurthy 1982 *J. Photochem.* **20** 47

Ramesh V and Ramamurthy V 1983 *J. Photochem.* **24** 395

Ramesh V and Ramamurthy V 1984 *J. Org. Chem.* **49** 536

Ramnath N and Ramamurthy V 1984 *J. Org. Chem.* (in press)

Teitei T, Wells D, Spurling T H and Sasse W H F 1978 *Aust. J. Chem.* **31** 85

Turro N J, Liu K C and Chow M F 1977 *Photochem. Photobiol.* **26** 413

Turro N J, Liu K C, Chow M F and Lee P 1978 *Photochem. Photobiol.* **27** 523

Turro N J and Krauetler 1980 *Acc. Chem. Res.* **13** 369

Turro N J 1983 *Proc. Natl. Acad. Sci. USA* **80** 609

Winkle J R, Worsham P R, Scharye K S and Whitten D G 1983 *J. Am. Chem. Soc.* **105** 3951

Wolff T 1981 *J. Photochem.* **16** 343

Wolff T 1982 *Bev. Bunsenges. Phys. Chem.* **86** 1132

Yamada K, Shigehiro K, Kujezuka and Tita H 1978 *Bull. Chem. Soc. Jpn.* **51** 2447