REGIOSELECTIVE PHOTODIMERIZATION OF POLAR 9-SUBSTITUTED ANTHRACENES IN MICELLAR SOLUTIONS

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Summary

The quantum yields of photodimerization and the ratios of head-to-tail to head-to-head dimerization rates were measured for 9-hydroxymethyl-anthracene, 9-anthracenecarboxylic acid and 9-anthracenepropionic acid in various homogeneous solvents and in micellar solutions. Higher quantum yields can be achieved in micellar solutions because of higher local monomer concentrations. Relatively more head-to-tail dimers are formed in solvents of higher polarity. Head-to-head dimerization is favoured in micellar solutions compared with homogeneous solutions. The product ratio of the two dimers depends on the micelle size and on the substituent in the 9 position. The results for 9-anthracenecarboxylic acid are complicated by dissociation effects. The activation energies of the thermal back reactions were determined.

1. Introduction

9-substituted anthracenes (Fig. 1, A) are known to form dimers on irradiation with light of wavelengths $\lambda > 300$ nm. Two isomeric dimers, the head-to-head photodimer (Dhh) and the head-to-tail-photodimer (Dht) [1 - 4] which can be split thermally and photochemically into the educts, are formed as shown in Fig. 1. An increase in the quantum yield of Dhh by a factor of 3 - 6 at the expense of Dht when dimer yields of 9-hydroxymethyl-anthracene (1) in aqueous micellar solutions of sodium dodecylsulphate (SDS) were compared with those obtained in homogeneous diethyl ether solutions was reported in a previous paper [3]. This result was ascribed to preorientation of the 9-hydroxymethylanthracene molecules in micelles in such a way that the polar substituent was predominantly directed to the polar micelle—water interface while the aromatic part of the molecule was directed to the micellar core.

In this paper we present a detailed study of the orientational effects of various polar substituents in various micelles. Photodimerization quantum yields and ratios ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head dimer yields were
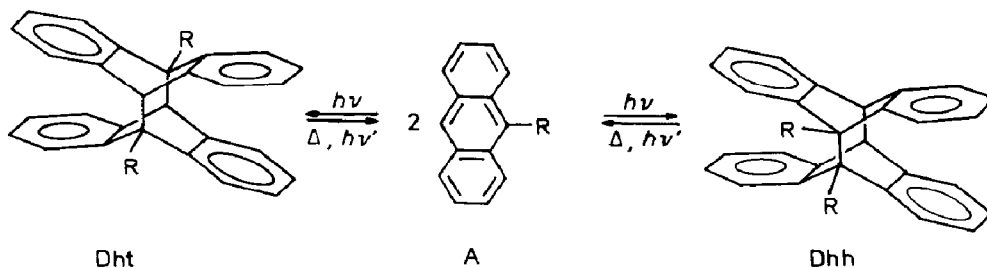
Fig. 1. The photodimerization of 9-substituted anthracenes: 1, $R \equiv CH_2OH$; 2, $R \equiv CH_2CH_2COOH$; 3, $R \equiv COOH$.

determined for 1, 9-anthracenepropionic acid (2) and 9-anthracenecarboxylic acid (3) in micellar solutions of cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC) and SDS. Homogeneous systems in solvents of various polarities were investigated for comparison. In addition the activation energies of the thermal back reactions were determined to characterize the stability of the products.

2. Experimental details

2.1. Materials

1 and most of the solvents and surfactants were available from previous investigations [3,5]. o-dichlorobenzene (Baker, pro analyse), ethanol (Merck, pro analyse), 3 (Ega; purity, 98% - 99%) and anthracene (Merck–Schuchhart; purity, 99%) were used as supplied. 2 was prepared as described by Stewart [6].

2.2. Irradiation and measurements

A detailed description of the sample preparation, the irradiation procedure, the determination of the quantum yields and the kinetic constants, and the spectrometers used is given elsewhere [5]. pH measurements were performed using a Philips PW 9414 ion activity meter. Relative vapour pressures were measured using a Knauer vapour pressure osmometer.

3. Results

3.1. Absorption and emission spectra

Absorption spectra of the compounds 1, 2 and 3 were measured in the homogeneous and micellar solutions used in the irradiation experiments. Only slight variations in the absorption maxima and the extinction coefficients were observed as shown in Table 1 for one of the absorption peaks.

TABLE 1

Wavelength λ_{max} and extinction coefficient ϵ of the absorption maximum near 365 nm of 9-substituted anthracenes in various solvents

| Solvent	9-hydroxymethyl-anthracene		9-anthracene-propionic acid		9-anthracene-carboxylic acid	
	λ_{max} (nm)	ϵ ($\times10^3$ M^{-1} cm^{-1})	λ_{max} (nm)	ϵ ($\times10^3$ M^{-1} cm^{-1})	λ_{max} (nm)	ϵ ($\times10^3$ M^{-1} cm^{-1})
Cyclohexane	365.5	9.7				
Diethyl ether	364.0	9.1	366.5	10.7	361.0	7.6
Benzene	367.5	9.1				
Methanol	364.0	9.1	366.5	10.1	361.5	7.3
Ethanol			367.0	9.4	361.5	7.8
0.125 M CTAB	367.0	8.6	371.0	8.8	368.5	8.1
0.123 M CTAC	367.0	8.4	370.0	8.7		
0.09 M SDS	366.5	8.5	369.0	8.7	364.5	8.4

TABLE 2

Wavelength λ of the fluorescence maximum near 415 nm of 9-substituted anthracenes in various solvents

Solvent	λ_{max} (nm) for the following compounds		
	9-hydroxymethyl-anthracene	9-anthracene-propionic acid	9-anthracene-carboxylic acid
Cyclohexane	409		
Diethyl ether	409	412	
Benzene	414		
Methanol	409	411	413
Ethanol			412
0.125 M CTAB	413	416	417
0.123 M CTAC	413	414	411
0.09 M SDS	413	414	411

The fluorescence maxima of 1, 2 and 3 do not differ much (Table 2). The emission spectrum of 3 is more complicated than those of 1 and 2 because the carboxylic acid is partially dissociated in some of the solvents so that the composite emission spectra of the anion and the undissociated molecule are measured. The anion has a typical anthracene-like fluorescence spectrum while the undissociated acid exhibits a structureless emission [7]. The emission of the anion is compared with that of the other substances in Table 2.

No ground state interactions other than the dissociation equilibrium of 3 were detected spectroscopically. However, measurements of the vapour pressure of solutions of 1 and of anthracene (as a reference) in cyclohexane and in benzene indicate that dimeric aggregates of 1 were present in the

solutions. Because of the low solubility of 1 in cyclohexane (less than 2×10^{-3} M) it was not possible to determine exactly the fraction of aggregated molecules in this solvent but it was larger than that in benzene. Since the UV spectra show no evidence of alternative structures, these dimeric aggregates are assumed to be hydrogen bridge bonded:

anthracene—CH$_2$

O—H

H—O

CH$_2$—anthracene
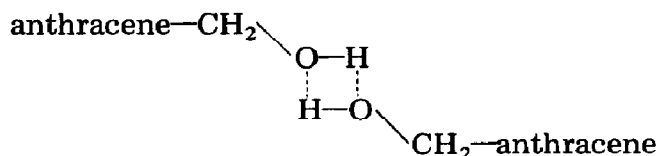
The appearance of a peak at $\lambda = 1415$ nm [8] in the near-IR spectrum of 1 in benzene which showed a concentration-dependent intensity supports the assumption of the presence of hydrogen bridges.

3.2. Quantum yields

Tables 3 - 5 give the dimerization quantum yields ϕ_D and the ratios ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head dimerization rates for the three compounds investigated in various solvents at various concentrations C_1, C_2 and C_3 of the educts. The published value [9] for ϕ_D of 3 in ethanol was reproduced. The tables show that higher quantum yields $\phi_D = \phi_{Dht} + \phi_{Dhh}$ can be achieved for a given concentration of the educts when the irradiations are performed in micellar solutions at suitable micelle concentrations given by

TABLE 3

Photodimerization quantum yields ϕ_D and ratios ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head dimerization rates at 25 ± 0.5 °C for 9-hydroxymethylanthracene in various homogeneous solutions and in micellar solutions at various micelle concentrations C_{Mi}

Solvent	C_{Mi} ($\times 10^{-3}$ M)	C_1 ($\times 10^{-3}$ M)	$\langle S \rangle$	$\phi_D \times 10^3$	ϕ_{Dht}/ϕ_{Dhh}
Cyclohexane	—	1.40		2.7	>15
Benzene	—	1.31		4.5	2.9
Diethyl ether[a]	—	1.50		6.2	1.2
	—	1.15		3.8	1.2
Methanol	—	1.25		3.3	3.2
CTAC	1.5	1.34	0.89	6.3	0.76
	3.0	1.34	0.45	2.2	0.96
CTAB	1.5	1.36	0.91	3.1	0.76
	0.75	1.34	1.79	6.5	0.70
	3.0	1.31	0.44	4.3	1.06
SDS	1.5	1.27	0.85	7.9	0.67
	0.75	1.30	1.73	13.0	0.62

C_1 is the overall concentration of 1 and $\langle S \rangle$ is the average occupation number of the micelles.
[a]At 20 ± 0.5 °C.

TABLE 4

Photodimerization quantum yields ϕ_D and ratios ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head dimerization rates at 25 ± 0.5 °C for 9-anthracenepropionic acid in various homogeneous solutions and in micellar solutions at various micelle concentrations C_{Mi}

Solvent	C_{Mi} ($\times 10^{-3}$ M)	C_2 ($\times 10^{-3}$ M)	$\langle S \rangle$	$\phi_D \times 10^3$	ϕ_{Dht}/ϕ_{Dhh}
Diethyl ether[a]	—	1.51	—	3.1	3.5
Methanol	—	1.47	—	4.6	8.9
CTAB	1.5	1.26	1.19	3.4	1.4
CTAC	1.5	1.26	1.20	3.7	1.9
SDS	1.5	1.28	1.17	5.8	0.91

C_2 is the overall concentration of 2 and $\langle S \rangle$ is the average occupation number of the micelles.
[a] At 20 ± 0.5 °C.

TABLE 5

Photodimerization quantum yields ϕ_D and ratios ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head dimerization rates at 25 ± 0.5 °C for 9-anthracenecarboxylic acid in various homogeneous solutions and in micellar solutions at various micelle concentrations C_{Mi}

Solvent	C_{Mi} ($\times 10^{-3}$ M)	C_3 ($\times 10^{-3}$ M)	$\langle S \rangle$	$\phi_D \times 10^3$	ϕ_{Dht}/ϕ_{Dhh}
Diethyl ether[a]	—	2.18	—	13.9	4.9
Methanol	—	2.01	—	4.2	6.5
	—	12.1	—	23.3	4.8
Ethanol	—	9.1	—	31.2	>15
	—	14.0	—	47.1	>15
CTAB	3.0	2.01	0.67	2.1	5.2
	1.5	2.11	1.41	3.9	15
	0.75	2.11	2.81	5.2	>15
SDS	3.0	1.72	0.57	1.2	6.8
	1.5	1.87	1.25	1.8	2.3
	0.75	1.50	2.00	2.3	1.4

C_3 is the overall concentration of 3 and $\langle S \rangle$ is the average occupation number of the micelles.
[a] At 20 ± 0.5 °C.

$$C_{Mi} = \frac{C_s - CMC}{n_{agg}} \qquad (1)$$

where C_s is the overall surfactant concentration, CMC is the critical micelle concentration and n_{agg} is the mean aggregation number of monomeric surfactant molecules per micelle which is taken as 60 for SDS [10], 84 for CTAB [11] and 82 for CTAC [12]. The observed effect is due to the high local concentrations of the anthracenes in the micelles as a consequence of their low solubility in water. The quantum yields in micellar solutions depend on the average numbers $\langle S \rangle$ of educt molecules per micelle given in

Tables 3 - 5. If intermicellar reactions are neglected ϕ_D is expected to increase with the probability of finding at least two monomeric educt molecules within the same micelle. This probability increases with increasing average number of educt molecules per micelle:

$$\langle S \rangle = C_i/C_{Mi} \tag{2}$$

where C_i is the bulk concentration of educt i.

Quantum yields ϕ_D are always lower in CTAB solutions than in CTAC solutions. This result can be explained in terms of a heavy atom effect of the bromide counter-ions [5, 13] which results in the conversion of some excited singlet states of the educt molecules into triplet states. Since the photodimerization of anthracenes is known to proceed via the excited singlet state (refs. 1 - 5 and references cited therein) the quantum yield is reduced by the heavy atom effect.

The ratio ϕ_{Dht}/ϕ_{Dhh} depends on each of the parameters varied in the investigations, *i.e.* the anthracene substituent, the type of homogeneous solution, the type of micelle and the occupation number $\langle S \rangle$. For anthracenes 1 and 2 more Dhh is generally produced in the micellar solutions than in the homogeneous solutions. This effect is more marked for the photodimerization of 1 than for that of 2 and is more pronounced in the smaller SDS micelles (micellar weight, 17 800 [14]) than in the larger CTAB and CTAC micelles (micellar weight, 31 000 [15]).

4. Discussion

It has been shown previously that micelles may favour the formation of head-to-tail dimers as in the non-polar 9-methylanthracene [5]. The present data, which pertain to polar 9-substituted anthracenes, suggest that micelle-directed photodimerization may also discriminate against the formation of the thermodynamically more stable Dht. These results are understood best when it is assumed that the dipolar structure of the micelle surface has an orienting effect which tends to align polar hydrophobic molecules and partially compensates their electrostatic repulsion. In this respect the smaller SDS micelles are more efficient than the larger CTAC or CTAB micelles. Also, the kind of polar anthracene substituent influences the orienting effect.

The ratios ϕ_{Dht}/ϕ_{Dhh} for homogeneous solutions of 1 and 2 in benzene, diethyl ether and methanol vary with the solvent in the same direction. The same type of solvent dependence was observed for 9-methylanthracene [5]. In contrast with the results for 9-methylanthracene, ϕ_D depends not only on the concentration but also significantly on the solvent as can be seen in Fig. 2 where $1/\phi_D$ is plotted against the reciprocal concentration of 1. The comparatively low quantum yield in cyclohexane can be explained by a reduced effective concentration due to the formation of hydrogen-bridge-bonded ground state aggregates. Inspection of molecular models suggests that these aggregates are
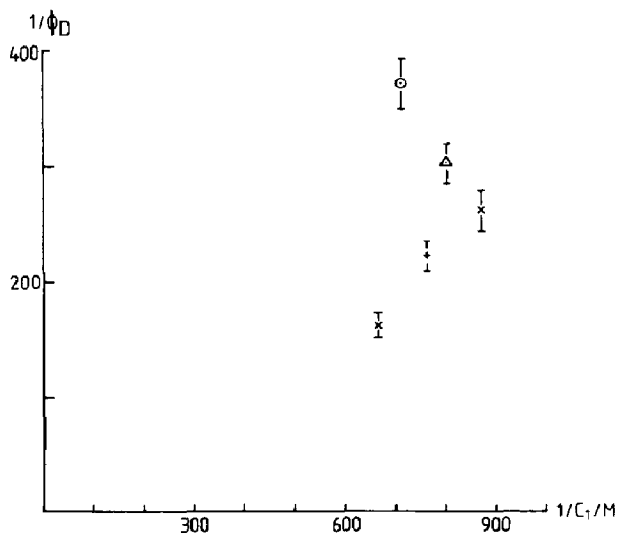
Fig. 2. Dependence of the reciprocal photodimer quantum yield ϕ_D on the concentration C_1 of 9-hydroxymethylanthracene in cyclohexane (⊙), benzene (+), diethyl ether (×) and methanol (△).

unlikely to form photodimers of the two bonded molecules. The models also indicate that Dht formation from two pairs of ground state dimers is much more likely than Dhh formation. This may explain the unusual ϕ_{Dht}/ϕ_{Dhh} ratio obtained for 1 in cyclohexane. Compounds 2 and 3 are not sufficiently soluble in cyclohexane to enable comparative experiments to be performed.

In compound 3 additional effects appear. Cowan and Schmiegel [9] found different dimerization quantum yields for the undissociated acid and for the anion. Therefore in solvents such as methanol and the surfactant solutions in which partial dissociation occurs ϕ_D is the sum of the quantum yields of three reactions: photodimerization of 3, photodimerization of its anion and mixed dimerization of 3 and the anion. The extent of dissociation was estimated from the pH dependence of the emission spectra. At the concentrations given in Table 5 the degree of dissociation is about 50% in surfactant solutions containing cetyltrimethylammonium (CTA) micelles and about 5% in the presence of SDS micelles. Furthermore, at high occupation numbers (at concentrations differing from those in Table 5 by higher occupation numbers) viscoelastic properties of the solutions have been observed [16] which are analogous to those reported for CTA solutions in the presence of salicylate counter-ions [17]. In the double layer surrounding the cationic CTA micelles the anion of 3 replaces a counter-ion and is therefore subjected to an environment which differs completely from that to which the other anthracene derivatives are exposed within the micelle. This situation leads to almost complete suppression of Dhh formation at high occupation numbers. In contrast, anionic SDS micelles suppress the dissociation of 3 so that the formation of Dhh becomes more favourable at high occupation numbers as observed for compound 1 (see Tables 3 and 5).

The results show that the extent of the photodimerization of 9-substituted anthracenes A is readily controlled when the reaction is carried out in micellar solutions. The total dimer yield ϕ_D should increase with the number of ground state monomer molecules A which an electronically excited anthracene molecule encounters within its lifetime. Since most A molecules are associated with micelles we can define a probability p_i of finding i A molecules within the same micelle. The total probability of encounters between excited and ground state A molecules is the sum [5]

$$P = p_2 + 2p_3 + 3p_4 + \ldots \tag{3}$$

If the photodimerization rate is assumed to be proportional to P a plot of $1/\phi_D$ versus $1/P$ should give a straight line. This is in fact confirmed by the results obtained (Fig. 3) when numerical values of P are estimated using Poisson statistics, i.e.

$$p_i = \frac{\langle S \rangle^i}{i!} \exp(-\langle S \rangle) \tag{4}$$

Since $\langle S \rangle$ is calculated using eqns. (1) and (2), the application of eqn. (4) depends on the assumption that n_{agg} is a constant. However, Almgren and Swarup [18] investigated some systems in which n_{agg} depends on the concentration of solubilizates. This may explain why $1/\phi_D$ versus $1/P$ is not linear when the results for 1 in CTAB solutions (see Table 3) are plotted as in Fig. 3.

Kinetic data for the thermal back reactions of Dhh and Dht are given in Table 6. The Dht compounds are more stable than the corresponding Dhh molecules as expected from previous results for other photodimers of 9-substituted anthracenes [1 - 5]. The kinetic data were used to calculate how
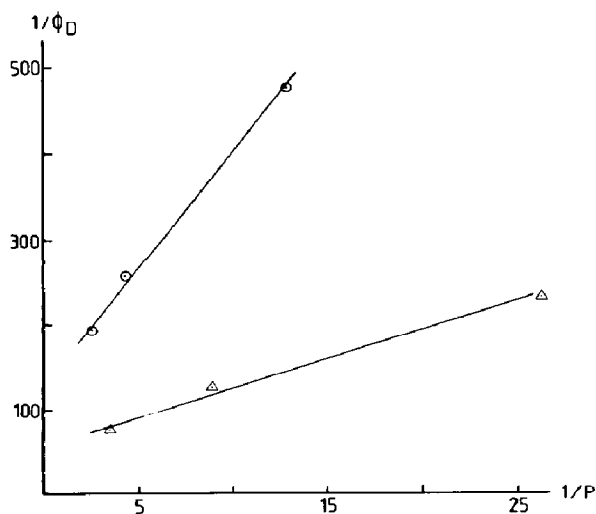

Fig. 3. Concentration dependence of the photodimerization of 1 in SDS solutions ($\triangle$) and of 3 in CTAB solutions ($\odot$). P is calculated from eqn. (3).

TABLE 6

Activation energies E_a and frequency factors F of the thermal cleavage of the head-to-head and head-to-tail photodimers Dhh and Dht of 9-hydroxymethylanthracene, 9-anthracenepropionic acid and 9-anthracenecarboxylic acid in various solvents

Solvent	Dhh of 1		Dht of 1		Dhh of 2		Dhh of 3		Dht of 3	
	E_a (kJ mol^{-1})	log F	E_a (kJ mol^{-1})	log F	E_a (kJ mol^{-1})	log F	E_a (kJ mol^{-1})	log F	E_a (kJ mol^{-1})	log F
Diethyl ether	113	15.0	—	—	90	12.6	117	16.9	—	—
0.2 M SDS	112	14.6	—	—	—	—	—	—	—	—
o-dichloro-benzene	—	—	153	15.2	—	—	—	—	144	14.5

The activation energies are correct to within ± 6 kJ mol^{-1} and the frequency factors accordingly. The error was calculated as the mean deviation. F is in reciprocal seconds.

much of the Dhh had decayed during the irradiations. All ϕ_{Dht}/ϕ_{Dhh} ratios given in this paper were corrected for this effect which turned out to be small (cf. ref. 5).

5. Conclusion

The regioselectivity of the photodimerization of polar 9-substituted anthracenes can be controlled by performing the reaction in aqueous micellar solutions. The effect is explained as a consequence of the micro-heterogeneous structure of the solutions which may even enable the thermodynamically unfavourable head-to-head-dimerization to be the dominant process.

Acknowledgments

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