Production and Reaction of Singlet Oxygen in Aqueous Micellar Solutions Using Pyrene as Photosensitizer

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Z. Naturforsch. **33b**, 622–627 (1978); received February 24, 1978

Singlet Oxygen, Pyrene, Diphenylisobenzofuran, Micelles

The reaction of singlet oxygen with 1,3-diphenylisobenzofuran was investigated in aqueous micellar solutions of sodium dodecyl sulfate and dodecyl trimethylammonium chloride using pyrene as photosensitizer. Singlet oxygen, produced by the photosensitization of pyrene bound to micelles, oxidized efficiently 1,3-diphenylisobenzofuran bound to micelles. The quantum yield for singlet oxygen production and the rate constant for furan oxidation were determined by the kinetic analysis for the oxidation reaction of furan. Quenching of singlet oxygen by sodium azide competed with the furan oxidation, and its rate constant was also determined.

Results obtained were compared with those in methanolic solutions. The quantum yield for singlet oxygen production and the rate constant for furan oxidation were much higher in micellar solutions than those in methanolic solutions. Empty micelles was found to act as a considerably strong scavenger for singlet oxygen. The penetration probability of singlet oxygen from aqueous phase into the interior of micelles which bound furan was also estimated.

Introduction

Singlet oxygen [1–5] has attracted a great attention of various workers as a reactive species from photochemical and photobiological importance. This molecule can be produced photochemically by direct excitation [1, 2, 6] of oxygen with laser or by energy transfer [1–4] from triplet state of sensitizer to oxygen. Various dyes and aromatic hydrocarbons such as rose bengal [7–9], eosine Y [10], thionine [9, 10], methylene blue [9, 10, 12, 14] and pyrene [15–21] are known as photosensitizer for singlet oxygen production. Among these, methylene blue is most popular as sensitizer, and has been widely employed for investigating the lifetime [7, 8] of singlet oxygen and the photooxidation reactions of many organic substrates in various solvents [12]. Usually, dye-sensitized photooxidations proceed with singlet oxygen mechanism (type II) and/or with radical mechanism (type I) involving the reaction of excited state of dye with substrate. Sodium azide [9, 17, 18], DF [6–8, 12], 9,10-di-

methylantracene [6, 7], tetramethylethylene [7], tetraphenylcyclopentadienone [6], carotenoids [12] and amines [17, 18] are known as effective quenchers for singlet oxygen. Reactions concerning with singlet oxygen have been investigated using the above quenchers; especially, sodium azide in polar solvents and DF in non-polar solvents.

Recently, photochemical reactions sensitized by methylene blue were kinetically studied with aqueous SDS micellar systems [21] containing DF, and the behaviour of singlet oxygen was discussed. Micellar solutions provide a hydrophobic environment (interior of micelles) in polar phase. Methylene blue may be bound to the surface of micelle and DF to the interior of micelle. Such micellar systems are of interest as a model of biological environment.

The present investigation deals with the kinetics of DF oxidation reactions photosensitized by P_y in aqueous micellar solutions of SDS and DTAC, and in methanolic solutions, containing P_y , DF and sodium azide. P_y and DF were controlled to be bound to different micelles in the reaction mixture by sample preparation. From kinetic data obtained, the effect of micelles on the production and reaction of singlet oxygen was discussed. The rate constant for singlet oxygen quenching by empty micelles was determined, and the penetration probability of singlet oxygen from aqueous phase into micellar interior was also estimated.

Abbreviations: SDS = sodium dodecyl sulfate; DTAC = dodecyl trimethylammonium chloride; P_y = pyrene; DF = 1,3-diphenylisobenzofuran; MeOH = methanol.

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Results and Discussion

Irradiation of the reaction mixture (aqueous micellar dispersion of 0.1 M SDS or 0.1 M DTAC containing solubilized P_y and DF; saturated with oxygen) with the filtered light (338 nm) decreased rapidly the concentration of DF; an initial linear decrease with the irradiation time followed by a saturation. P_y and DF, hydrophobic molecules, in the reaction mixture are presumed to be bound to different micelles separated each other, under the present sample preparation. DF is known to be highly reactive with singlet oxygen and to be oxidized into dibenzoyl benzene [22]. For this reason, the above decrease in DF concentration is considered to have been caused by the oxidation of DF by the singlet oxygen produced by the photosensitization of P_y , possibly through the triplet energy transfer from P_y to oxygen. In the absence of P_y , the DF concentration was unchanged with a several min-irradiation of the filtered light employed.

When NaN_3 , a scavenger for singlet oxygen, was added to the reaction mixture, the oxidation of DF was considerably inhibited depending on the NaN_3 concentration. NaN_3 is watersoluble, and may be distributed in the aqueous phase as the ionized form.

The reaction mixture used in the present investigation contained various micelles; P_y -bound (M_{Py}), DF-bound (M_{DF}) and empty (M_{empty}) micelles. The total micelle (M_{total}) concentration was estimated to be $1.6 \cdot 10^{-3}$ and $2.0 \cdot 10^{-3}$ M for 0.1 M SDS and 0.1 M DTAC, respectively, assuming the aggregation numbers of 62 for SDS micelle [23, 24] and 50 for DTAC micelle [25]. The maximum concentrations of M_{Py} and M_{DF} are equal to those of P_y ($1 \cdot 10^{-4}$ M) and DF ($\leq 6 \cdot 10^{-5}$ M), respectively. Therefore, a large amount of empty micelles was present in the reaction mixture. In order to examine whether empty micelles behave as scavenger for singlet oxygen, the quantum yield (Φ_{DF}) for DF oxidation was measured as a function of DF concentration changing the concentration of empty micelles. The concentration of DF-bound micelles could be neglected compared with that of empty micelles. Results obtained in SDS micellar solutions are shown in Fig. 1. The curves indicate a considerable quenching effect of empty micelles for singlet oxygen. Such a quenching effect was also seen in empty micelles of DTAC. Φ_{DF} was determined

using the initial velocity of the decrease in DF concentration and the number of photons absorbed by P_y per min.

Fig. 1. Quantum yield (Φ_{DF}) for DF oxidation as a function of DF concentration at various concentrations of empty SDS micelles. Concentration of P_y , $1 \cdot 10^{-4}$ M; concentration of empty SDS micelles for Curves 1, 2, 3, and 4, $1.5 \cdot 10^{-3}$, $1.3 \cdot 10^{-3}$, $1.2 \cdot 10^{-3}$ and $0.9 \cdot 10^{-3}$ M, respectively.

Simplified diagram for the photochemical reaction in aqueous micellar solutions containing P_y , DF and NaN_3 is shown in Fig. 2, assuming that P_y and DF are bound to the interior of micelles. Then, the reciprocal of the quantum yield for DF oxidation is represented as follows.

Fig. 2. Simplified diagram for photochemical reaction in aqueous micellar solutions containing P_y , DF and NaN_3 . Φ_{O_2} , quantum yield for singlet oxygen production in aqueous phase; k_r , overall rate constant for DF oxidation by singlet oxygen produced in aqueous phase; k_q , rate constant for singlet oxygen quenching by NaN_3 ; k_q' , rate constant for singlet oxygen quenching by empty micelles (M_{empty}); k_d , rate constant for physical decay of singlet oxygen in aqueous phase. $k_r = k_{en} \cdot p \cdot k / (k + k_d')$, where k_{en} , k and k_d' are rate constants for encounter between singlet oxygen and micelle, for DF oxidation by singlet oxygen in interior of micelle and for physical decay of singlet oxygen in interior of micelle, respectively, and p is penetration probability of singlet oxygen from outside into inside of micelle. 3P_y , triplet P_y .

$$\Phi_{DF}^{-1} = \Phi_{102}^{-1} \left(1 + \frac{k_d + k_q[M_{empty}] + k_q[NaN_3]}{k_r} \cdot \frac{1}{[DF]} \right), \quad (1)$$

where the overall rate constant for the oxidation reaction of singlet oxygen in aqueous phase with DF bound to micelle,

$$k_r = k_{en} \cdot p \cdot k / (k + k_d'). \quad (2)$$

Φ_{102} , k_{en} , k_q , k_d' , k_d , k and p are illustrated in the legend of Fig. 2. Under the present experimental conditions, the concentration of empty micelles, $[M_{empty}]$, could be approximated to be nearly equal to that of the total micelles, $[M_{total}]$, because the concentrations of P_y and DF were much less than that of the total micelles as mentioned above. From eq. (1), Φ_{DF}^{-1} should be proportional to the reciprocal of DF concentration ($k_d' = 0$ for methanolic solution). This linear relation was hold for the experimental values obtained in micellar and methanolic solutions as shown in Fig. 3. Plots of Φ_{DF}^{-1} in DTAC and methanolic solutions are shown only in the absence of NaN_3 . The intercepts of the curves with the ordinate give Φ_{102}^{-1} in micellar and methanolic solutions. Obtained values of Φ_{102} are given in Table I. The values of Φ_{102} in micellar solutions were higher than that in methanolic solution.

The difference (ΔS) between slopes for curves in the presence and absence of NaN_3 in Fig. 3 is represented as follows,

$$\Delta S = \Phi_{102}^{-1} \cdot k_q[NaN_3]/k_r. \quad (3)$$

ΔS values were determined experimentally at various NaN_3 concentrations, and were plotted in Fig. 4 for SDS micellar solutions. The curve obtained

Fig. 3. Plots of reciprocal of quantum yield (Φ_{DF}) for DF oxidation against reciprocal of DF concentration. Concentration of P_y , $1 \cdot 10^{-4}$ M; Curves 1, 2 and 3 in the absence of NaN_3 , 0.1 M SDS, 0.1 M DTAC and methanolic solutions, respectively; NaN_3 concentrations for Curves a, b, c and d in 0.1 M SDS solutions, $2 \cdot 10^{-4}$, $4 \cdot 10^{-4}$, $6 \cdot 10^{-4}$ and $8 \cdot 10^{-4}$ M, respectively.

Table I. Quantum yield (Φ_{102}) for singlet oxygen production, rate constant (k_r) for oxidation reaction of DF by singlet oxygen and rate constant (k_q) for singlet oxygen quenching by NaN_3 in methanolic and micellar solutions, and rate constant (k_d') for singlet oxygen quenching by empty micelles and penetration probability (p) of singlet oxygen from outside into interior of micelle in micellar solutions.

Solutions	Φ_{102}	k_r [M ⁻¹ sec ⁻¹]	k_q [M ⁻¹ sec ⁻¹]	k_d' [M ⁻¹ sec ⁻¹]	p
SDS	0.9	$2.2 \cdot 10^{10}$	$7.9 \cdot 10^8$	$1.0 \cdot 10^9$	0.38
DTAC	1.0	$2.8 \cdot 10^{10}$	$1.8 \cdot 10^9$	$1.7 \cdot 10^8$	0.48
MeOH	0.6	$7.8 \cdot 10^8$	$2.3 \cdot 10^8$	—	(1.0)

Fig. 4. Difference (ΔS) between slopes for the curves in the presence and absence of NaN_3 in Fig. 3 as a function of NaN_3 concentration in 0.1 M SDS solutions. $\Delta S = \Phi_{102}^{-1} \cdot k_q[NaN_3]/k_r$.

was linear again, and its slope gave $\Phi_{102}^{-1} \cdot k_q/k_r$. Next, the slope for the curve in the absence of NaN_3 shown in Fig. 3 was determined as a function of $[M_{total}]$, and was plotted in Fig. 5 for SDS micellar solutions. The curve obtained was linear with an intercept of $\Phi_{102}^{-1} \cdot k_d/k_r$ and a slope of $\Phi_{102}^{-1} \cdot k_q'/k_r$. The same treatment could be made for DTAC micellar solutions. The value of $\Phi_{102}^{-1} \cdot k_d/k_r$ for methanolic solution was determined from the slope of the curve in the absence of NaN_3 in Fig. 3.

Merkel *et al.* [12] described that the lifetime ($1/k_d$) of singlet oxygen was $2 \mu\text{sec}$ in water and

Fig. 5. Slope (S) for the curve in the absence of NaN_3 shown in Fig. 3 as a function of SDS micelle concentration.

7 μsec in methanol. Accordingly, assuming that the lifetime of singlet oxygen in aqueous phase of micellar solution is the same as 2 μsec in water, k_r , k_q and k_q' were determined using the obtained values of $\Phi_{102}^{-1} \cdot k_q/k_r$, $\Phi_{102}^{-1} \cdot k_d/k_r$ and $\Phi_{102}^{-1} \cdot k_q'/k_r$, as given in Table I. The magnitude of k_r values was in the order of DTAC solution > SDS solution > methanolic solution. Using methylene blue as sensitizer, Merkel *et al.* [12] obtained $k_r = 8 \cdot 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ in methanolic solution, and Young *et al.* [8] obtained $k_r = 1.3 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in methanolic solution and $k_r = 1.2 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in dioxanic solution. Gorman *et al.* [21] estimated $k_d/k_r = 9.7 \cdot 10^{-5} \text{ M}$ in SDS micellar solutions with methylene blue as sensitizer, which is higher than our k_d/k_r value of $2.3 \cdot 10^{-5} \text{ M}$. The high k_d/k_r value obtained by them may be due to neglect of singlet oxygen quenching by empty micelles. The magnitude of k_q values was also in the above order. Hasty *et al.* [17] obtained $k_q = 2.2 \cdot 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ in methanolic solution using methylene blue as sensitizer. A larger k_q value in DTAC micellar solution than that in SDS micellar solution might be derived from the difference in distribution of azide ions due to counter-ion effect. DTAC micelles are cationic and SDS micelles anionic. The rate constants for singlet oxygen quenching by empty micelles were surprisingly large comparable to those by NaN_3 , especially in SDS micellar solution.

Gorman *et al.* [21] calculated the rate constant for encounter between excited oxygen and SDS micelles from the expression of Weston and Schwarz [26], $k_{en} = 4\pi a(D_A + D_m)$, assuming that the diffusion coefficients of oxygen (D_A) [26] and SDS micelles (D_m) [27] in water are $5 \cdot 10^{-9}$ and $1 \cdot 10^{-10} \text{ m}^2 \text{ sec}^{-1}$, respectively, and the collision radius of the encounter pair (a) is nearly equal to the micellar radius ($1.5 \cdot 10^{-9} \text{ m}$). They obtained $k_{en} = 5.8 \cdot 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. We estimated the penetration probability (p) of singlet oxygen from aqueous phase into the interior of micelle from eq. (2) with the assumption of $k \gg k_d'$ in the interior of micelle and $k_{en} = 5.8 \cdot 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for SDS and DTAC micellar solutions, using the k_r values obtained. The lifetime of singlet oxygen seems to be larger in non-polar solvents than that in polar solvents [12]. Calculated p values are given in Table I. Of course, p value for methanolic solution without micelles corresponds to unity. From p values obtained, singlet oxygen in aqueous phase seems to penetrate

into the interior of DTAC micelle more efficiently than into that of SDS micelle.

The quantum yield for singlet oxygen production sensitized by methylene blue has been estimated to be 0.52 in methanolic solution [28]. This value is comparable to the quantum yield obtained with sensitizer P_y in methanolic solution. The quantum yield for singlet oxygen production in micellar solutions has not been obtained so far as we know. P_y , a hydrophobic molecule, was a good photosensitizer for singlet oxygen production in SDS and DTAC micellar solutions, and the quantum yield (Φ_{102}) was very close to unity. Gorman *et al.* [21] estimated the penetration probability of ~ 0.1 for SDS micellar solutions, using $k_r = 5.2 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. ($k_d = 5 \cdot 10^5 \text{ sec}^{-1}$ was assumed.) The quantum yield (Φ_{102}) in the present investigation was defined as the yield of singlet oxygen produced in aqueous phase (not in micellar interior). Next, it is notable that k_q' values were large comparable to k_q values. Empty micelles seem to act as efficient scavenger for singlet oxygen. P_y -bound micelles may also trap singlet oxygen. In this case, the singlet oxygen trapped may be regenerated by the photosensitization of P_y even if it is quenched to the ground state in the interior of micelle.

In conclusion, P_y bound to micelles effectively photosensitized the oxidation of DF bound to micelles with large rate constants and high quantum yields for singlet oxygen production. At present, the detailed mechanism for these can not be given merely from the results obtained. The micellar structure, the distribution of molecular oxygen, the production site of singlet oxygen, the lifetime of singlet oxygen in aqueous phase and interior of micelle, and the binding site of P_y and DF are still open to be elucidated. To clarify these points may lead to the full understanding of the mechanism of photochemical reactions caused in micellar solutions.

Materials and Methods

SDS and DTAC were obtained from Nakarai Chemical Co. and Maruwaka Kagaku Co., respectively, and were used without further purification. P_y , NaN_3 and MeOH purchased from Katayama Chemical Co. were guaranteed reagents. DF was of special grade for analytical use and was obtained from Aldrich Chemical Co. Laboratory-distilled water was further distilled from alkaline KMnO_4 solution.

Crystalline P_y or DF was dissolved by stirring the crystals in warm 0.1 M aqueous solution (60 °C) of SDS or DTAC in the dark. Sufficient dissolution was obtained in 4–7 h. The concentrations of P_y and DF in the original micellar solutions were $1 \cdot 10^{-3}$ and $1 \cdot 10^{-4}$ M, respectively. The reaction mixture was prepared by mixing the original micellar solutions containing P_y and DF separately before irradiation. When necessary, the mixed solution was diluted with P_y and DF free micellar solution or water. The concentrations of P_y and DF were determined by absorbances at 338 and 415 nm, respectively.

The reaction mixture in a quartz vessel ($1 \times 1 \times 4$ cm³) was irradiated with the ultra-violet light isolated from a 150 W xenon lamp through an interference filter (peak, 338 nm; half width, 22 nm; Nippon Shinku Kogaku type S) at 40 °C. Fig. 6 shows the absorption spectra of solubilized P_y and DF in aqueous micellar solution of 0.1 M SDS and the transmission of the interference filter. The concentrations of P_y and DF employed in the present investigation were $1 \cdot 10^{-4}$ and $5 \cdot 10^{-6}$ – $6 \cdot 10^{-5}$ M, respectively. Therefore, in the reaction mixtures (SDS, DTAC and MeOH solutions containing P_y and DF) used, the amount of photons absorbed directly by DF was estimated to be less than 2% of the photons absorbed by P_y . DF is oxidizable with direct excitation, but the present experimental conditions could neglect this kind of DF oxidation. The amount of photooxidized DF was determined by the decrease in absorbance at 415 nm. The number of photons absorbed by P_y was determined by the potassium ferrioxalate method (sensitive to 334 nm light) of Hatchard and

Parker [29]. The actinometer cell containing 1.25 mM potassium ferrioxalate in 0.1 N H_2SO_4 was placed just behind the target cell. Under the present experimental conditions, $1 \cdot 10^{-4}$ M P_y in MeOH and micellar solutions of SDS and DTAC absorbed $3.8 \cdot 10^{18}$, $3.3 \cdot 10^{18}$ and $3.6 \cdot 10^{18}$ photons per min at the target position, respectively.

Fig. 6. Absorption spectra of P_y and DF in SDS micellar solutions, and transmission of the interference filter used. Concentrations of SDS, P_y and DF, 0.1, $1 \cdot 10^{-4}$ and $1 \cdot 10^{-4}$ M, respectively; Curve 1, P_y ; Curve 2, DF; Curve 3, transmission.

Absorption spectra were measured with a Hitachi spectrophotometer type 124, and the fluorescence spectra with a Hitachi spectrofluorimeter type 203 modifying the irradiating and recording parts.

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