Quenching of Singlet Oxygen by Sodium Azide in Reversed Micellar Systems

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Z. Naturforsch. 34b, 339-343 (1979); received October 4, 1978

Singlet Oxygen, Sodium Azide, Diphenylisobenzofuran, Reversed Micelles

The oxidation reaction of singlet oxygen with 1,3-diphenylisobenzofuran was investigated in cyclohexanic reversed micellar solutions of dodecylammonium propionate, using pyrene as photosensitizer. The furan oxidation was effectively inhibited by azide ion-bound reversed micelles. Empty reversed micelles also inhibited the furan oxidation to some extent. The inhibition of the furan oxidation was due to the quenching of singlet oxygen by azide ion-bound and empty reversed micelles. Such singlet oxygen quenching was dependent on the concentration of water added.

Results obtained were discussed in connection with the polarity in the interior of reversed micelles, micellar size, the state of water solubilized in reversed micelles and the lifetime of singlet oxygen. The heavy atom effect on the quenching of singlet oxygen was also studied using heavy water.

Introduction

The DF oxidation by singlet oxygen in various aqueous micellar solutions has been studied using \( P_y \) as photosensitizer and \( \text{NaN}_3 \) as singlet oxygen quencher [1, 2]. Aqueous micellar solutions provided a hydrophobic environment (interior of micelles) in polar phase. Therefore, in the reaction mixtures, \( P_y \) and DF were bound to the interior of micelles, and \( \text{NaN}_3 \), in ionized form, was distributed in the aqueous phase.

Recently, reversed micelles are attracting a great attention of various workers [3-8] from chemical and biological interest, since they offer very specific environments for chemical reactions. Reversed micelles can solubilize various polar molecules and partition molecules solubilized inside micelles depending on their molecular character. Fendler et al. found many interesting chemical reactions in reversed micellar systems [3, 4, 7, 8].

Reactions concerning with singlet oxygen have been investigated using quenchers for singlet oxygen such as \( \text{NaN}_3 \) [9-11], DF [12, 15], 9,10-dimethylanthracone [12, 13], tetramethylethylene [13], tetraphenylessuperoxide [12], carotenoids [15] and amines [10, 11]. Most of the quenchers are characterized to be hydrophobic molecules except for few quenchers such as \( \text{NaN}_3 \) and amines. \( \text{NaN}_3 \) is most popular as singlet oxygen quencher in aqueous solutions. We found that \( \text{NaN}_3 \) could be employed in non-polar solvents as effective quencher for singlet oxygen when bound to DAP reversed micelles.

The present investigation deals with the DF oxidation by singlet oxygen formed by \( P_y \) photosensitization in cyclohexanic DAP reversed micellar solutions, containing \( P_y \), DF and \( \text{NaN}_3 \). The reaction mixture was an interesting solution composed of \( P_y \), DF and azide ion-bound DAP reversed micelles in cyclohexane. The quenching of singlet oxygen by azide ion-bound and -unbound (empty) reversed micelles was investigated at various water concentrations, monitoring the DF oxidation. Results obtained were discussed in connection with the structure of DAP reversed micelles (polarity in micellar interior, micellar size and state of solubilized water) and the lifetime of singlet oxygen in reversed micelles. The heavy atom effect on the quenching of singlet oxygen was also examined using D\( _2 \)O instead of H\( _2 \)O.

Materials and Methods

\( P_y \), \( \text{NaN}_3 \), potassium ferrioxalate, ethanol, cyclohexane and DAP obtained from Katayama Chemical Co. were guaranteed or extra pure reagents. DAP was used without further purification. \( P_y \) was purified by recrystallization twice from ethanol. DF purchased from Aldrich Chemical Co. was of special grade for analytical use. Laboratory-distilled water was further distilled from alkaline KMnO\( _4 \) solutions.

Reversed micellar solution was prepared by dissolving DAP in cyclohexane at room temperature, \( P_y \) and DF were separately dissolved in cyclohexane. These three original solutions, after adequate dilution, were mixed in the dark before use. The mixed solution was stirred for several minutes in the dark after adding a light or heavy aqueous...
NaN₃ solution and/or an adequate amount of light or heavy water. The final concentration of DAP was 0.08 M in the reaction mixture. The concentrations of Py and DF were determined by absorbances at 338 and 410 nm, respectively.

The reaction mixture in a quartz vessel (1 × 1 × 4 cm³) was irradiated with the ultraviolet 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 30 °C.

DF is oxidizable with direct excitation, but this kind of DF oxidation could be neglected under the present optical conditions. The amount of photons absorbed directly by DF in the reaction mixture was less than 2% of the photons absorbed by Py. The amount of oxidized DF was determined by the decrease in absorbance at 410 nm. The absorbance was measured with a Hitachi spectrophotometer type 356.

The number of photons absorbed by Py was determined by the potassium ferrioxalate method (sensitive to 334 nm light) of Hatchard and Parker [16] as described in the previous paper [1]. Under the present experimental conditions, 1 × 10⁻⁵ M Py in the micellar solution of 0.08 M DAP absorbed 2.2 × 10¹⁷ photons per min at the target position.

Results and Discussion

Irradiation of the cyclohexanic solution (oxygen-saturated) containing Py and DF with the filtered light (338 nm) absorbed by Py caused a rapid decrease in DF concentration. This concentration decrease is due to the DF oxidation by singlet oxygen produced by Py-photosensitization. The DF oxidation was inhibited to some extent when the above reaction mixture contained DAP reversed micelles. Namely, DAP reversed micelles (empty micelles) operated as a scavenger for singlet oxygen although their scavenging efficiency was not high.

On adding an aqueous solution of NaN₃ to the reaction mixture containing DAP reversed micelles, the DF oxidation was remarkably inhibited. Azide ion may be bound to the interior of DAP reversed micelles. Azide ion-bound DAP reversed micelles are a new type of effective quencher for singlet oxygen in non-polar solvents. We found that the inhibition of the DF oxidation by azide ion-bound DAP reversed micelles depended strongly on the water content in the reaction mixture. The initial rate of the DF oxidation is shown in Fig. 1 as a function of NaN₃ concentration. R, initial rate; concentrations of Py, DF and DAP, 1 × 10⁻⁵, 5 × 10⁻⁵ and 0.08 M, respectively; temperature, 30 °C; Curves 1 and 2, DAP reversed micellar solutions containing 0.2 and 0.6 M H₂O, respectively; Curves 3 and 4, DAP reversed micellar solutions containing 0.2 and 0.6 M D₂O, respectively.

Correll et al. [7] calculated average sizes of reversed micelles for 0.08 M DAP in cyclohexane as a function of solubilized water concentration, assuming spherical geometry. According to them, at the stoichiometric H₂O concentrations below 0.37 M, all the water molecules are bound to the surfactant head groups (‘bound water range’). With increasing stoichiometric H₂O concentration above 0.37 M, the average aggregation number and the number of free water molecules entrapped in a reversed micelle increased rapidly (‘free water range’). The data obtained by Correll et al. [7] are plotted in Fig. 2. From Curves 1 and 2, the average aggregation number and the number of the free water molecules are estimated to be about 10 and 0 at 0.2 M H₂O and about 80 and 250 at 0.6 M H₂O, respectively.

Fig. 1. The initial rate (R) of DF oxidation as a function of NaN₃ concentration. R, initial rate; concentrations of Py, DF and DAP, 1 × 10⁻⁵, 5 × 10⁻⁵ and 0.08 M, respectively; temperature, 30 °C; Curves 1 and 2, DAP reversed micellar solutions containing 0.2 and 0.6 M H₂O, respectively; Curves 3 and 4, DAP reversed micellar solutions containing 0.2 and 0.6 M D₂O, respectively.

Fig. 2. The average aggregation number, N, (Curve 1) of 0.08 M DAP reversed micelles in cyclohexane and the number (Curve 2) of free water per micelle as a function of H₂O concentration. These curves are the plot of the data obtained by Correll et al. [7].
Next, the initial rate of the DF oxidation was measured in the absence and presence of NaN₃ as a function of H₂O or D₂O concentration. Results obtained are shown in Fig. 3. In the absence of NaN₃, the initial rate exhibited a slight decrease in the free water range in either case of H₂O or D₂O (Curves 1 and 2) comparing with that in the bound water range. In the presence of NaN₃, the initial rate was considerably low in the bound water range but it increased in going from bound water range to free water range, in the case of H₂O (Curve 3). Curves a and b are the initial rate for 0.06 and 0.10 M DAP micellar solutions, respectively. However, D₂O caused a slight decrease in the initial rate of the DF oxidation with increasing its concentration (Curve 4).

![Fig. 3. The initial rate (R) of DF oxidation as a function of H₂O or D₂O concentration. R, initial rate; concentrations of P₇, DF, DAP and NaN₃, 1 • 10⁻⁵, 5 • 10⁻⁵, 0.08 and 4 • 10⁻⁴ M, respectively; temperature, 30 °C; Curves 1 and 2 in the absence of NaN₃, H₂O and D₂O solubilized, respectively; Curves 3 and 4 in the presence of NaN₃, H₂O and D₂O cosolubilized, respectively; Curves a and b in the presence of NaN₃, 0.06 and 0.10 M DAP reversed micellar solutions, respectively, and H₂O cosolubilized.]

Simplified diagram for photochemical reaction in DAP reversed micellar solutions containing P₇, DF and NaN₃ is shown in Fig. 4. Then, the reciprocal of the quantum yield for the DF oxidation (Φ⁻¹) is represented as follows.

\[
\Phi_{DF}^{-1} = \Phi_{O_{3}}^{-1} \left( 1 + \frac{k_a + k'_q [M_{\text{empty}}] + k_q [M_{\text{NaN}_3}]}{k_r} \right) \cdot \frac{1}{[DF]},
\]

where Φ₀₂, k₁, k₂, k₃ and k₄ are illustrated in the legend of Fig. 4. [M_{NaN₃}] and [M_{empty}] denote the concentrations of NaN₃-bound and -unbound reversed micelles, respectively. Using eq. (1), k₄ and k₃ can be determined according to the usual procedure described in the previous paper [1]. Here, we assumed that one micelle bound one azide ion. The concentration of NaN₃ used was less than that of reversed micelles. The micellar concentration was determined using the aggregation number obtained from Curve 1 in Fig. 2 and the stoichiometric DAP concentration. The lifetime of singlet oxygen is 17 μsec in cyclohexane [15]. k₉ was determined to be 5.3 • 10⁻⁵ M⁻¹ sec⁻¹ from the kinetic analysis for the DF oxidation in the absence of reversed micelles.

Assuming that the dependences of the aggregation number and number of free water per reversed micelle on water concentration are same for H₂O and D₂O, the rate constants, k₄ and k'₄ were determined at various water concentrations. Results obtained are shown in Fig. 5. k₄ for empty micelles was very small in the bound water range, but it increased slightly in the free water range in

![Fig. 4. Simplified diagram for photochemical reaction in reversed micellar solutions containing P₇, DF and NaN₃. 3P₇, triplet state of P₇; Φ₀₂, quantum yield for singlet oxygen production in cyclohexane; k₁, rate constant for DF oxidation by singlet oxygen; k₂, rate constant for physical decay of singlet oxygen in cyclohexane; k₃, rate constant for the quenching of singlet oxygen by NaN₃-bound DAP reversed micelles; k₄, rate constant for the quenching of singlet oxygen by empty DAP reversed micelles.]

![Fig. 5. Rate constants for the quenching of singlet oxygen by empty micelle (k₄) and azide ion-bound micelle (k₄') as a function of H₂O or D₂O concentration. Concentrations of P₇ and DAP, 1 • 10⁻⁵ and 0.08 M, respectively; temperature, 30 °C; Curves 1 and 3 in the absence of NaN₃, H₂O and D₂O solubilized, respectively; Curves 2 and 4 in the presence of NaN₃, H₂O and D₂O solubilized, respectively; Curve 5, k₄(D₂O)/k₄(H₂O), obtained from (Curve 4)/(Curve 2); k₄(H₂O) and k₃(D₂O), rate constants for the quenching of singlet oxygen by NaN₃ when H₂O and D₂O were solubilized, respectively.]

\[\text{Cyclohexanic phase}\]

- Curve a: Empty reversed micelle
- Curve b: NaN₃-bound reversed micelle

\[\text{Empty reversed micelle}\]

\[\text{NaN₃-bound reversed micelle}\]
either case of H_2O or D_2O (Curves 1 and 3). However, k_q(H_2O), the rate constant for singlet oxygen quenching by N_3-bound micelles cosolubilized H_2O suddenly decreased from about 6 \times 10^8 M^{-1} \cdot sec^{-1} in the bound water range to about 2 \times 10^8 M^{-1} \cdot sec^{-1} in the free water range. On the contrary, k_q(D_2O), the quenching rate constant of N_3-bound micelles cosolubilized D_2O exhibited a slight change from about 6 \times 10^8 M^{-1} \cdot sec^{-1} to about 7.5 \times 10^8 M^{-1} \cdot sec^{-1} at about 0.4 M D_2O. k_q(D_2O)/k_q(H_2O) obtained from (Curve 4)/(Curve 2) is shown as Curve 5.

Fendler et al. [8] estimated solvent polarity parameters (\varepsilon_0(\infty)) in the 0.2 M DAP reversed micelles in benzene at various concentrations of solubilized water, using a linear relation between the absorption maximum of vitamin B_12a and the solvent polarity parameter. They described that the polarity in the interior of DAP reversed micelles was same as that of methanol at the water concentration of 1.1 M and that of pyridine at the water concentration of 0.033 M.

It is known that the lifetime of singlet oxygen decreases with increasing solvent polarity. The lifetime is determined to be 17 \mu sec in cyclohexane [15], 7 \mu sec in methanol [15] and 2 \mu sec in water [15]. Thus, the lifetime of singlet oxygen in DAP reversed micelles at the water concentration of 1.1 M is estimated to be about 7 \mu sec. The lifetime of singlet oxygen may be shortened when singlet oxygen in cyclohexane is trapped in the interior of the DAP reversed micelles containing solubilized water. The degree of the shortening of the lifetime may depend on the water concentration. More strictly speaking, whether the solubilized water is in the state of bound water or free water, and the amount of free water may be important factors for controlling the lifetime of singlet oxygen through the polarity of the environment of singlet oxygen. The quenching of singlet oxygen by empty reversed micelles may be caused by the degradation of singlet state of oxygen to triplet ground state in micelles. The slight increase in k_q values with increasing water concentration (Curves 1 and 3 in Fig. 5) seems to be due to the shortening of the lifetime of singlet oxygen in the free water range. In addition to this, the size of reversed micelles, which increases with increasing water concentration, is considered to be another important factor for understanding the dependence of k_q on water concentration. Larger size of the reversed micelle gives larger collisional cross-section between singlet oxygen and the reversed micelle. The quenching reaction of singlet oxygen by azide ion bound to the interior of reversed micelle may depend on the lifetime of singlet oxygen and the binding state of azide ion. As mentioned above, the lifetime of singlet oxygen is shorter in the free water range than in the bound water range. This leads to the lowering of k_q value in the former range than that in the latter (Curve 2 in Fig. 5), overcoming the factor of collisional cross-section. At present, the binding state of azide ion is not clear, so we can not go into the relation between the quenching efficiency and the binding state of azide ions.

It is known that the lifetime of singlet oxygen is about 20 \mu sec in D_2O (ten times longer than that in H_2O) [15]. The lengthening of the lifetime of singlet oxygen may result in a decrease in the quenching of singlet oxygen by empty micelles and an increase in that by azide ion-bond micelles. k_q values in the free water range was remarkably enhanced by the deuterium effect, but those in the bound water range remained unchanged (Curve 4 or 5). It is presumed that the lifetime of singlet oxygen was considerably longer in the bound water range than in the free water range and D_2O had no room for displaying the heavy atom effect.

In the present investigation, the quenching of singlet oxygen by azide ion-bond and empty DAP reversed micelles, and the deuterium effect on these singlet oxygen quenchings were found to be strongly dependent on the micellar structure and the state of solubilized water. However, detailed explanation for these phenomena awaits further experiment.