CHEMISTRY LETTERS, pp. 743-744, 1973. Published by the Chemical Society of Japan

DETERMINATION OF QUANTUM YIELD OF SINGLET OXYGEN FORMATION BY PHOTOSENSITIZATION

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Quantum yield of singlet oxygen formation for some sensitizers in aqueous solution has been determined by analyzing the concentration dependence of the quantum yield of 2,5-dimethylfuran oxidation in reference to that of methylene blue as a sensitizer.

In recent years there has been a surge of interest in the kinetic behaviors of singlet oxygen in solution as shown in many reports on the lifetime and its reactions with some substrates.1) For a quantitative interpretation of photodynamic effect in various biological systems and for the investigation to organic synthesis by photosensitized oxygenation, the determination of quantum yield for singlet oxygen formation ($\Phi_{^1O_2}$) and the evaluation of a singlet oxygen formation efficiency ($\gamma_{^1O_2}$) in the reaction between sensitizer triplet and oxygen are keenly required in addition to the intersystem crossing probability ϕ_{st} of sensitizer. The present paper describes the expedient of the determination of $\Phi_{^1O_2}$ for some sensitizers in reference to that of methylene blue (MB) by an analysis of the concentration dependence of the quantum yield of 2,5-dimethylfuran (DMF) oxidation.

According to the mechanism previously introduced in the present reaction system2,1-c) the following main processes for the photosensitization in aqueous solution are proposed by a kinetical analysis,

$$
\begin{array}{lllll}
 & MB & \xrightarrow{h\nu} & MB^T & \phi_{st} \\
MB^T + & ^3O_2 & \longrightarrow & MB + {}^1O_2 & \gamma_{^1O_2} \\
 & ^1O_2 & \longrightarrow & ^3O_2 & k_d \\
^1O_2 + & A & \longrightarrow & AO_2\ ,\ (A + {}^3O_2) & k_Q \\
AO_2 + & A & \longrightarrow & \text{diketone etc.} &
\end{array}
$$

where A is an acceptor (DMF) and AO_2 is assumed as an intermediate.

To confirm the possibility of two stage contributions of A,using 9,10-dimethylanthracene (DMA) and 1,3-diphenylisobenzofuran (DPBF) as a selective acceptor to singlet oxygen, the dependence of quantum yield of acceptor oxidation (Φ_{-A}) on the concentration was investigated by a crossing illumination method of a steady light. Since a linear relationship between reciprocals of Φ_{-A} and [A] is observed in Fig.1, Φ_{-A} could be given under a favorable conditions by,

$$\Phi_{-A} = \phi_{st}\gamma_{^1O_2} \frac{\alpha\,[\,A\,]}{\beta + [\,A\,]} \qquad (1)$$

where $\Phi_{^1O_2} = \phi_{st}\gamma_{^1O_2}$ and $\beta = k_d/k_Q$. α could be the product of trapping effeciency (γ_A) of singlet oxygen by A multiplied by the reaction efficiency proceeding forward of A. As shown in Fig.1, it seems that two molecules of these acceptors react effectively to one singlet oxygen molecule as similar with the results in the case of DMF, i.e., $\alpha = 2\gamma_A$ because the saturation values of Φ_{-A} are $2\phi_{st}\gamma_{^1O_2}\gamma_A$ ($\doteqdot$ 1.2) in Eq.(1). Although it was supposed that $\gamma_{^1O_2}$ might be equal to one approximately with a large saturation values of Φ_{-A}, this was supported by the result of pulsed ruby laser technique recently.[1-b)] Putting ϕ_{st} of MB as 0.52,[3)] γ_A could be unity within experimental error in all acceptors of DMF, DMA and DPBF. Consequently in aqueous, methanol and ethanol solutions, $\Phi_{^1O_2}$ value (0.52 ± .03) which equals to ϕ_{st} value for MB is able to be used as standard. (a little larger in dichloromethane; 0.57)

To determine $\Phi_{^1O_2}$ value to other sensitizers, a linear relation of $\Phi_{-A} = 2\Phi_{^1O_2}\beta^{-1}[A]$ in Fig,1 can be approximately employed when $\beta >> [A]$. This equation really held for the moderate concentration of DMF and $\Phi_{^1O_2}^{(X)}$ value of a given sensitizer (X) to that of MB was relatively estimated by using the ratio of slopes (S) of the linear portions on Φ_{-A} against [A] plots; that is,

$$\Phi_{^1O_2}^{(X)} = \frac{S^{(X)}}{S^{(MB)}} \Phi_{^1O_2}^{(MB)} \qquad (2)$$

From Eq.(2), $\Phi_{^1O_2}$ and $\gamma_{^1O_2}$ values for some sensitizers determined comparatively in terms of those of MB are listed in Table 1. $^1\Sigma_g^+$ oxygen which might be produced by energy transfer from some triplet sensitizers converts promptly into $^1\Delta_g$ state[1-a)] and then reacts with DMF as shown in the above scheme.

Gollnick and Schenck have previously estimated the quantum yield of the singlet oxygen formation for some xanthene dyes in methanol preliminarily. Although their values agree well with ours in Table 1, further investigation is of course necessary before a difinite interpretation is proposed for the solvent effect.

ACKNOWLEDGMENT: The author is indebted to Professor Masao Koizumi, Tohoku University for his valuable discussions.

Table 1. $\Phi_{^1O_2}$ and $\gamma_{^1O_2}$ in water(A;DMF)

sensitizer	$\Phi_{^1O_2}$		ϕ_{st}	$\gamma_{^1O_2}$
MB	0.52*		0.52	1.0*
thionine	0.58		0.55	1
erythrosine	0.68	0.6[4)]	1.0	0.68
eosine	0.57	0.3[4)]	0.64	0.89
fluorescein	0.06	0.03[4)]	0.05	1
proflavine	0.12		(0.47)**	(0.25)

*) Reference, $\beta = 3.2 \times 10^{-4}$ M
**) In ethanol

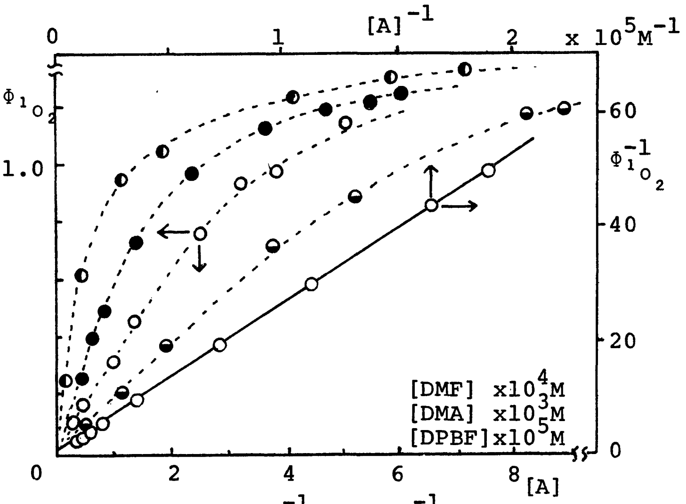

Fig.1 Φ_{-A} vs [A] and Φ_{-A}^{-1} vs $[A]^{-1}$ plots; DMF(○ in H_2O), DMA(● in EtOH), DPBF(◒ in MeOH, ◐ in CH_2Cl_2)

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(Received April 20, 1973)