## Communications to the Editor

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# PATICIPATION OF OXYGEN IN PHOTODEGRADATION OF METHYL ORANGE IN MICELLAR SOLUTION

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It has been observed that oxygen participates in the photodegradation of methyl orange in aqueous micellar solutions. The specific superoxide ion scavenger, superoxide dismutase, is not concerned in the reaction. The replacement of $H_2O$ by $D_2O$ results in a tenfold acceleration in the reaction rate. It is concluded that the singlet oxygen generated by the photosensitizer, tetraphenyl porphyrin, has an important role in the reaction.

KEYWORDS — tetraphenyl porphyrin; photosensitizer; singlet oxygen; methyl orange; micellar solution

In the previous report of this series, we described the photodegradation of azo dyes sensitized by porphyrin derivatives in micellar solution.1) In recent investigations, we have found that oxygen participates in the reaction.

Porphyrins act as sensitizers of various photoreactions including oxidation and reduction.2) When atmospheric oxygen is admitted a cuvette, a considerable amount of oxygen( $2.5 \times 10^{-4}$ M) is dissolved in the aqueous solution.3) Either superoxide ions, $O_2^{\cdot-}$, or singlet oxygen molecules, $^1O_2$, generated by the sensitizer, may take part in the photoreaction. Therefore, it is interesting to investigate the reaction in the presence of the specific scavenger of superoxide ion or the stabilizer of singlet oxygen.

Tetraphenyl porphyrin (TPP) ($1 \times 10^{-6}$ M) and methyl orange (MO) ($5 \times 10^{-5}$ M) were solubilized in a micellar solution of heptaethyleneglycol dodecylether (HED) ($2 \times 10^{-3}$M). Tris-HCl ($1 \times 10^{-3}$ M) was used to maintain the pH of the solution at 7.3 . The TPP was solubilized in the aqueous solution only with the help of the surfactant, HED, and was incorporated exclusively in the micellar phase. The irradiation source used was a 1 kW halogen lamp. The sample solution was contained and well stirred in a quartz vessel equipped with a jacket to keep the temperature at 20°C. Atmospheric oxygen was available to the solution in an open cuvette. The decrease of absorbance of MO was monitored with a Hitachi model 100-10 spectrophotometer at 450 nm. Detailed measurements are given elsewhere.1)

In Fig. 1, the decrease in the absorbance, A, of MO is represented as a function of irradiation time. The following results were obtained:

1. The purging of oxigen by nitrogen stopped MO degradation, strongly indicating the participation of oxygen in the reaction.
2. The specific superoxide ion scavenger (quencher),4) superoxide dismutase, SOD

(800 unit/ml), had no effect on the reaction rate. Therefore, $O_2^{\bar{\cdot}}$ was not concerned in the reaction.

3. A tenfold higher reaction rate resulted when $H_2O$ was replaced with $D_2O$. This is in accord with the already known fact that the singlet oxygen, $^1O_2$, has a lifetime 10 times longer in $D_2O$ ($2 \times 10^{-5}$ s) than in $H_2O$ ($2 \times 10^{-6}$ s).[5]

4. TPP was an indispensable component in the reaction and no degradation of TPP occurred after the complete degradation of MO by irradiation.

These observations indicate the participation of the singlet oxygen, $^1O_2$, generated by the photosensitization of TPP in the HED micellar phase, in MO degradation.

A reaction mechanism is proposed as follows, referring to equations in the previous report[1]

$$
\begin{array}{llll}
{}^1\mathrm{TPP} & \xrightarrow{h\nu} & {}^1\mathrm{TPP}^* & (1) \\
{}^1\mathrm{TPP}^* & \longrightarrow & {}^3\mathrm{TPP}^* & (2) \\
{}^3\mathrm{TPP}^* + {}^3O_2 & \longrightarrow & {}^1\mathrm{TPP} + {}^1O_2 & (3) \\
{}^1O_2 + \mathrm{MO} & \longrightarrow & \text{CT complex} & (4) \\
\text{CT complex} & \longrightarrow & \text{degradation products} & (5)
\end{array}
$$

Here, the CT complex is a charge transfer complex of $^1O_2$ and MO. The charge transfer complexes with $^1O_2$ have been reported in other photoreactions.[6] The higher reaction rate is obtained when the reagents are located at the more polar environment of the micelle,[1] even though the lifetime of $^1O_2$ is shorter in the polar environment.

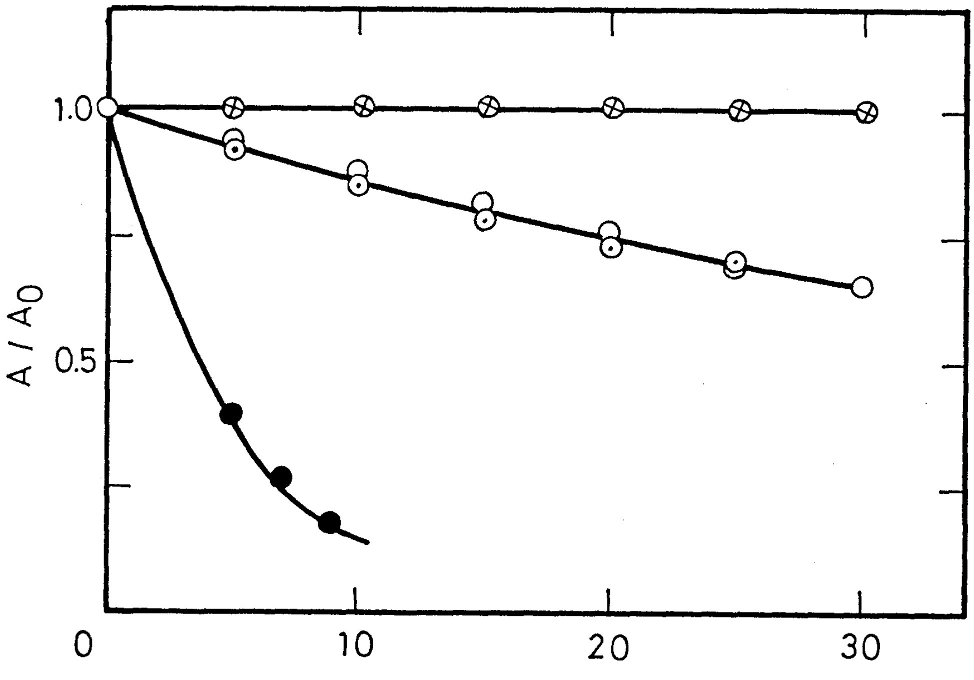

Fig.1. Degradation of MO by TPP Solubilized in the HED Micellar Phase

○: $1 \times 10^{-6}$ M TPP and $5 \times 10^{-5}$ M MO in $2 \times 10^{-3}$ M HED micellar solution at pH = 7.3 (control); ⊗ : oxygen was purged by nitrogen; ⊙ : SOD (800 unit/ml) was added in the control solution; ●: $H_2O$ was replaced by $D_2O$ in the control solution.

The singlet oxygen, $^1O_2$ ($^1\Delta_g$) is said to have a more ionic nature than the triplet oxygen because of the localization of two electrons in an antibonding orbital($\pi_x^*$ or $\pi_y^*$ ),[7] and it is expected to form the CT complex with an MO molecule in the polar environment of micelle. The highly polarized CT complex is presumed to act as the rate-determining transition state.

In conclusion, the singlet oxygen generated by TPP sensitization plays an important role in the photosensitized degradation of MO in HED micellar solutions.

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