Application of Laser Flash Photolysis to Determine Association Constants between Zn–TPPS3 and Viologens

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(Received July 30, 1984)

Synopsis. The association behavior between zinc 5,10,15,20-tetraphenylporphyrintrisulfonate (Zn–TPPS3) and viologens was investigated from the T-T absorption band of the triplet Zn–TPPS3 by laser-flash photolysis. The association constants of Zn–TPPS3 with methylviologen and propylviologen-3,3′-sulfonate (PVS) were 1.7×10^4 and 7.3×10^2 $mol^{-1}\cdot dm^3$, respectively.

Water-soluble zinc meso-tetraphenylporphyrintrisulfonate (Zn–TPPS3) has been found to be a suitable photosensitizer in the photoinduced hydrogen evolution system, consisting of a photosensitizer, an electron donor, an electron acceptor, and a catalyst.[1] Zn–TPPS3, however, has been reported to form a complex with viologen and it has been clarified that the complex does not take part in the photoreduction of viologen, and that only the uncomplexed Zn–TPPS3 plays an important role in the reaction.[2] The determination of the association constant between Zn–TPPS3 and viologen provides suitable reaction conditions. As it is difficult to determine the association constant from the visible spectra (the visible spectra of the complex is very similar to that of Zn–TPPS3) a laser-flash photolysis was applied to determine the association constant in this study.

Experimental

Methylviologen was purchased from Tokyo Kasei Kogyo Co., and PVS was prepared according to the literature.[3] The sample solution, which consisted of Zn–TPPS3 and viologen (if included), was deaerated by repeated freeze-pump-thaw cycles. Conventional laser photolysis was carried out using a Nd-YAG Laser, Model HY-500 from JK Lasers Ltd., equipped with second, third, and fourth harmonic generators. The second harmonic (532 nm), of *ca.* 100 mJ cm^{-2} and a flash duration of 20 ns was used to excite the sample solutions throughout this study. The analyzing light beams from a xenon lamp (Ushio UXL-150 D, 150 W) were intensified by a factor of *ca.* 20 during the detection of the transient spectra. Transient spectra having a lifetime longer than 200 μs were measured without intensification of the analyzing light. The light, after passing through a sample cell, was focused onto the entrance slit of a monochromator (Model MC-20 N from Ritsu Appl. Opt. Co.). The output from a Hamamatsu photomultiplier (R 758) attached to the exit slit of the monochromator was displayed on a Tektronix oscilloscope, Model 7904.

Results and Discussion

Figure 1-(a) shows an oscilloscopic photograph monitored at 470 nm (the peak wavelength of the T-T absorption band due to the triplet Zn–TPPS3) after a laser flash. In the presence of methylviologen, the decay rate of the transient spectrum measured at 470 nm increased, as shown in Fig. 1-(b) and 1-(c). The methylviologen cation radical (MV^+, $\lambda_{max}=605$ nm) initially increased and then decreased as shown in Fig. 1-(e) and 1-(f). The absorbance of the triplet spectrum at 470 nm measured immediately after the laser flash decreased with an increase in methylviologen concentration (Fig. 1-(a), 1-(b), and 1-(c)), and the T-T absorption was not detected at concentrations higher than 5.01×10^{-3} $mol\cdot dm^{-3}$. As a consequence of the decrease in the absorbance at 470 nm, the concentration of MV^+ formed after the laser flash decreased, and MV^+ formation was not observed in the absence of T-T absorption as shown in Fig. 1-(g). These results can be expressed by the following reaction scheme, suggesting the 1:1 complex (PQ) formation between Zn–TPPS3 (P) and MV^{2+} (Q).

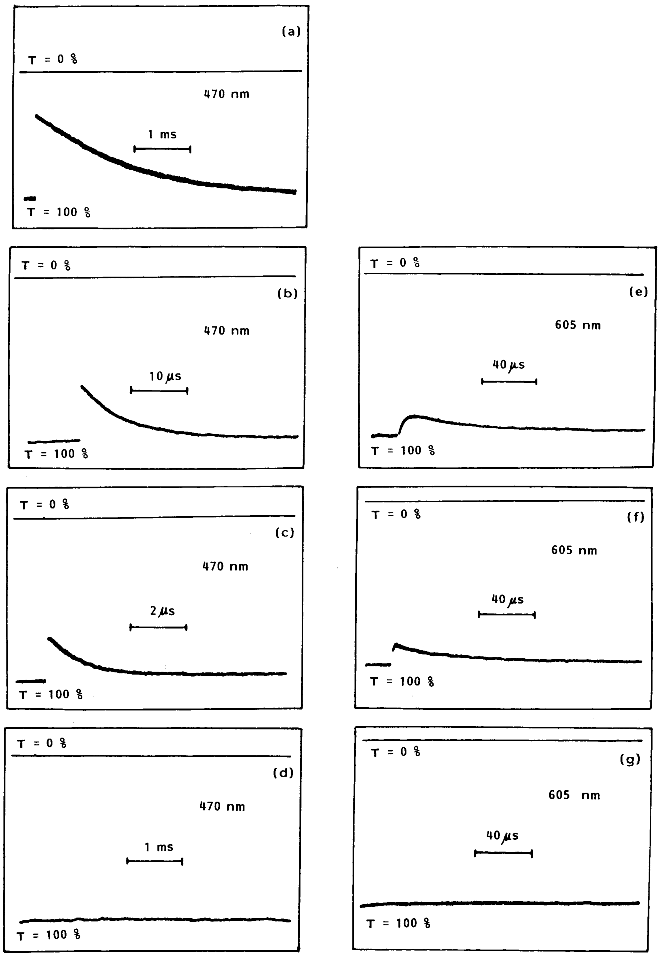

Fig. 1. Oscilloscopic photographs obtained from laser flash photolysis of aqueous solutions of (a) Zn–TPPS3, (b)—(g) Zn–TPPS3+MV^{2+}. Zn–TPPS3: 3.03×10^{-5} $mol\cdot dm^{-3}$; concentration of viologens, (a): 0, (b), (e): 1.21×10^{-5} (c), (f): 5.01×10^{-5}, (d), (g): 5.01×10^{-3} $mol\cdot dm^{-3}$.

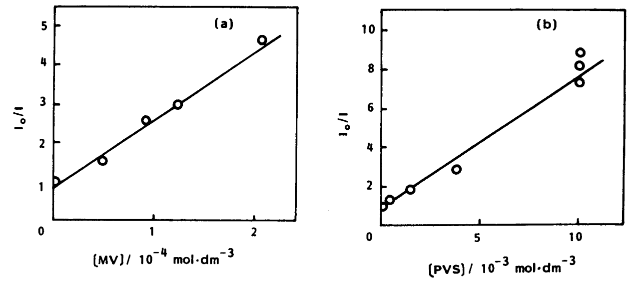

Fig. 2. Relation between I_0/I and the concentration of methylviologen or PVS.

$$\mathrm{P} + \mathrm{Q} \overset{K}{\rightleftarrows} \mathrm{PQ}$$

$$\mathrm{P} \xrightarrow{h\nu} {}^3\mathrm{P}^*$$

$$ {}^3\mathrm{P}^* + \mathrm{Q} \longrightarrow \mathrm{P}^{\dagger} + \mathrm{Q}^{\overline{\cdot}}$$

$$\mathrm{P}^{\dagger} + \mathrm{Q}^{\overline{\cdot}} \longrightarrow \mathrm{P} + \mathrm{Q}$$

$$\mathrm{PQ} \xrightarrow{h\nu} \mathrm{PQ}^* \xrightarrow{\text{fast}} \mathrm{PQ}$$

where K is the association constant.

According to such a reaction scheme, the concentration of PQ increases with the increase of the Q concentration. The absorbance of the T-T absorption at 470 nm is considered to be proportional to the concentration of uncomplexed Zn–TPPS$_3$ on the assumption that the photoexcited complex (PQ*) may convert to PQ very rapidly. We, therefore, obtain,

$$I_0/I = 1 + K[\mathrm{Q}]$$

where I_0 and I are the absorbance at 470 nm measured immediately after the laser flash in the absence and in the presence of methylviologen, respectively. This equation is the same as that reported previously[4] in the case of the static quenching of fluorescence.

As shown in Fig. 2-(a), the fairly linear relationship between I_0/I and [Q] indicates that the above proposed scheme is adequate. From the slope of the straight line, the K value was obtained as $1.7\times10^4\,\mathrm{mol^{-1}\cdot dm^3}$. For propylviologen-3,3′-sulfonate(PVS), a similar linear relationship was also obtained (Fig. 2-(b)), and the K value was $7.3\times10^2\,\mathrm{mol^{-1}\cdot dm^3}$. The difference in the K values between PVS and methylviologen is explained by the difference of electrostatic force between Zn–TPPS$_3$ and viologens or the redox potentials of each viologen.

The difference between the redox potential of methyl-viologen (−0.44 eV *vs* NHE) and that of PVS (−0.41 eV *vs* NHE) is so small that the larger K value of methylviologen compared with PVS may be mainly due to an electrostatic effect. Since the positively charged methylviologen is more favorable to associate with the negatively charged Zn–TPPS$_3$, the larger K value detected for methylviologen (compared with PVS) is plausible.

References

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