November, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *55*, *3637—3638 (1982)* 3637

The Photoreduction of Viologen Dyes with Palladium *meso*-Tetraphenylporphyrintrisulfonate

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(Received April 1, 1982)

Synopsis. Pd–TPPS$_3$ was found to be an effective photosensitizer for the photoreduction of viologen dyes, such as methyl, ethyl, propyl, butyl, and heptyl viologens. The order of the reduction rate was as follows: Ethyl>Butyl>Methyl>Propyl>Heptyl. The respective complex formation was observed between Pd–TPPS$_3$ and viologen dyes, and electron transfer from photoexcited Pd–TPPS$_3$ to viologen dye was discussed.

Various attempts have been made to develop suitable redox systems for the photochemical utilization of solar energy. Recent works have shown that three-component systems containing a photosensitizer, an electron donor, and an electron acceptor can be used to evolve hydrogen from water when a suitable catalyst is present.[1)] The metallo porphyrins employed almost exclusively in these studies as photosensitizers are zinc porphyrins.[2)] It is desirable to explore other, suitable photosensitizers. In this study, palladium *meso*-tetraphenylporphyrintrisulfonate (Pd–TPPS$_3$) was found to be an effective photosensitizer for the photoreduction of viologen dyes; the reason for its effect was discussed.

Experimental

The methyl viologen and heptyl viologen were purchased from the Tokyo Kasei Kogyo Co. and the Aldrich Chemical Co. respectively, while the other chemicals, obtained from the Wako Pure Chemical Co., were of the highest available purity. The ethyl, propyl, and butyl viologens were synthesized according to the literature.[3)] Pd–TPPS$_3$ was synthesized by refluxing *meso*-tetraphenylporphyrintrisulfonic acid and equimolar palladium acetate in methanol for 1 h.

The sample solution, which consisted of Pd–TPPS$_3$, viologen dye and 2-mercaptoethanol (RSH) in a Tris–HCl buffer (pH 7.0), was deaerated by repeated freeze-pump-thaw cycles. A typical experiment was performed as follows under anaerobic conditions. To 1.20×10^{-8} mol of Pd–TPPS$_3$ and 8.25×10^{-7} mol of viologen dye, 6.41×10^{-4} mol of RSH was added. The volume of the mixture was adjusted to 6.5 ml with a 0.02 M Tris–HCl buffer (pH 7.0). In the photolysis with continuous irradiation, the sample in a Pyrex cell with a magnetic stirrer was irradiated with light from a 150-W tungsten lamp (from a slide projector). Light of wavelength less than 390 nm was cut off by means of a Toshiba L-39 filter.

Results and Discussion

When an aqueous solution containing Pd–TPPS$_3$, methyl viologen, and RSH was irradiated, the growth of the cation radical of methyl viologen, which has characteristic absorption bands at 395 and 605 nm, was observed. The concentration of the reduced form of methyl viologen (MV$^+$) increased rapidly at the beginning of the reaction and then reached a constant value. When irradiation ceased, the concentration of MV$^+$ gradually decreased until it reached zero. MV$^+$ was reformed by re-irradiating the system, and the MV$^+$ formation rate was almost the same as the initial rate, for MV$^+$ returns to its original (oxidized) form in the absence of light. When other viologens, such as ethyl, propyl, butyl and heptyl viologens, were used instead of methyl viologen, the respective cation-radical formation was established by the irradiation. The order of the reduction rate was as follows:

Ethyl (2.40×10^{-5} M) > Butyl (1.8×10^{-5} M) > Methyl (1.56×10^{-5} M) $\simeq$ Propyl (1.55×10^{-5} M) > Heptyl ($\simeq$0 M).

The figures in the parentheses indicate the concentration of cation radicals formed by a 40-min irradiation. As the reduced forms of these viologens have redox potentials high enough for the decomposition of water, they may be useful as electron carriers to evolve hydrogen from water. In practice, hydrogen evolution by the reduction of water has been confirmed by the addition of hydrogenase as a catalyst to the reduced viologen dye formed by the reduction with $Na_2S_2O_4$.

Pd–TPPS$_3$ was a very active photosensitizer such one which was equal to Zn–TPPS$_3$ and far better than popular photosensitizers as ruthenium complexes. The photoreduction rate of methyl viologen with Pd–TPPS$_3$ was 12 times as large as that with palladium tetraphenylporphyrin (Pd–TPP), though it contains the same metal in the porphyrin ring. The difference in these activities may depend on the relative hardness of a complex formation between porphyrin and vi-

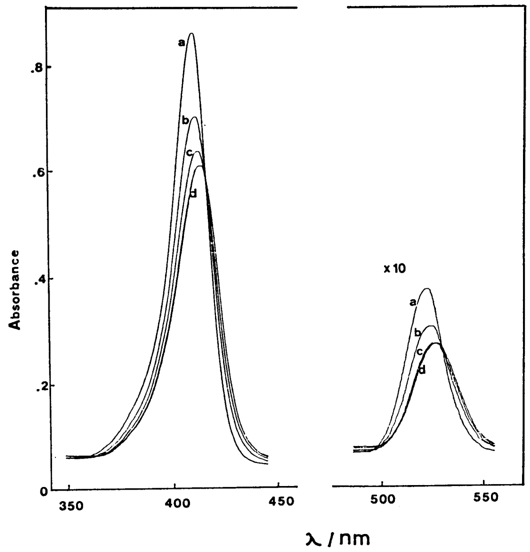

Fig. 1. Spectrum change of Pd–TPPS$_3$ by the addition of methyl viologen.
Sample solution contains 6.85×10^{-6} M of Pd–TPPS$_3$ and methyl viologen (a: 0 M; b: 2.03×10^{-5} M; c: 1.01×10^{-4} M; d: 5.07×10^{-4} M).

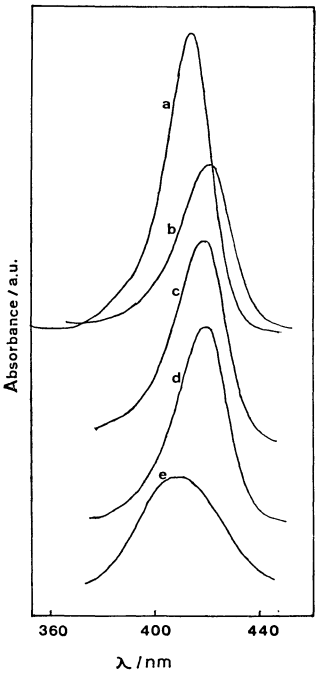

Fig. 2. Spectrum change of Pd–TPPS$_3$ by the addition of viologens.
a: Pd–TPPS$_3$, b: Pd–TPPS$_3$+ethyl viologen, c: Pd–TPPS$_3$+propyl viologen, d: Pd–TPPS$_3$+butyl viologen, e: Pd–TPPS$_3$+heptyl viologen.

ologen dye. Though a complex formation between Pd–TPPS$_3$ and viologens was observed as follows, no complex was formed in the case of Pd–TPP. When Pd–TPPS$_3$ was mixed with methyl viologen, the characteristic absorption bands at 409 and 521 nm of Pd–TPPS$_3$ decreased with the increase in the methyl viologen concentration, and a new spectrum appeared which has characteristic absorption bands at 414 and 527 nm through isosbestic points at 361, 417, 498, and 530 nm (Fig. 1). When other viologen dyes were used, the respective complex formation was observed, as is shown in Fig. 2. In the case of copper uroporphyrin, complex formation with methyl viologen was observed by Shelnutt.[4] The red shift in the Soret band of the complex is usually associated with a decrease in π-electron density in the porphyrin ring. The π-density in the ring follows this order: heptyl>methyl>propyl>butyl>ethyl. The lower the π-density of the ring, the larger the photoreduction rate of viologens, except for methyl viologen. The finding that the porphyrin ring acts as a donor in the ground state of the complex may show that photoinduced electron transfer from Pd–TPPS$_3$ to viologen dyes is apt to occur. Thus, viologens may be easily photoreduced. In the case of Pd–TPP, electron transfer from the photoexcited Pd–TPP to viologens may not proceed easily; a low reduction rate of methyl viologen is observed as a result.

Recently Matsuo *et al.*[5] prepared viologen-linked photosensitizers and found that electron was easily transferred from the photosensitizer to viologen dye and any undesirable back reaction was suppressed. In the cases of these Pd–TPPS$_3$–viologen complexes, easy electron transfer may also be found as a result of a similar effect.

We wish to express our appreciation to Professor Tominaga Keii and Professor Yoshio Ono for their stimulating and helpful discussions.

References

1) a) J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, **1**, 449 (1977); b) M. Kirch, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979); c) K. Kalyanasundaram, J. Kiwi, and M. Gratzel, *ibid.*, **61**, 2720 (1978); d) K. Kalyanasundaram and M. Gratzel, *J. Chem. Soc., Chem. Commun.*, **1979**, 1137; e) A. Moradpour, E. Amouyal, P. Keller, and H. Kagan, *Nouv. J. Chim.*, **2**, 547 (1978); f) A. I. Krasna, *Photochem. Photobiol.*, **29**, 267 (1979); g) I. Okura and N. Kim-Thuan, *J. Mol. Catal.*, **5**, 311 (1979); h) I. Okura, S. Nakamura, N. Kim-Thuan, and K. Nakamura, *ibid.*, **6**, 261 (1979); i) I. Okura and N. Kim-Thuan, *J. Chem. Soc., Chem. Commun.*, **1980**, 84; j) I. Okura and N. Kim-Thuan, *J. Chem. Soc., Faraday Trans. 1*, **76**, 2209 (1980).

2) a) K. Takuma, M. Kajiwara, and T. Matsuo, *Chem. Lett.*, **1977**, 1199; b) I. Okura and N. Kim-Thuan, *J. Mol. Catal.*, **6**, 227 (1979); c) I. Okura, M. Takeuchi, and N. Kim-Thuan, *Chem. Lett.*, **1980**, 765; d) K. Kalyanasundaram and M. Gratzel, *Helv. Chim. Acta*, **63**, 478 (1980).

3) A. G. Evans, J. C. Evans, and M. W. Baker, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1787.

4) J. A. Shelnutt, *J. Am. Chem. Soc.*, **103**, 4275 (1981).

5) T. Matsuo, T. Sakamoto, K. Takuma, K. Sakura, and T. Ohsako, *J. Phys. Chem.*, **85**, 1277 (1981).