

## Photoredox Reaction in Micellar Solutions Sensitized by Surfactant Derivative of Tris(2,2'-bipyridyl)ruthenium(II)

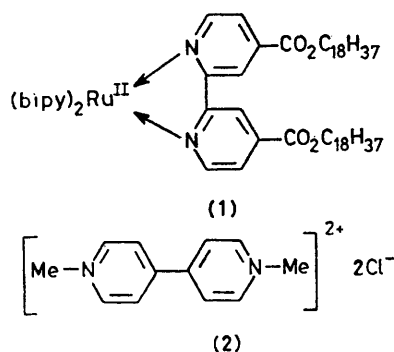
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*Summary* The photoreduction of Methyl Viologen sensitized by the surfactant derivative of tris(2,2'-bipyridyl)-ruthenium (II) in anionic sodium lauryl sulphate micelles with cysteine as donor has been demonstrated by steady state *ir* adiation methods.

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RECENTLY there has been a growing interest in the visible light sensitized photoredox reactions as a means of solar energy conversion and storage. In order to overcome the major limitation of the fast thermodynamically favourable back reactions of redox products, attention has been focused on the use of multiphase systems such as micelles



and lipid vesicles. The surfactant derivative (1) of tris-(2,2'-bipyridyl)ruthenium(II) recently received wide attention<sup>1</sup> as a possible photo-sensitizer for the photolysis of water. We report here the visible light sensitized reduction of the dye Methyl Viologen (2) in anionic micelles with the surfactant derivative (1) as the sensitizer and cysteine or ascorbate as donors. Formation of redox products by photosensitization through  $[\text{Ru}(\text{bipy})_3]^{2+}$  has been observed only as transients in flash photolysis studies<sup>2</sup> and, as far as we are aware, this is the first example of a case where a photoredox reaction between a donor-acceptor pair (neither of them absorb in the visible) has been brought about by steady state irradiation methods using a transition metal complex as a sensitizer.<sup>†</sup> In the present case, the reduced acceptor is quite stable for a few hours in the dark.

The surfactant derivative  $[(\text{bipy})_2\text{Ru}^{\text{II}}(\text{bipy})(\text{CO}_2\text{C}_{18}\text{H}_{37})_2]^{2+}$  (1),<sup>‡</sup> which is water-insoluble, can be solubilised readily in anionic sodium lauryl sulphate (NaLS) micellar solution. The absorption spectrum of (1) in aqueous NaLS<sup>§</sup> shows maxima at 415 and 500 nm and an emission maximum at 693 nm. Irradiation of a micellar solution containing (1) ( $1 \times 10^{-5} \text{ mol l}^{-1}$ ), cysteine ( $0.02 \text{ mol l}^{-1}$ ), and Methyl Viologen ( $2 \times 10^{-3} \text{ mol l}^{-1}$ ) with visible light ( $\lambda \geq 440 \text{ nm}$ ) leads to the development of a blue colour, due to the formation of reduced Methyl Viologen ( $\text{MV}^{\cdot+}$ ). While cysteine, cystine, and Methyl Viologen do not absorb above 350 nm, the one-electron reduction product  $\text{MV}^{\cdot+}$  has two distinct absorption maxima in the visible region:  $\lambda 395$  ( $\epsilon 38,000$ ) and 605 nm ( $\epsilon 10,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). The Figure presents a typical absorption spectrum of the solution before and after various times of continuous irradiation with visible light ( $\lambda \geq 440 \text{ nm}$ ) using an 800 W tungsten-halogen lamp as the light source, used in conjunction with a water (heat) filter and a 440 nm cut-off glass filter. The increased absorption at 395 and 605 nm are due to  $\text{MV}^{\cdot+}$  formed by photosensitized electron transfer from cysteine.

Under degassed conditions,  $\text{MV}^{\cdot+}$  absorptions persist for a few hours in the dark. We have observed the above sensitized reduction also in non-ionic micellar systems composed of Triton X-100 or Igepal (CO-630). In both systems, reduction is more efficient with cysteine than with ascorbate.

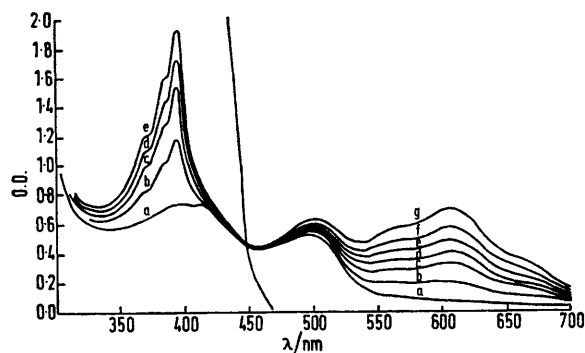


FIGURE. Absorption spectrum of the three-component system, cysteine-sensitizer-Methyl Viologen, in the anionic micellar solutions of NaLS before (a) and after 5 min (b), 15 min (c), 25 min (d), 40 min (e), 55 min (f), and 70 min (g), irradiation with visible light ( $\lambda > 440 \text{ nm}$ ). Sensitizer =  $1 \times 10^{-5} \text{ mol l}^{-1}$ ; cysteine =  $0.02 \text{ mol l}^{-1}$ ; Methyl Viologen  $5 \times 10^{-3} \text{ mol l}^{-1}$ , and NaLS =  $0.1 \text{ mol l}^{-1}$ .

The main features of this sensitized reduction of  $\text{MV}^{2+}$  using (1) are very similar to the reductions we examined earlier<sup>3</sup> using chlorophyll-a as the sensitizer in non-ionic micelles: (i) there is no formation of  $\text{MV}^{\cdot+}$  in the dark or on steady irradiation in the cysteine- $\text{MV}^{2+}$  system without the sensitizer and also in the sensitizer- $\text{MV}^{2+}$  system without the donor cysteine, (ii) there is also no reduction of  $\text{MV}^{2+}$  in the dark or on irradiation of aerated three-component (donor-acceptor) solutions, (iii) the role of (1) is strictly that of a photocatalyst in that it is not consumed and there is considerably more  $\text{MV}^{\cdot+}$  formed than the amount of (1) present, and (iv) the reduction is energy storing, in that part of visible light is converted into useful chemical energy as reduced Methyl Viologen ( $E'_0$  for cysteine and Methyl Viologen are  $-0.240$  and  $-0.440 \text{ V}$ , respectively). In aqueous micellar systems, hydrogen gas can be released<sup>4</sup> from  $\text{MV}^{\cdot+}$  through the use of enzymes such as hydrogenase.

It is to be pointed out that this photosensitized reduction employs cysteine as a donor, a fuel not readily available. For any practical application on a large scale one must use donors which are more readily available.

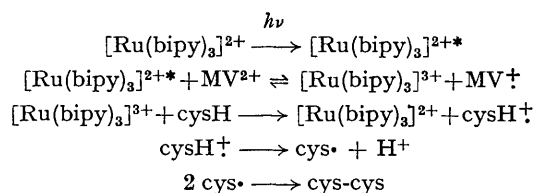
It is most likely that the oxidative mechanism in the Scheme is operative<sup>¶</sup> in the photosensitized electron transfer from cysteine to Methyl Viologen.

<sup>†</sup> Since the submission of this communication, a referee has brought our attention to a related work in which  $\text{Ru}^{\text{II}}$  has been used as a donor: D. M. Headstrand, W. H. Kruizinga, and R. M. Kellogg, *Tetrahedron Letters*, 1978, 1255.

<sup>‡</sup> Purified sample of (1) used in this study was prepared according to the procedures outlined in the literature (G. L. Gaines and S. J. Valenty, *J. Amer. Chem. Soc.*, 1977, **99**, 1285; A. Harriman, *J.C.S. Chem. Comm.*, 1977, 777; K. P. Seefeld, D. Möbins, and H. Kuhn, *Helv. Chim. Acta*, 1977, **60**, 2608) and gave satisfactory elemental analysis and absorption spectral features in chloroform.

<sup>§</sup> In order to avoid hydrolysis of the sensitizer, the pH of the solution was kept at  $6.5 \pm 0.2$ .

<sup>¶</sup> Based on the quenching of the sensitizer emission at 694 nm under the concentrations employed for cysteine and Methyl Viologen, the oxidative quenching of emission by  $\text{MV}^{2+}$  is much more efficient than reductive quenching by cysteine.



We are grateful to Dr. A. Harriman for a generous gift of a sample of (1) and also for stimulating discussions during the course of this work and to Professor Sir George Porter, F.R.S. for providing laboratory facilities and financial support.

SCHEME. For brevity, the surfactant derivative (1) is shown as  $[\text{Ru}(\text{bipy})_3]^{2+}$ , cysteine as cysH, and cystine as cys-cys.

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<sup>1</sup> G. Sprintschnik, H. W. Sprintschnik, P. D. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1976, **98**, 2337.

<sup>2</sup> J. K. Nagle, R. C. Young, and T. J. Meyer, *Inorg. Chem.*, 1977, **16**, 3366; R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1975, **97**, 4781.

<sup>3</sup> K. Kalyanasundaram and G. Porter, *Proc. Roy. Soc.*, to be submitted.

<sup>4</sup> A. A. Krasnovskii, V. V. Nikandrov, G. P. Brin, I. N. Gogotov, and V. P. Oshchepkov, *Doklady Akad. Nauk S.S.S.R.*, 1975, **225**, 711; J. R. Benemann and N. M. Weare, *Science*, 1974, **184**, 174.