Photoinduced Reduction of Potassium Hexacyanoferrate(III) by Iron(II) Chloride in the Liposome System

By Yukio Sudo and Fujio Toda*

(*Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo* **113**, *Japan*)

Summary The photoinduced reduction of potassium hexacyanoferrate(III) by iron(II) chloride was carried out in the liposome system using Methylene Blue as a photosensitizer.

Investigation of photoinduced electron transport across membranes is important for simulating the primary process of photosynthesis. Active transport of electrons from the lower energy side of the membrane to the higher energy side is also useful for simulating solar energy conversions. Although there have been many reports of photoinduced electron transport models using liposome[1–3] or black membrane,[4,5] almost all reported reactions are 'down-hill' as far as the gradient of the redox potential is concerned. They can also take place in the homogeneous system without using either liposome or black membrane.

We have previously reported that photoinduced electron transport across the phospholipid wall of liposome can take place using Methylene Blue as a photosensitizer (without using any quinone or carotene).[6] Using this system, we report here the photoinduced reduction of hexacyanoferrate(III) by iron(II) chloride sensitized by Methylene Blue. This reaction is 'up-hill' and will not occur either in the homogeneous system or in the ordinary micellar system.

The reaction was carried out in a single wall liposome system (Figure) with Methylene Blue acting as both a photosensitizer and an electron carrier. The single wall liposome system containing potassium hexacyanoferrate(III) only in the inner aqueous phase of each vesicle was treated as follows. Lecithin (isolated from egg yolk[7]) was dispersed in buffered 1 M potassium hexacyanoferrate(III). After the dispersion was subjected to ultrasonic radiation, the untrapped potassium hexacyanoferrate(III) was completely removed by gel filtration over Sephadex G-50. Then a known amount of Methylene Blue and iron(II) chloride was added. The photoreaction was carried out under nitrogen at room temperature by irradiating the solution with a super-high pressure mercury lamp. Light of shorter wavelength than 460 nm was completely removed by the u.v.-46 filter.

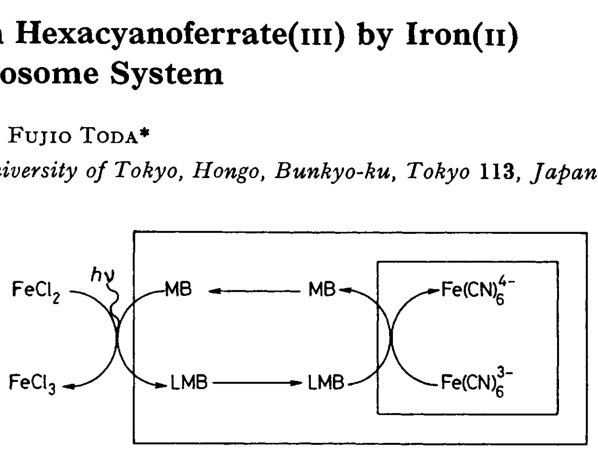

Figure. Schematic diagram of the liposome system. MB, Methylene Blue; LMB, leuco Methylene Blue.

Only one major spectral change was observed when the solution was irradiated. The hexacyanoferrate(III) absorption at 420 nm decreased as the hexacyanoferrate(III) was reduced. Changes in absorption for other components of the system were negligible.

The Table shows the relative reduction rates of hexacyanoferrate(III) under different conditions. The reduction rate was determined by measuring the decrease in absorption at 420 nm. When the reaction was carried out without

TABLE. Relative reduction rates of hexacyanoferrate(III) under different conditions

Methylene Blue/ 10^{-5} M	$FeCl_2$/M	Light[a]	Relative rates
4·0	0·01	+	4·0
2·4	0·01	+	2·5
1·2	0·01	+	1·0
0	0·01	+	0
1·2	0	+	0
1·2	0·01	−	0

[a] + Irradiated, − non-irradiated.

either hexacyanoferrate(III), iron(II) chloride or light no reduction was observed. The reduction rate was found to increase linearly with Methylene Blue concentration. Neither hexacyanoferrate(III) nor iron(II) chloride penetrated the phospholipid wall. Self reduction of Methylene Blue and hexacyanoferrate(III) does not occur, as described previously. From these results, it is clear that hexacyanoferrate(III) is an electron acceptor and iron(II) chloride is an electron donor. The reaction is thought to proceed via steps (1)—(4).

$$\mathrm{MB(out)} + h\nu \rightarrow \mathrm{MB^{*}(out)} \qquad (1)$$

$$\mathrm{MB^{*}(out)} + \mathrm{Fe^{2+}} \rightarrow \mathrm{LMB(out)} + \mathrm{Fe^{3+}} \qquad (2)$$

$$\mathrm{LMB(out)} \rightarrow \mathrm{LMB(in)} \qquad (3)$$

$$\mathrm{LMB(in)} + \text{hexacyanoferrate(III)} \rightarrow \mathrm{MB} + \text{hexacyanoferrate(II)} \qquad (4)$$

where MB = Methylene Blue, LMB = leuco Methylene Blue, out = outside, in = inside.

This electron transfer does not occur under ordinary conditions for the following reasons. First, the redox potential of iron(II) chloride (E_0' 0·77 V) is higher than that of hexacyanoferrate(III) (E_0' 0·33 V). Secondly, iron(II) chloride reacts rapidly with potassium hexacyanoferrate(III) to form a deep blue precipitate of iron(II) hexacyanoferrate(III) (Turnbull's Blue). When the vesicle containing potassium hexacyanoferrate(III) inside and iron(II) chloride outside was destroyed by the addition of detergent, the dispersion soon turned deep blue and Turnbull's Blue was precipitated.

Thus we have carried out a photosensitized reduction of hexacyanoferrate(III) by iron(II) chloride in the liposome system. This reaction is noteworthy because it cannot be observed in the ordinary system.

(*Received*, 19*th June* 1979; *Com.* 654.)

[1] M. Mangel, *Biochim. Biophys. Acta*, 1976, **430**, 459.
[2] Y. Toyoshima, M. Morino, H. Motoki, and M. Sukigara, *Nature*, 1977, **265**, 187.
[3] J. W. Otvos and M. Calvin, *Nature*, 1978, **274**, 507; *Internat. J. Energy Res.*, 1979, **3**, 80.
[4] M. Mangel, D. Bevns, and A. Ilani, *J. Membrane Biol.*, 1975, **20**, 171.
[5] H. Ti. Tien and S. P. Verna, *Nature*, 1969, **227**, 1232.
[6] Y. Sudo and F. Toda, *Nature*, 1979, **279**, 807.
[7] C. H. Lea, D. H. Rhodes, and R. D. Stoll, *Biochemistry*, 1975, **60**, 353.