Photosensitized Electron Transport across a Liquid Membrane containing Photosensitizer, Electron Mediator, and Carrier

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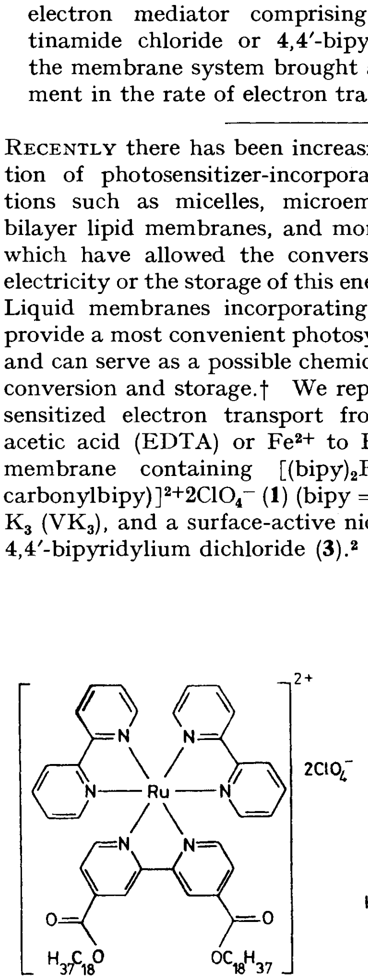
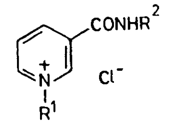
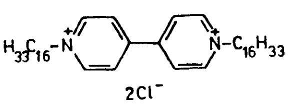
Summary Photosensitized electron transport from ethylenediaminetetra-acetic acid or Fe^{2+} to $Fe(CN)_6^{3-}$ proceeded across a liquid membrane containing both a surface active ruthenium(II) complex and vitamin K_3, supported on a millipore filter; the incorporation of an electron mediator comprising a surface-active nicotinamide chloride or 4,4′-bipyridylium dichloride into the membrane system brought about a marked enhancement in the rate of electron transport.

RECENTLY there has been increasing interest in the formation of photosensitizer-incorporated molecular organizations such as micelles, microemulsions, vesicles, planar bilayer lipid membranes, and monomolecular layer arrays, which have allowed the conversion of solar energy into electricity or the storage of this energy in chemical products. Liquid membranes incorporating various photosensitizers provide a most convenient photosynthetic membrane model and can serve as a possible chemical device for solar energy conversion and storage.† We report here the visible light-sensitized electron transport from ethylenediaminetetra-acetic acid (EDTA) or Fe^{2+} to $Fe(CN)_6^{3-}$ across a liquid membrane containing $[(bipy)_2Ru^{II}(4,4'\text{-bisoctadecyloxycarbonylbipy})]^{2+}2ClO_4^-$ (**1**) (bipy = 2,2′-bipyridyl),[1] vitamin K_3 (VK_3), and a surface-active nicotinamide chloride (**2**) or 4,4′-bipyridylium dichloride (**3**).[2]


(**1**)


(**2**)

a; $R^1 = C_{16}H_{33}$, $R^2 = H$
b; $R^1 = R^2 = C_{18}H_{37}$


(**3**)

The electron-transport system consisted of EDTA (1 mmol) with (a) phosphate buffer (pH 7·0; 50 ml) or (b) $FeCl_2.4H_2O$ (3 mmol)–H_2O (50 ml) (Red. phase) and $K_3Fe(CN)_6$ (50 μmol) with phosphate buffer (pH 7·0; 50 ml) for Red. phase (a) and H_2O (50 ml) for Red. phase (b) (Ox. phase), separated by a liquid membrane (M. phase) comprising VK_3 alone (40 μmol), VK_3 (40 μmol) + (**1**) (0·15 μmol), or VK_3 (40 μmol) + (**1**) (0·15 μmol) + (**2**) or (**3**) (0·15 μmol) in Ph_2O–$Cl_2CHCHCl_2$ (10:3) (w/w) (0·12 ml), supported on a Fluorinert millipore filter with a pore size of 0·2 μm (Millipore Ltd.).‡ Equilibrations were conducted at 35 ± 1 °C and the aqueous phases were vibrated gently to facilitate mixing by argon bubbling. The extent of electron transport was determined spectrophotometrically by continuously monitoring the decrease in the absorbance of $Fe(CN)_6^{3-}$ at 421 nm.

Without irradiation there was no electron transport between the two aqueous phases for any of the membrane systems VK_3, VK_3 + (**1**), or VK_3 + (**1**) + (**2**) or (**3**) during 5 h. However, electron transport did occur when the membrane system was irradiated with visible light. Transport rates for the membrane systems containing VK_3 + (**1**), and VK_3 + (**1**) + (**2**) or (**3**) were 2—7 times higher than those for the membrane containing VK_3 alone when EDTA was used as a reductant (Table 1). The membrane containing VK_3 + (**1**) + (**3**) was the most effective. The increased transport rates remained constant during an initial period of *ca.* 1 h, but then decreased markedly probably because of dimer formation from the radicals of (**2**) and an unknown reaction of (**3**). However,

TABLE 1. Photosensitized electron transport from EDTA to $Fe(CN)_6^{3-}$ across various liquid membrane systems at 35 ± 1 °C.

Red. phase	M. phase[b]	Transport rate[a]/ μmol h^{-1}
EDTA	VK_3[b]	1·6
”	VK_3 + (**1**)[b]	4·0
”	VK_3 + (**1**)[b,c]	7·5
”	VK_3 + (**1**) + (**2a**)[b]	5·9[d]
”	VK_3 + (**1**) + (**2b**)[b]	7·8[d]
”	VK_3 + (**1**) + (**3**)[b]	11·6[d]
”	VK_3 + (**1**) + (**3**)[b,c]	7·2
EDTA + (**4**)	VK_3[b]	3·8
”	VK_3 + (**2a**)[b]	3·5
”	VK_3 + (**2b**)[b]	2·2
”	VK_3 + (**3**)[b]	4·8
”[e]	VK_3 + (**3**)[b]	3·6

[a] Transport rates are those for an initial 1 h period. Electron transport was not observed for the systems EDTA with VK_3, VK_3 + (**1**), or VK_3 + (**1**) + (**2**) or (**3**), and EDTA + (**4**) with VK_3 or VK_3 + (**2**) or (**3**) in the dark. [b] Irradiated (λ >400 nm). [c] The Ox. phase was kept in contact with one side of the filter covered with VK_3 and (**1**) or VK_3 and (**1**) + (**3**). In the other experiments the covered side was in contact with the Red. phase. [d] After *ca.* 1 h the rates decreased to 3·8, 3·6, and 1·8 μmol h^{-1} for (**2a**), (**2b**), and (**3**), respectively. [e] 107 μmol of (**4**).

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† There are previous reports that electron transport across a liquid membrane containing an electron carrier is driven by the irradiation of a photosensitizer dissolved in the aqueous phase [J. J. Grimaldi, S. Boileau, and J.-M. Lehn, *Nature (London)*, 1977, **265**, 229; I. Tabushi, A. Yazaki, N. Koga, and K. Iwasaki, *Tetrahedron Lett.*, 1980, 373].

‡ In the usual manner one side of the filter covered with a mixture of the membrane components was kept in contact with the Red. phase, with irradiation from the Red. phase from a 500 W halogen lamp (λ >400 nm) in all experiments.

electron transport driven by the irradiation of $[(bipy)_3Ru^{II}]^{2+}2Cl^-$ (**4**) dissolved in the Red. phase presented a striking contrast to the above observation. The use of (**4**) in an equal amount led to a rate comparable to that obtained by the (**1**)-incorporated membrane. The incorporation of electron mediators as above into the membrane brought about no large enhancement in rate. Use of a large amount of (**4**) (107 μmol)§ led to a decrease in rate. This suggests that the quenching rate of (**4**) in the photoexcited state increases with increasing concentration. We assume that (**1**) is located at the Red.–M. interface of the membrane in an extremely high concentration, but (**1**) in the photoexcited state transfers an electron to VK_3 efficiently in the presence of electron mediators as above. It was also found in the photosensitized electron transport with an $FeCl_2$ reductant that the incorporation of both (**1**) and (**2**) or (**3**) into the membrane containing VK_3 alone increased the transport rate, although the observed rates were small as compared with those with EDTA (Table 2).

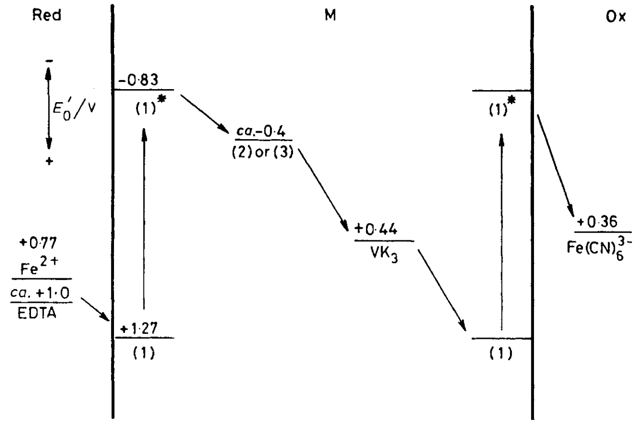

FIGURE. Schematic representation of the photosensitized electron transport from EDTA or Fe^{2+} to $Fe(CN)_6{}^{3-}$ across a liquid membrane containing VK_3 + (**1**) + (**2**) or (**3**), supported on a 0·2 μm pore-sized Fluorinert millipore filter.

TABLE 2. Photosensitized electron transport from Fe^{2+} to $Fe(CN)_6{}^{3-}$ across various liquid membrane systems at 35 ± 1 °C.

M. phase	Transport rate/ μmol h^{-1}
VK_3, VK_3 + (**1**), VK_3 + (**1**) + (**2**) or (**3**)^a	0
$VK_3{}^b$	0·4
VK_3 + (**1**)^b	0·6
VK_3 + (**1**)^{b,c}	1·5
VK_3 + (**1**) + (**2a**)^b	0·6
VK_3 + (**1**) + (**2b**)^b	1·0
VK_3 + (**1**) + (**3**)^b	0·6

^{a} In the dark. ^{b} Irradiated (λ >400 nm). ^{c} The Ox. phase was kept in contact with one side of the filter covered with VK_3 and (**1**).

A large rate-enhancement was obtained when one side of the filter covered with a mixture of VK_3 and (**1**) was kept in contact with the Ox. phase, with irradiation by visible light from the Red. phase. This shows that the electron transfer at the Ox.–M. interface is greatly accelerated by the photosensitization of (**1**) located at the interface. The electron transfer was not influenced by the further incorporation of an electron mediator which exhibited rate-enhancement in the electron transfer at the Red.–M. interface.

From the above results the photosensitized electron transport across a liquid membrane containing VK_3 + (**1**) + (**2**) or (**3**) can be schematically depicted as shown in the Figure. Photoexcited (**1**), (**1**)* (E_0' −0·83 V),[3] located at the Red.–M. interface, transfers an electron to VK_3 (E_0' +0·44 V)[4] *via* the electron mediator (**2**) or (**3**) (*ca.* −0·4 V),[4,5] and the oxidized form of (**1**), $(\mathbf{1})_{OX}$ (+1·27 V),[6] is reduced by EDTA¶ or Fe^{2+} (+0·77 V)[4] to regenerate (**1**). The reduced VK_3 diffuses to the Ox.–M. interface and reduces the $(\mathbf{1})_{OX}$ resulting from the electron transfer of (**1**)* to $Fe(CN)_6{}^{3-}$ (+0·36 V)[4] at the interface. EDTA is irreversibly oxidized to lead to efficient electron transport from the Red. to the Ox. phase. In the case of $FeCl_2$ the reverse electron transport can proceed, since the redox reaction between Fe^{2+} and Fe^{3+} is reversible, and this probably causes the overall electron transport rate to be small. The use of either reductant leads to the storage of chemical energy of *ca.* 42 kJ/mol by this electron-transport process.

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§ 50 ml of a buffer solution of (**4**) (107 μmol) has an equal concentration to that of (**1**) (0·15 μmol) in the membrane (0·12 ml).

¶ The oxidation potential of EDTA is *ca.* +1·0 V at pH 7·8 (H. Tsubomura, Y. Shimoura, and S. Fujiwara, *J. Phys. Chem.*, 1979, **83**, 2103).

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