CHEMISTRY LETTERS, pp. 1835-1838, 1991.

Formation of Proton Gradients in Electron Transport between Two Proton-Conducting Acetonitrile Phases Separated by an Insulating Carbon Disulfide Phase

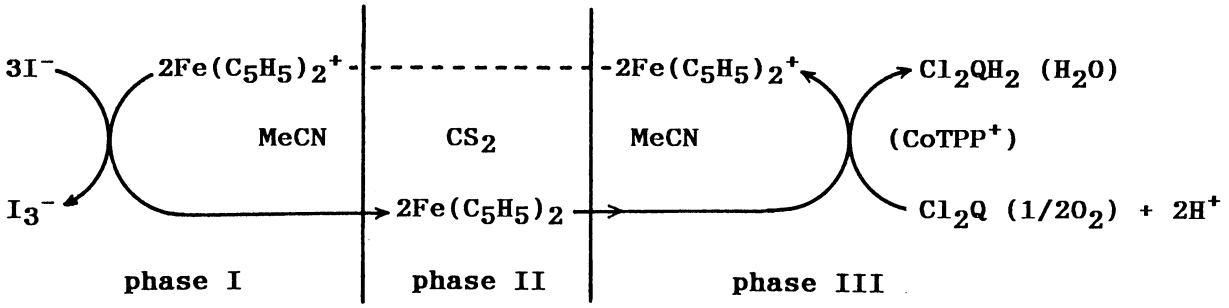
Shunichi FUKUZUMI* and Tomohiro YORISUE
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

Proton gradients are formed efficiently, coupled with electron transport from iodide ion to electron acceptors (quinone, nitrite, and dioxygen) between two acetonitrile phases, which are separated by a proton-insulating CS_2 phase, by using ferrocenium ion as an electron carrier.

Artificial electron transport systems between two aqueous phases have been studied extensively by using liquid membranes[1] or bilayer lipid membranes.[2,3] Electron transport across the membrane can be coupled with the generation of proton gradients which are a central inter-convertible currency of free energy in biological systems.[4] On the other hand, the activity of proton is much higher in an aprotic polar solvent such as acetonitrile (MeCN) than in H_2O because of the large difference in the solvation.[5,6] Thus, electron transport to generate proton gradients would be much more efficient in an aprotic polar solvent than in H_2O. However, no electron transport systems using an aprotic solvent have so far been reported. The most difficult problem in constructing such an aprotic membrane system is to find an appropriate membrane being a proton insulator that can separate two aprotic polar phases. We report herein that CS_2 is successfully used as a proton-insulating liquid membrane that can separate two MeCN phases and that proton gradients are formed efficiently, coupled with electron transport between two MeCN phases across the CS_2 phase.

Mixing of CS_2 with MeCN results in formation of two phases.[7] Then, two MeCN phases can be separated by the CS_2 phase. It was confirmed that no appreciable permeation of proton from the MeCN phases (I and III) to the CS_2 phase II takes place. Thus, the CS_2 phase can act as a proton insulator between the two proton-conducting MeCN phases. By using the liquid membrane is constructed an electron transport system from I^- being an electron donor in phase I to an electron acceptor, 2,6-dichloro-p-

benzoquinone (Cl_2Q) in phase III across the CS_2 phase II. The liquid membrane system consists of two MeCN phases, I (8 cm^3) and III (8 cm^3) together with a CS_2 phase II (16 cm^3), which is inserted between the two MeCN phases by using a H type cell. Equilibrations were conducted at 298 K and the CS_2 solution at the bottom of each side of the H type cell was stirred magnetically. Ferrocenium ion ($Fe(C_5H_5)_2^+$) is used as an electron carrier as shown in Scheme 1, where $Fe(C_5H_5)_2$ formed by the reduction of



Scheme 1.

$Fe(C_5H_5)_2^+$ by I^- in phase I is more soluble in phase II (CS_2) than in phase I. The $Fe(C_5H_5)_2$ is thereby transported across phase II to phase III, where it is oxidized by Cl_2Q, accompanied by the consumption of protons to regenerate $Fe(C_5H_5)_2^+$. The extent of electron transport from I^- in phase I to Cl_2Q in phase III, together with the concomitant change of $[H^+]$ in phase I and phase III is shown in Fig. 1 (part a), where $[Fe(C_5H_5)_2^+]$ in phase III increases with time, accompanied by the corresponding decrease in $[H^+]$ in phase III. The change in the proton concentration in the two MeCN phases was determined by monitoring the pH of the diluted aqueous solution (x50) of the two MeCN phases. The extent of electron transport was determined spectrophotometrically by monitoring the increase in the absorbance due to $Fe(C_5H_5)_2^+$ at λ = 618 nm,[8] or that due to $CoTPP^+$ at 434 nm[8] in the diluted MeCN solution (x50) of the phase III MeCN solution. In Fig. 1 no change in $[H^+]$ is observed with time in phase I, where no proton is consumed in the reduction of $Fe(C_5H_5)_2^+$ by I^- in phase I (Scheme 1). Thus, proton gradients are formed efficiently, coupled with the electron transport form I^- in phase I to Cl_2Q in phase III. Essentially the same result was obtained when Cl_2Q was replaced by nitrite (NO_2^-). The $Fe(C_5H_5)_2$ transported to phase III is oxidized by NO_2^- in the presence of $HClO_4$,[9] accompanied by the decrease in $[H^+]$ to yield $Fe(C_5H_5)_2^+$ and NO.

Ferrocene is stable toward dioxygen in MeCN. We have recently reported, however, that the four-electron reduction of dioxygen by $Fe(C_5H_5)_2$ proceeds efficiently in the presence of $HClO_4$ in MeCN containing

a catalytic amount of $CoTPP^+$ (Eq. 1).[10] The $CoTPP^+$-catalyzed

$$4Fe(C_5H_5)_2 + O_2 + 4H^+ \xrightarrow{CoTPP^+} 4Fe(C_5H_5)_2^+ + 2H_2O \quad (1)$$

reduction of O_2 by $Fe(C_5H_5)_2$ in the presence of $HClO_4$ can be applied to the present $MeCN/CS_2$ liquid membrane system in order to achieve the formation of proton gradients, coupled with electron transport from I^- to O_2. In fact, efficient formation of proton gradients takes place, accompanied by electron transport from I^- in phase I to O_2 in phase III where a catalytic amount of $CoTPP^+$ is initially dissolved, as shown in Fig. 1 (part b). The $Fe(C_5H_5)_2$ formed by the reduction of $Fe(C_5H_5)_2^+$ by I^- in phase I is transported across phase II to phase III, where the efficient $CoTPP^+$-catalyzed reduction of O_2 by $Fe(C_5H_5)_2$ occurs to generate proton gradients between the two MeCN phases as also shown in Scheme 1 (parentheses).

In each case, however, the flow of electron of the electron carrier is one-direction, i.e., from phase I to phase III, since $Fe(C_5H_5)_2^+$ is sparingly soluble in phase II. Nonetheless this study has demonstrated for the first time the efficient formation of proton gradients in an aprotic medium. It should be

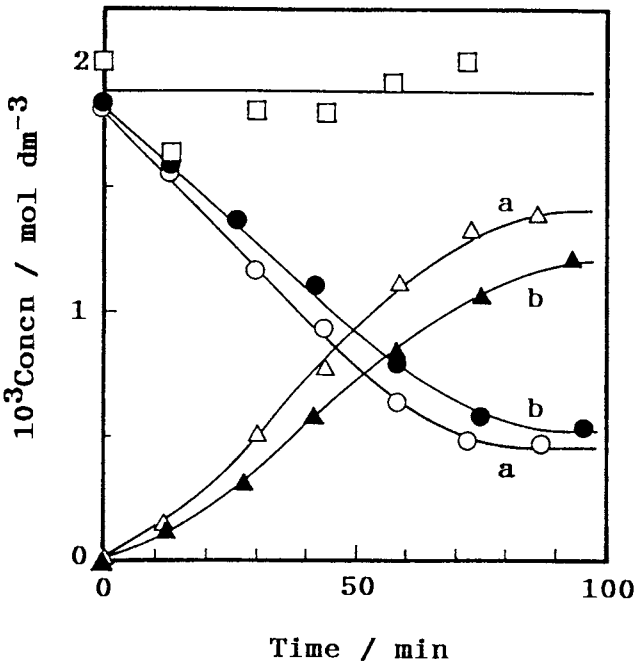


Fig. 1. (a) Formation of proton gradients between phase I, $[H^+]_I$ (□), and phase III, $[H^+]_{III}$ (○) in MeCN, coupled with electron transport from I^- ($Pr_4N^+I^-$: 6.0 x 10^{-2} mol dm^{-3}) in phase I to Cl_2Q (1.0 x 10^{-2} mol dm^{-3}) in phase III by using $Fe(C_5H_5)_2^+$ as an electron carrier, which is transported from phase I to phase III, $[Fe(C_5H_5)_2^+]_{III}$ (△), across the CS_2 phase II. (b) Formation of proton gradients between phase I, $[H^+]_I$ (□), and phase III, $[H^+]_{III}$ (●) in MeCN, coupled with electron transport from I^- (4.0 x 10^{-2} mol dm^{-3}) in phase I to O_2 (2.6 x 10^{-3} mol dm^{-3}) in phase III by using $Fe(C_5H_5)_2^+$ as an electron carrier, which is transported from phase I to phase III, $[Fe(C_5H_5)_2]_{III}$ (▲) in MeCN containing $CoTPP^+$ (1.0 x 10^{-4} mol dm^{-3}), across the CS_2 phase II.

emphasized that no appreciable electron transport has occurred when a normal liquid membrane system consisting of two aqueous solutions separated by CH_2Cl_2 was applied to the present electron transport systems.

The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References

1) T. Shinbo, K. Kurihara, Y. Kobatake, and N. Kamo, Nature, **270**, 277 (1977); J. J. Grimaldi and J. M. Lehn, J. Am. Chem. Soc., **101**, 1333 (1979); I. Tabushi, A. Yazaki, N. Koga, and K. Iwasaki, Tetrahedron Lett., **21**, 373 (1980); T. Sugimoto, J. Miyazaki, T. Kokubo, S. Tanimoto, M. Okano, and M. Matsumoto, J. Chem. Soc., Chem. Commun., **1981**, 210; E. Ozeki, S. Kimura, and Y. Imanishi, ibid., **1988**, 1353.

2) I. Tabushi and M. Funakura, J. Am. Chem. Soc,. **98**, 4684 (1976); M. S. Tunuli and J. H. Fendler, ibid., **103**, 2507 (1981); P. C. Hinkle, Fed. Proc., **32**, 1988 (1973); G. Hauska, FEBS Lett., **79**, 345 (1977).

3) J. A. Runquist and P. A. Loach, Biochim. Biophys. Acta, **637**, 231 (1981); I. Tabushi, T. Nishiya, M. Shimomura, T. Kunitake, H. Inokuchi, and T. Yagi, J. Am. Chem. Soc., **106**, 219 (1984); I. Tabushi and S. Kugimiya, ibid., **107**, 1859 (1985); M. Nango, A. Mizusawa, T. Miyake, and J. Yoshinaga, ibid., **112**, 1640 (1990).

4) P. Michel, Trans. Biochem. Soc., **4**, 399 (1976); F. M. Harold, "The Vital Force: A Study of Bioenergetics," W. H. Freeman, New York (1986), Chap. 7.

5) S. Fukuzumi, K. Ishikawa, K. Hironaka, and T. Tanaka, J. Chem. Soc., Perkin Trans. 2, **1987**, 751; S. Fukuzumi, S. Mochizuki, and T. Tanaka, J. Am. Chem. Soc., **111**, 1497 (1989).

6) D. T. Sawyer and J. L. Roberts, Jr., Acc. Chem. Res., **21**, 469 (1988).

7) "Solubilities of Inorganic and Organic Compounds," ed by H. Stephan, T. Stephan, Pergamon Press, New York (1963), Vol. 1, Binary Systems, Part 2, No. 4151.

8) S. Fukuzumi, S. Mochizuki, and T. Tanaka, Inorg. Chem., **28**, 2459 (1989).

9) S. Fukuzumi and T. Yorisue, Chem. Lett., **1990**, 871.

10) S. Fukuzumi, S. Mochizuki, and T. Tanaka, Inorg. Chem., **29**, 653 (1990).

(Received July 25, 1991)