CHEMISTRY LETTERS, pp. 1825-1828, 1985.

INCLUSION, SOLUBILIZATION, AND STABILIZATION OF TWO-ELECTRON REDUCED SPECIES OF METHYL VIOLOGEN BY CYCLODEXTRINS

Tomokazu MATSUE, Tetsuya KATO, Uichi AKIBA, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

An electrochemical investigation of methyl viologen-cyclodextrin (CD) system has revealed that β-CD has outstanding ability to include the 2e reduced species of methyl viologen in aqueous solution (formation constant: 1400 dm^3 mol^{-1}) in comparison with other CDs and the inclusion solubilizes and stabilizes the electrogenerated species.

Dipyridium salts (Viologens) are one of the rare organic materials which show reversible redox character with remarkable color change[1] in aqueous solution and therefore have widely explored as electron acceptors, electron carriers[2] and materials for electrochromic displays.[3] Viologens undergo two succesive one-electron reduction as shown below:

$$V^{2+} + e^- \rightleftharpoons V^{+\cdot} \qquad (1)$$
$$V^{+\cdot} + e^- \rightleftharpoons V \qquad (2)$$

The two-electron reduced species (neutral quinoid form, V) is usually sparingly soluble in aqueous solution, which makes practical use of it very narrow as compared with that of the one-electron reduced species, $V^{+\cdot}$. Another major demerit of V resides in its unstability in the presence of reactive chemicals.

We report here that these fatal disadvantages of V can greatly be diminished by addition of cyclodextrins (CDs). Recently, Okuno and coworkers demonstrated[4] that complexation of long tails in viologen molecule with CD prevented consumption of viologen in photochemical hydrogenation. They also suggested no inclusion of methyl viologen (N,N′-dimethyl-4,4′-dipyridinium dichloride, $MV^{2+}2Cl^-$) due to its short tails. Our present results have supported their suggestion. However, we have found that β-CD includes the two-electron reduced species (MV) strongly and, more importantly, the inclusion solibilizes and stabilizes the electrogenerated species. These finding would provide a way to utilize the two-electron reduced viologens for various purposes. The electrochemical reaction of MV^{2+} in the presence of CD in the solution proceeds via a mechnism shown in Scheme 1. We have used cyclic voltammetric technique to investigate this reaction.

$$MV^{2+} + e^- \rightleftharpoons MV^{+\cdot} \qquad (3)$$
$$MV^{+\cdot} + e^- \rightleftharpoons MV \qquad (4)$$
$$MV^{2+} + CD \rightleftharpoons MV^{2+}\text{-}CD \qquad K\ (\text{Equilibrium constant}) \qquad (5)$$
$$MV^{+\cdot} + CD \rightleftharpoons MV^{+\cdot}\text{-}CD \qquad K_1(\text{Equilibrium constant}) \qquad (6)$$
$$MV + CD \rightleftharpoons MV\text{-}CD \qquad K_2(\text{Equilibrium constant}) \qquad (7)$$

Scheme 1.

The measurement was carried out using conventional instruments at 25 °C in a phosphate buffer (pH 7.0). The voltammogram was recorded at the scan rate of 50 mV s^{-1}; this scan rate is considered to be slow enough to maintain equilibrium concentration in the electrolyte solution.[5)] The working electrode was a 3 mm diameter glassy carbon disk (GC-20, Tokai Carbon Co.) epoxidized in a glass tube. The electrode was polished finally with 0.3 μm alumina powder (Buehler Co.) to give a mirror-like surface (area: 0.071 cm^2). Methyl viologen and CDs were obtained commercially and recrystallized with ethanol and water, respectively. The circular dichroism measurement was also carried out.

β-CD had a dramatic effect on a cyclic voltammogram of MV^{2+} as shown in Fig. 1. Since the two-electron reduced species of MV^{2+} has very poor solubility in aqueous solution, the voltammogram shows a typical adsorption wave on the reverse scan in the absence of CD. However, the addition of β-CD altered the adsorption shape to a well-defined, diffusion-controlled one with two successive one-electron reduction. In addition to the change in shape, the second reduction peak potential was shifted to the positive direction. By contrast, only small influence was observed on the first electron transfer step corresponding to the $MV^{2+}/MV^{+\cdot}$ redox couple. These findings clearly demonstrate that MV is solubilized by its inclusion in β-CD.

Next we have carried out a quantitative investigation of this system by the electrochemical method. As proposed previously,[6)] the electrochemical determination of formation constants of CD complexes can be accomplished by using the two phenomena induced by complexation; one phenomenon is the decrease in peak or diffusion current and the other the shift in peak or half-wave potential. The latter was used for the determination of the formation constant of CD comlexes. The cyclic voltammetry was carried out with 0.45 mmol dm^{-3} of MV^{2+} in a phosphate buffer (pH 7.0). Under this low concentration of the substrate the reoxidation wave of the electrogenerated MV to $MV^{+\cdot}$ shows quite normal shape with the half-wave potentials for the first ($E_{1/2}^1$) and the second ($E_{1/2}^2$) electron transfer of -0.702 V and -1.018 V vs. SCE, respectively. The addition of β-CD resulted in the shift in the apparent half-wave potential for the second electron transfer step, $E_{1/2,app}^2$, to the positive direction

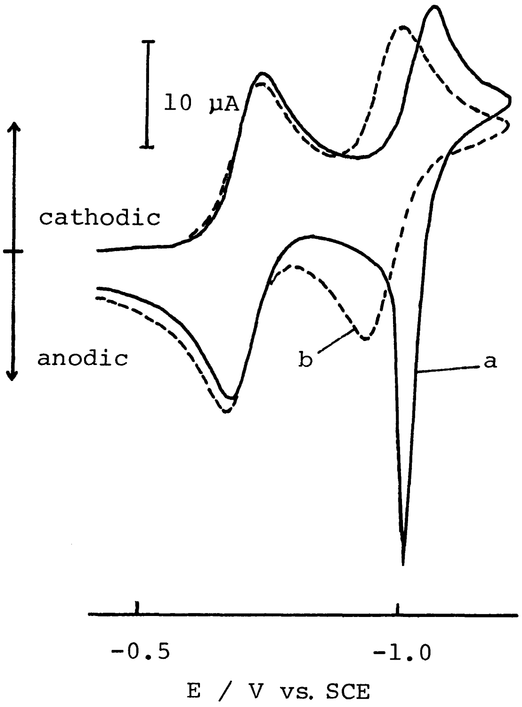

Fig. 1. Cyclic voltammograms of 1.36 mmol dm^{-3} methyl viologen in the absence (a) and presence (b) of 15.1 mmol dm^{-3} β-CD. Electrode: Glassy carbon disk. Electrolyte: Phosphate buffer (pH 7.0). Scan rate: 50 mV s^{-1}. Temperature: 25 °C.

whereas the first one, $E_{1/2,app}{}^{1}$, showed only small potential changes. These observation indicates that β-CD binds the species in the order of MV > $MV^{+\bullet}$ > MV^{2+}. The independent measurement using circular dichroism showed no inclusion of MV^{2+} into β-CD. The determination of the formation constants was performed by the comparison of the experimental shifts in the apparent half-wave potentials with the theoretical ones from an analytical equation[6b)] and a digital simulation analysis.[7)] Figure 2 shows the results. The experimental shifts in the apparent half-wave potential agree beautifully with the theoretical ones calculated with K=0, K_1=30, and K_2=1400 dm^3 mol^{-1}. The line obtained from the analytical equation deviates slightly upward in the low CD concentration range, since it is only applicable when the concentration of CD is in great excess over that of methyl viologen. These shifts were explained on the basis of a 1:1 (guest:host) complexation very well. Therefore, it can be concluded that the contribution from other types (e. g., 1:2 or 2:1 complexation) is, if any, small. Table 1 summarizes the results including those with α- and γ-CD as the host compounds. Among CDs investigated, β-CD showed the outstanding ability for inclusion of MV. The inclusion ability of α-CD for $MV^{+\bullet}$ and MV is very small although it was expected from consideration with a molecular model. γ-CD may be too large to include these species. The formation constant can also be determined from the change in the peak current induced by addition of CD.[6)] However, this method is not applicable to the present case since MV^{2+} and $MV^{+\bullet}$ were hardly included in CD as shown in Table 1. This system is contrast well with the ferrocene derivatives-CD one where ferrocenes are much more strongly included in CD than the electrogenerated ferricinium species.[7,8)]

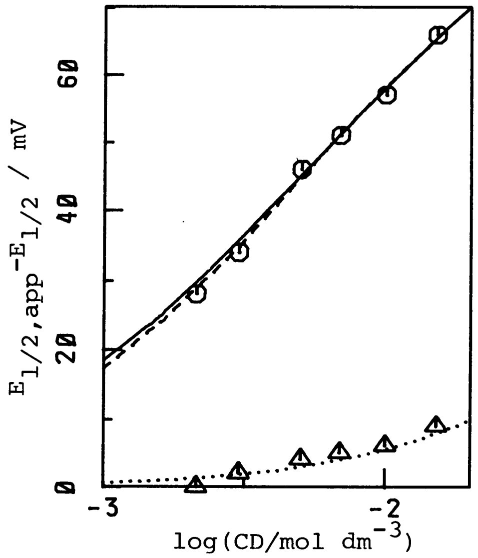

Fig. 2. Shift in the apparant half-wave potential as a function of total concentration of β-CD.

△ : Experimental for $MV^{2+}/MV^{+\bullet}$ couple.

○ : Experimental for $MV^{+\bullet}/MV$ couple.

—— : Theoretical from the analytical equation[6b)] with K_1=30 and K_2=1400 dm^3 mol^{-1}. ...... : Theoretical from the analytical equation[6b)] with K=0 and K_1=30 dm^3 mol^{-1}. --- : Theoretical from the digital simulation with K_1=30 and K_2=1400 dm^3 mol^{-1}.

Table 1. Formation constants CD complexes

Type of CD	K	K_1	K_2
		dm^3 mol^{-1}	
α-	0	10	50
β-	0	30	1400
γ-	0	40	60

Another major disadvantage of MV for practical use is its unstability. As shown in Fig. 3, the reoxidation peak of MV to $MV^{+\bullet}$ disappeared in the presence of 94 mmol dm^{-3} propionaldehyde due to chemical reactions between MV and the aldehyde.[9] The addition of β-CD reproduced the well-defined reoxidation peak. This phenomenon clearly demonstrates that the inclusion of MV into the interior of the CD cavity protects the unstable MV from reactive chemicals. Further investigation of the present system is now in progress.

This work was supported by Grant-in-Aid for Scientific Research (No. 59350052).

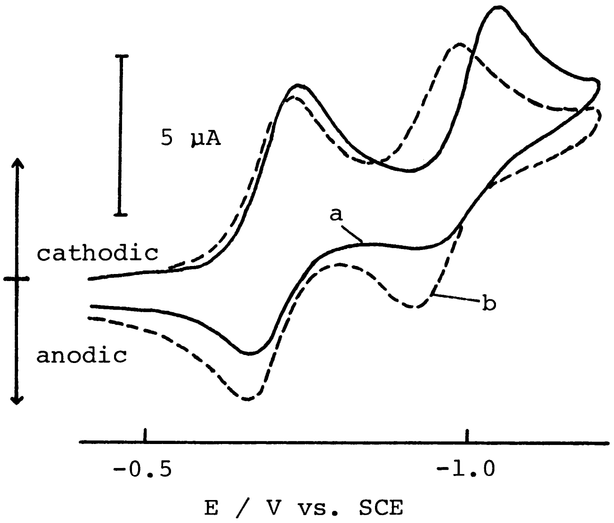

Fig. 3. Cyclic voltammograms of 0.45 mmol dm^{-3} methyl viologen in the presence of 94 mmol dm^{-3} propionaldehyde. (a): Without CD. (b): With saturated β-CD (ca. 20 mmol dm^{-3}). Electrode: Glassy carbon disk. Electrolyte: Phosphate buffer (pH 7.0). Scan rate: 50 mV s^{-1}. Temperature:25 °C.

References

1) T.Osa and T.Kuwana, J.Electroanal.Chem., 22, 389(1969).
2) R.Szentrimay, R.Yeh, and T.Kuwana, "Electrochemical studies of biological systems," ed by D.T.Sawyer, American Chemical Society, Washington D.C. (1977), Chap. 9; M.D.Ward, J.R.White, and A.J.Bard, J.Am.Chem.Soc., 105, 27(1983); D.Mandler and I.Willner, ibid., 106, 5352(1984); T.Sugimoto, I.Miyazaki, T.Kubota, S.Tanimoto, M.Okano, and M.Matsumoto, Tetrahedron Lett., 22, 1119(1981); and references therein.
3) T.Uchida, Denki Kagaku, 52, 49(1984) and references therein.
4) Y.Okuno, Y.Chiba, and O.Yonemitsu, J.Chem.Soc., Chem.Commun., 1984, 1638.
5) The association and dissociation rate constants of CD complexes are usually large (see Ref. 6). Therefore, the concentration of CD and guest compound are considered to be at an equilibrium state at slow scan rates in cyclic voltammetry. We have not observed any distortion of the voltammetric shape. This indicates appropriateness of the assumption.
6) a) T.Osa, T.Matsue, and M. Fujihira, Heterocycles, 6, 1833(1977); b) T. Matsue, T.Osa, and D.H.Evans, J.Inclus.Phenom., 2, 547(1984).
7) T.Matsue, D.H.Evans, T.Osa, and N.Kobayashi, J.Am.Chem.Soc., 107, 3411(1985).
8) T.Matsue, U.Akiba, K.Suzufuji, and T.Osa, Denki Kagaku, 53, 508(1985).
9) The electrogenerated MV may in part reduce propionaldehyde as suggested by K.Ageishi, T.Endo, and M.Okawara, J.Polym.Sci.Polym.Chem.Ed., 21, 175(1983). However, the cyclic voltammetric behavior could not be accounted for by the simple EC catalytic process. The present case probably contains other complicated chemical reactions.

(Received September 9, 1985)