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ELECTROCHEMICALLY SWITCHED CATION BINDING IN PENTAOXA [13] FERROCENOPHANE

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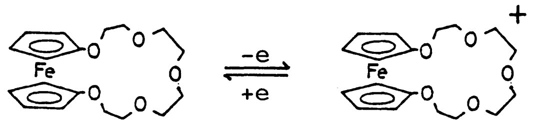
The effects of cations on the half-wave potential for oxidation of pentaoxa [13] ferrocenophane (**1**) in dichloromethane were studied. The shift of the half-wave potential by the addition of alkaline cations shows the abrupt decrease of the binding constant of **1** with cations upon electrochemical oxidation.

Numerous reports have dealt with the application of functional crown ether to ion transport. Ionization of acidic functions,[1)] photoswitching,[2)] and oxidation dimerization of sulfhydryl-substituted crown[3)] have been utilized to ion-transport. Recently, the binding strength enhancement upon electrochemical reduction of redox active neutral crown ether or cryptand have been proposed for a candidate for ion-transport.[4)] We report here the first evidence for the abrupt decrease of cation binding strength by electrochemical oxidation of pentaoxa [13] ferrocenophane (**1**).

1 was prepared by the method found in the literature and identified on the basis of its melting point and elemental analysis on C, H, and N.[5)] Voltammetric measurements were carried out at 25 ± 1 °C. Other experimental procedures have been described.[6)]



1 $\quad$ **1**$^+$

The cyclic voltammogram for 0.2 mM **1** (mmol dm^{-3}) in 0.1 M tetrabutylammonium hexafluorophosphate-dichloromethane in the absence of alkali metal ions showed the reversible one-electron oxidation wave at -0.23 V (half-wave potential)(Fig. 1-a). The half-wave potential was identified with the midpoint of the cathodic peak potential (E_{pc}) and anodic one (E_{pa}) of a cyclic voltammogram ((E_{pa}+E_{pc})/2). The potential was reffered to the half-wave potential of the redox system of ferrocene/ferricenium ion (Fc/Fc$^+$). The reversibilities of the redox steps were judged on the basis of the separation (ΔE_p) between E_{pc} and the E_{pa} and the ratio of the anodic peak current to the cathodic one. When 1 mM $NaClO_4$ was added to the solution of 0.2 mM **1** and the solution was stirred for 5 min, a new oxidation wave appeared at -0.06 V, which was quasi-reversible one-electron process (Fig. 1-b). When this solution was stirred for 1 h, the wave at -0.23 V disappeared and only the wave at -0.06 V was observed (Fig. 1-c). The oxidation peak current of this wave was nearly identical with that of **1** in the absence of $NaClO_4$. The results of cyclic voltammetry for **1** in the presence of $LiClO_4$ were almost the same except for the smaller shift of the half-wave potential. A new oxidation wave appeared at -0.12 V.

The positive shift of the half-wave potential by the addition of alkali metal ions reflects the abrupt decrease of metal ion binding of $\mathbf{1}^+$ compared with that of $\mathbf{1}$. The difference in stability constants is calculated from[4)]

$$E^{complex} - E^{free} = RT/nF\left[\ln(K_{\mathbf{1}}/K_{\mathbf{1}^+})\right]$$

where $K_{\mathbf{1}}$ and $K_{\mathbf{1}^+}$ are the stability constants of $\mathbf{1}$ and $\mathbf{1}^+$ with metal ions, $E^{complex}$ and E^{free}, the half-wave potentials in the presence and in the absence of alkali metal ions , respectively. The other symbols have their usual meanings. The values of $K_{\mathbf{1}}/K_{\mathbf{1}^+}$ for Na^+ and Li^+ are 740 and 72, respectively. The decrease of the stability constant for $\mathbf{1}^+$ compared with that of $\mathbf{1}$ may be explained by the electro-static repulsion between the charge on ferrocene moiety and that of alkali metal ions.

The large values of $K_{\mathbf{1}}/K_{\mathbf{1}^+}$ for Na^+ and Li^+ mean that most of the metal ion binding in $\mathbf{1}$ may dissociate completely to metal ion and $\mathbf{1}^+$ by electrochemical oxidation of $\mathbf{1}$. Such a means to turn on and turn off ion binding offers the possibility of driving ion transport against a chemical concentration gradient. Specially, this ferrocene/ferricenium type redox system may be a good candidate for ion transport because both of the oxidant and the reductant are stable in both nonaqueous and aqueous solvents.

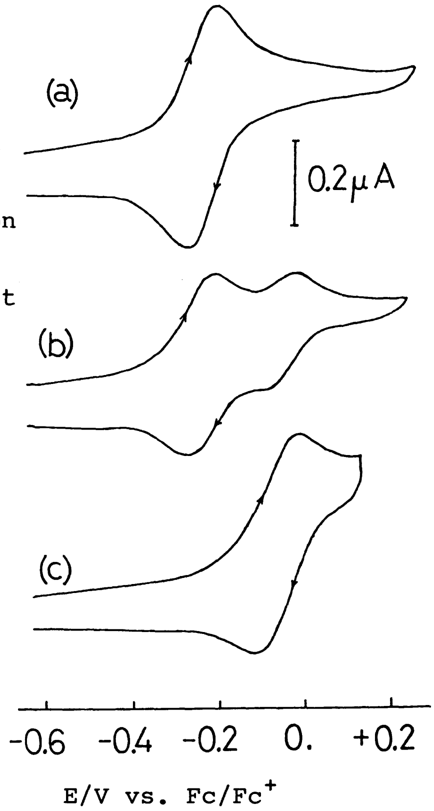


Fig. 1. Cyclic voltammograms for 0.2 mM pentaoxa 13 ferrocenophane in the absence of $NaClO_4$ (a), and in the presence of 1 mM $NaClO_4$ (partially precipitated) in the course of stirring a solution for (b) 5 min and (c) 1 h. Scan rate: 40 mV s^{-1}.

References

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