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Electrochemical Confirmation of Disproportionation of μ-Oxo-bis[(*N,N'*-ethylenebis(salicylideneaminato))vanadium(IV)] Tetrafluoroborate

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μ-Oxo-bis[(*N,N'*-ethylenebis(salicylideneaminato))vanadium(IV)] tetrafluoroborate is prepared from (*N,N'*-ethylenebis(salicylideneaminato)) oxovanadium(IV) (VO(salen)) through an electrophilic reaction by triphenylmethyl tetrafluoroborate (Ph_3CBF_4) in dichloromethane. The voltammetric analysis of the binuclear complex in dichloromethane revealed a one-step two-electron transfer at 0.58V (vs Ag/AgCl) based on the disproportionation ($2V^{IV}OV^{IV} \rightleftharpoons V^{III}OV^{IV} + V^{IV}OV^{V}$).

Multi-electron transfer process$^{1)}$ plays an important role in biosynthesis and photosynthesis. Our goal in this study is to elucidate multi-electron transfer processes through the disproportionation to develop catalytic systems for new syntheses. Recent interesting work has shown the possible function of vanadium in nitrogenase as multi-electron transfer agents involving the mixed-valence state,$^{2)}$ and the VO-catalyzed O_2-oxidative polymerization of thiophenol derivatives$^{3)}$ as a laccase-like reaction. Such multi-electron transfer reactions are critical not only in the biological reduction or fixation of oxygen or nitrogen, but also in the redox catalysts for organic syntheses.

Our present work reports the first example of a vanadium binuclear complex which displays the reversible redox process based on disproportionation. The net reaction of this redox process is the transfer of two electrons.

The synthesis of μ-oxo-bis[(*N,N'*-ethylenebis(salicylideneaminato))vanadium(IV)] tetrafluoroborate ($[\{V(salen)\}_2(\mu\text{-}O)](BF_4)_2$) was carried out under a dry argon atmosphere. VO(salen) (0.208 g, 0.62 mmol) was dissolved in 20 cm^3 of degassed dry dichloromethane. Dichloromethane (5 cm^3) containing triphenylmethyl tetrafluoroborate (0.204 g, 0.62 mmol) was added to the solution at 0 °C. The solution immediately turned dark blue, and black powder precipitated after a few minutes. The stoichiometry was confirmed as follows by using the titration with an electrophile such as triphenylmethyl tetrafluoroborate (Ph_3CBF_4) or trifluoromethanesulfonic acid (CF_3SO_3H).

$$2\,VO(salen) + 2\,Ph_3C^+ \longrightarrow [\{V(salen)\}_2(\mu\text{-}O)]^{2+} + Ph_3COCPh_3 \qquad (1)$$

$[\{V(salen)\}_2(\mu\text{-}O)](BF_4)_2$ was isolated with >95% yield as black powder having the empirical formula

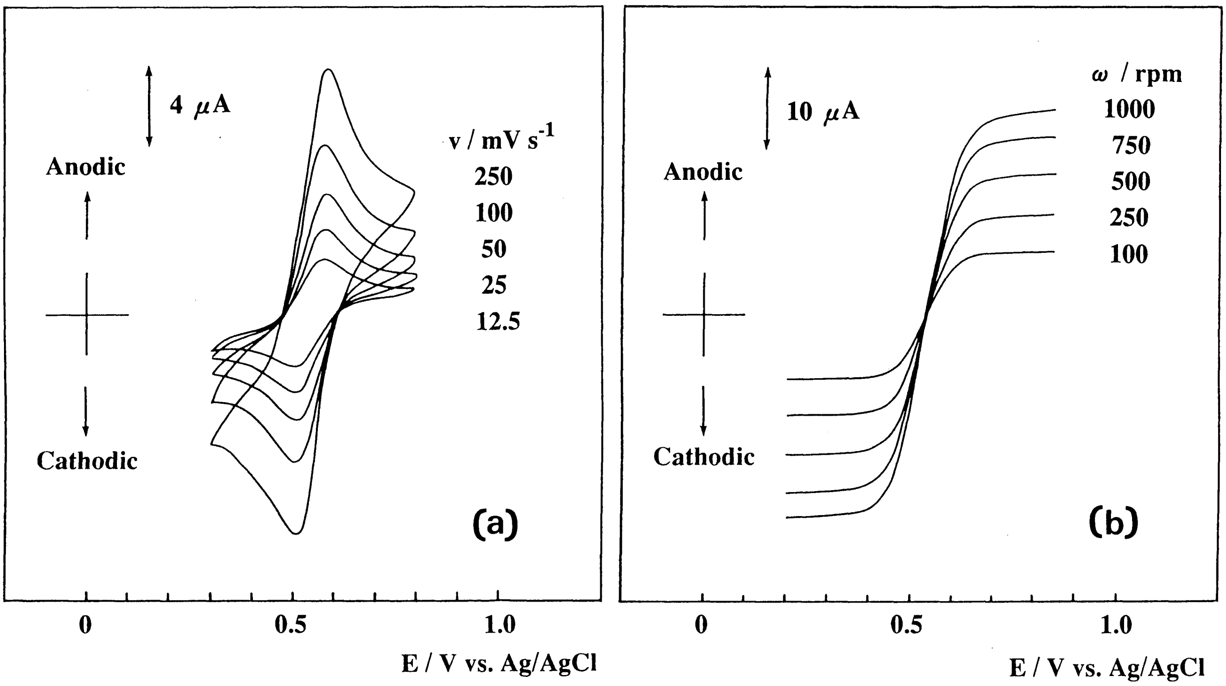

Fig. 1. Cyclic voltammograms (a) and rotating disk voltammograms (b) of [{V(salen)}$_2$(μ-O)](BF$_4$)$_2$ (0.5 mmol dm^{-3}) under anaerobic conditions in dichloromethane containing tetrabutylammonium tetrafluoroborate (0.5 mol dm^{-3}) on Pt disk electrode (4 mmϕ).

of $C_{32}H_{24}N_4V_2B_2F_8$.[4] The fragments of 650,[5] 333, 315(+1) were observed in FAB MAS spectroscopy. The electronic spectrum of [{V(salen)}$_2$(μ-O)](BF$_4$)$_2$ displays the absorption band at λ_{max} = 579 nm (ε_{max} = 365 mol^{-1} dm^3 cm^{-1}) with 200 nm of half-band width.[6] The typical V-O-V stretching band is observed at 655 cm^{-1} which is assigned by the use of V^{18}O(salen) complex. The spectroscopic data indicate the formation of μ-oxo dimer, [{V(salen)}$_2$(μ-O)](BF$_4$)$_2$. The contamination with Ph_3C^+ group was not detected by spectroscopic measurements.

The cyclic voltammograms in Fig. 1(a) shows the redox of [{V(salen)}$_2$(μ-O)](BF$_4$)$_2$ (0.5 mmol dm^{-3}) in dichloromethane containing 0.5 mol dm^{-3} of tetrabutylammonium tetrafluoroborate using the platinum disk electrode. Reversible redox wave is observed at 0.58 V(vs. Ag/AgCl)[7] with a potential separation (ΔEp) of 75 mV between cathodic and anodic peaks which is smaller than that for VO(salen) (85 mV) at the same conditions.[8] The redox potential of the μ-oxo dimer shifts more positive potential than the one-electron oxidation potential of VO(salen) (0.56 V vs. Ag/AgCl).[9]

As an additional check on the system, the rotating disk voltammetry of VO(salen) and [{V(salen)}$_2$(μ-O)](BF$_4$)$_2$ were measured at the same conditions. The rotating disk voltammetry (Fig. 1(b)) shows symmetric waves at $E_{1/2}$ = 0.58 V vs. Ag/AgCl, *i.e.* the cathodic current is equal to the anodic one regardless of the rotation rate. The limiting currents, i_{la}, i_{lc}, are identified to be the oxidation and the reduction of V^{IV}-O-V^{IV} complex, respectively. A plot of the plateau current ($i_l = i_{la} + i_{lc}$) vs. the square root of the rotation rate

(Levich plot)[10] yields a straight line. The electrode potential at i=0 was equal to the half wave potential regardless of the rotation rate. The plateau current for $[\{V(salen)\}_2(\mu\text{-}O)]^{2+}$ was about two times larger than the one-electron oxidation (V^{IV}/V^{V}) current of VO(salen). The diffusion coefficient of the binuclear complex was determined to be 5.2 x 10^{-6} $cm^2\ s^{-1}$, which is slightly smaller than that of VO(salen) (7.9 x 10^{-6} $cm^2\ s^{-1}$).

These results support the idea that the following disproportionation takes place (Eq. 2), which is caused by the fact that $E_{1/2}$[III-IV/IV-IV] and $E_{1/2}$[IV-IV/IV-V] are located at close potentials.[11]

$$2[V^{IV}\text{-O-}V^{IV}]^{2+} \rightleftharpoons [V^{III}\text{-O-}V^{IV}]^{+} + [V^{IV}\text{-O-}V^{V}]^{3+} \qquad (2)$$

The disproportionation of the μ-oxo binuclear complex(V^{IV}-O-V^{IV}) results in the transfer of two electrons as the net redox reaction of the system.

In the presence of acid such as trifluoroacetic acid the μ-oxo binuclear complex is sensitive to dioxygen and is oxidized, which is confirmed by the decrease of i_{la} under aerobic conditions. In contrast the mononuclear VO(salen) complex is not oxidized with oxygen in the same conditions. The disproportionation of the dimer to mixed-valence states (V^{III}-O-V^{IV} and V^{IV}-O-V^{V}) in the solution plays an important role on the two electron transfer in the reduction of dioxygen.

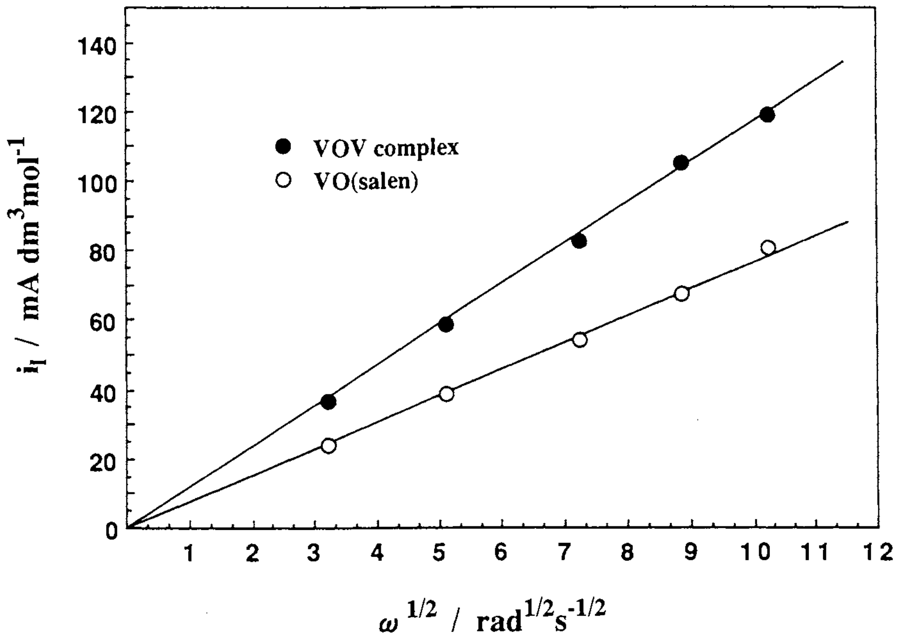

Fig. 2. Levich plots of the plateau current vs. $\omega^{1/2}$ for VO(salen) (0.5 mmol dm^{-3}) and $[\{V(salen)\}_2(\mu\text{-}O)](BF_4)_2$ (0.5 mmol dm^{-3}) on Pt disk electrode (4 mmϕ).

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4) Anal. Found: C, 46.58; H, 3.66; N, 6.84; V, 12.12; F, 18.33%. Calcd for $C_{32}H_{24}N_4V_2B_2F_8$: C, 46.75; H, 3.43; N, 6.82; V, 12.39; F, 18.49%.

5) The fragment of 650 in FAB MAS is attributed to $[\{V(salen)\}_2(\mu\text{-}O)]^{2+}$.

6) The *d-d* absorption for VO(salen)(λ_{max} = 587 nm, ε_{max}= 197 $mol^{-1}\ dm^3\ cm^{-1}$).

7) The electrode potential of the reference electrode (Ag/AgCl) was determined to be 0.21 V vs. NHE by the adjustment with a ferrocene/ferrocenium redox couple with the scanning rate of 20 $mV\ s^{-1}$.

8) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966). One of the reason that ΔEp for VO(salen) (V^{IV}/V^{V}) is larger than the calculated value for one-electron transfer is the the uncompensated resistance of the electrolyte solution.

9) J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.*, **108**, 4088 (1986).

10) $i_l = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C^*(298\ K)$, where n is the number of electron transferred, F is the Faraday constant, A is the electrode area, D is the diffusion coefficient, ω is the rotating rate of the electrode, and ν is the kinetic viscosity of the electrolyte solution. In this experiment F, A, ω, ν, and C^* in RDV of VOV are equal to that for VO(salen). The diffusion coefficient of the binuclear complex is generally smaller than that of $V^{IV}O$(salen) due to the increase in the charge and the molecular size. Therefore the two-electron transfer was concluded from the slope of the binuclear complex in the Levich plot which is larger than that of VO(salen).

11) The isolated binuclear complex (V^{IV}-O-V^{IV}) should contain V^{III}-O-V^{IV} and V^{IV}-O-V^{V} due to the disproportionation equilibrium (Eq. 2). The quantitative description of the equilibrium remains to be clarified.

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