Chiral Recognition in the Electron-Transfer Reaction between Optically Active Schiff Base-Oxovanadium(IV) and -Oxovanadium(V) Complexes

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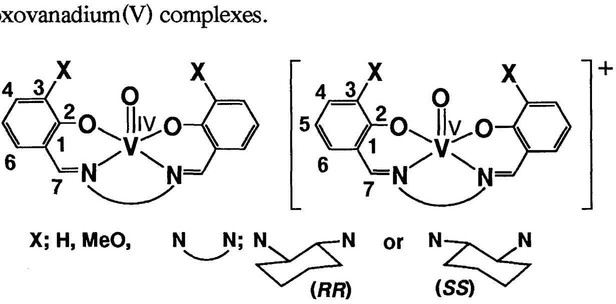
The kinetics of the electron-transfer reaction between [VO{3-MeOsal-(*RR*) or (*SS*)-chxn}] and [VO{sal-(*RR*)-chxn}]$^+$ were studied using the stopped-flow method in acetonitrile over the temperature range of 5 – 25 °C. The reactions were enantioselective. The ratio of the rate constant of the electron-transfer between [VO{3-MeOsal-(*SS*)-chxn}] and [VO{sal-(*RR*)-chxn}]$^+$ ($k_{SS\text{-}RR}$) and that between [VO{3-MeOsal-(*RR*)-chxn}] and [VO{sal-(*RR*)-chxn}]$^+$ ($k_{RR\text{-}RR}$) was 2.0 ($k_{SS\text{-}RR}$ / $k_{RR\text{-}RR}$) at 25 °C.

The investigation of the electron-transfer reaction involving optically active metal complexes and/or metalloproteins has attracted increasing interest. Stereoselectivity and chiral recognition in such electron-transfer reactions have mainly been studied[1] on the outer-sphere electron-transfer of cobalt and iron complexes, and few examples of the inner-sphere reactions have been reported. Mostly, stereoselectivity is not large, and discussion in terms of the structures of intermediates is difficult. In our recent studies,[2] we have shown that the isomerization between the diastereomeric pair of an optically active Schiff base-oxovanadium(IV) complex is catalyzed by the oxidized oxovanadium(V) species. The electron-transfer reaction between the oxovanadium(IV) and oxovanadium(V) complexes was suggested to have an important role in the isomerization. Chiral Schiff base-oxovanadium(IV) complexes such as [VO{sal-(*RR*)-chxn}] (**1**)[3] have been found to be enantioselective catalysts for the asymmetric oxidation of sulfides to sulfoxides.[4] Accordingly, we studied the electron-transfer reaction between [VO{sal-(*RR*)-chxn}]Cl (**2**) and [VO{3-MeOsal-(*RR*) or (*SS*)-chxn}] (**3-a** or **3-b**)[3] which gives **1** and [VO{3-MeOsal-(*RR*) or (*SS*)-chxn}]Cl (**4-a** or **4-b**) at equilibrium. In this letter, we report the chiral recognition in the electron-transfer reaction between optically active Schiff base-oxovanadium(IV) and -oxovanadium(V) complexes.



The complexes were synthesized in the same way as previously reported.[4] The complexes are green (**1**, **3-a**, and **3-b**) or dark green (**2**, **4-a**, and **4-b**). The absorption spectra in acetonitrile are shown in Figure 1. The electron-transfer reaction between **2** and **3-a** or **3-b** in acetonitrile was fast, and their kinetics were investigated using the stopped-flow method.

The change in absorbance at 314 nm was monitored for 100 ms after the acetonitrile solutions of **2** (8.30×10^{-5} mol dm^{-3}) and **3-a** (8.30×10^{-5} mol dm^{-3}) had been mixed at 5, 15, or 25 °C. Since, **3-a** and **4-a** have the same molar absorption coefficient at 314 nm, the absorbance change should be regarded as being caused by the reduction reaction from **2** to **1**. Absorbance-time traces were analyzed by the non-linear least-squares fit to determine the second-order rate constant according to the literature.[5]

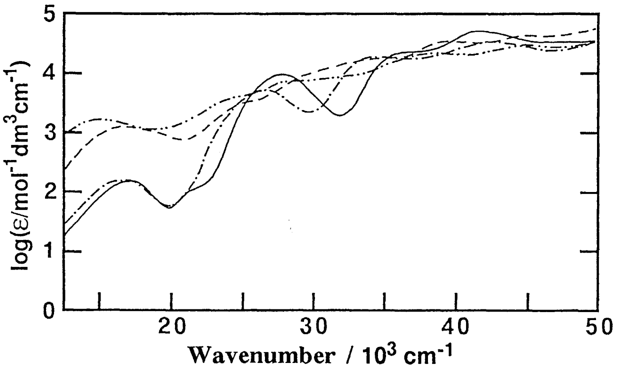
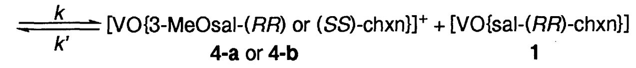


Figure 1. The absorption spectra of **1**; ——, **2**; - - - -, **3-a**; — · —, and **4-a**; — ·· — in CH_3CN.



$$[\mathrm{VO\{3\text{-}MeOsal\text{-}}(RR)\ \mathrm{or}\ (SS)\mathrm{\text{-}chxn\}}] + [\mathrm{VO\{sal\text{-}}(RR)\mathrm{\text{-}chxn\}}]^+ \underset{k'}{\overset{k}{\rightleftharpoons}} [\mathrm{VO\{3\text{-}MeOsal\text{-}}(RR)\ \mathrm{or}\ (SS)\mathrm{\text{-}chxn\}}]^+ + [\mathrm{VO\{sal\text{-}}(RR)\mathrm{\text{-}chxn\}}]$$

3-a or **3-b** **2** **4-a** or **4-b** **1**

k denotes $k_{RR\text{-}RR}$ or $k_{SS\text{-}RR}$, and k' denotes $k'_{RR\text{-}RR}$ or $k'_{SS\text{-}RR}$.

From the absorption spectra of the equilibrated solution, the equilibrium constant ($K = k_{RR\text{-}RR}/k'_{RR\text{-}RR}$) was calculated to be 1.0. The reaction of **2** and **3-b** was carried out under the same conditions. Table 1 shows the rate constants of these reactions, and their Eyring plots for $\ln(k_{RR\text{-}RR}/T$ or $k_{SS\text{-}RR}/T)$ vs $1/T$ are given in Figure 2. The stereoselectivity of the reaction depends on temperature. For example, **3-b** reacts 2.0 times faster than **3-a** at 25 °C, while 1.6 times at 5 °C. The activation parameters were $\Delta H^{\ddagger}_{RR\text{-}RR} = 15.2 \pm 0.6$ kJ mol^{-1}, $\Delta S^{\ddagger}_{RR\text{-}RR} = -70.2 \pm 1.9$ J mol^{-1} K^{-1}, $\Delta H^{\ddagger}_{SS\text{-}RR} = 21.4 \pm 2.4$ kJ mol^{-1}, and $\Delta S^{\ddagger}_{SS\text{-}RR} = -43.7 \pm 8.1$ J mol^{-1} K^{-1}. The observed activation parameters

Table 1. The rate constants of the electron-transfer reactions

t / °C	$k_{RR\text{-}RR}$ / mol^{-1} dm^3 s^{-1}	$k_{SS\text{-}RR}$ / mol^{-1} dm^3 s^{-1}
5	$(1.7 \pm 0.1) \times 10^6$	$(2.8 \pm 0.4) \times 10^6$
15	$(2.3 \pm 0.1) \times 10^6$	$(4.3 \pm 0.3) \times 10^6$
25	$(2.8 \pm 0.1) \times 10^6$	$(5.6 \pm 0.7) \times 10^6$

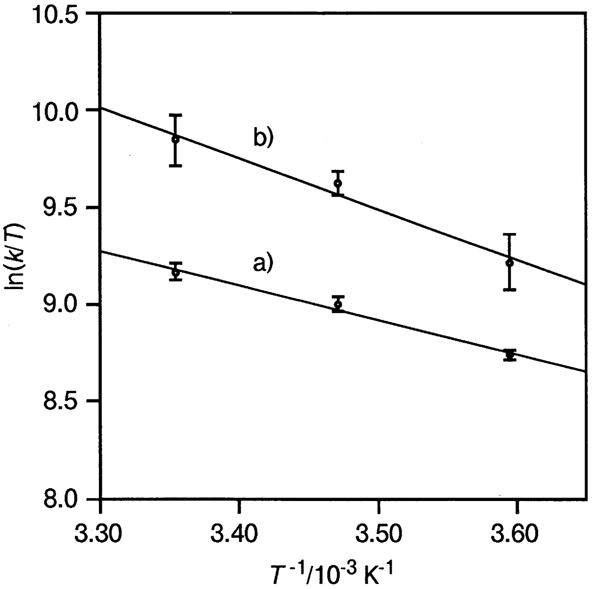


Figure 2. Eyring plots of the reactions. a); the reaction of **2** and **3-a**, b); the reaction of **2** and **3-b**.

suggest that the reaction between **2** and **3-b** requires more thermal energy than that between **2** and **3-a** to bring the reactants into the transition state. Though the $\Delta H^{\ddagger}_{SS\text{-}RR}$ value is larger than the $\Delta H^{\ddagger}_{RR\text{-}RR}$ value, a rather large difference in the activation entropy, $\Delta\Delta S^{\ddagger}_{(SS\text{-}RR)\text{-}(RR\text{-}RR)}$ = 26.5 J mol^{-1} K^{-1}, overcompensates the effect of the activation enthalpy, $\Delta\Delta H^{\ddagger}_{(SS\text{-}RR)\text{-}(RR\text{-}RR)}$ = 6.2 kJ mol^{-1}, on the free activation energy. Two mutually competing effects of the activation enthalpy and the activation entropy in stereoselectivity are well known in reactions involving proteins and have been observed in electron-transfer reactions between metalloproteins and several metal complexes. Bernauer *et al.*[6] reported the electron-transfer between spinach ferredoxin and optically active cobalt(III) complexes, and explained the compensation behavior by the combination of stereochemical interactions and desolvation processes upon formation of the precursor complex or the transition state. But, the structures of the intermediates for these reactions are too complicated to elucidate the reaction mechanism. It is notable that the $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation was also observed in the electron-transfer reactions between these oxovanadium(IV) and (V) complexes.

Although we do not have any conclusive evidence which determines that the present reaction proceeds by the inner-sphere mechanism, the two reacting vanadium atoms must be brought sufficiently close together when the electron-transfer occurs. It should be reasonable that the oxo ligand of oxovanadium(IV) complex interacts at the position trans to the oxo ligand of the oxovanadium(V) complex because the latter prefers a six-coordinate structure. The dinuclear structure of [(salen)$V^{IV}OV^{V}O$(salen)]$I_5\cdot CH_3CN$[7] (H_2salen=*N,N'*-disalicylidene-1,2-ethanediamine) was reported, which has a V^{IV}=O··· V^{V}=O bond. A similar dinuclear structure may be expected for the intermediate of the electron-transfer reaction. Figure 3 is a schematic representation of the proposed structures of the intermediate. The chiral recognition must be due to the difference in the non-bonding steric interaction between the ligands in the two intermediate structures.

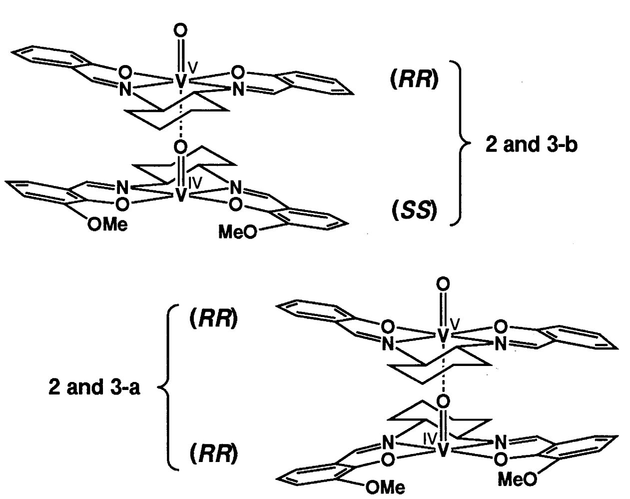


Figure 3. Proposed structures of the intermediate in the electron-transfer reaction.

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References and Notes

1 For example, A. G. Lappin and R. A. Marusak, *Coord. Chem. Rev.*, **109**, 125 (1991), and the references cited therein.
2 K. Nakajima, M. Kojima, M. Tsuchimoto, Y. Yoshikawa, and J. Fujita, *Chem. Lett.*, **1994**, 1593.
3 H_2{sal-(*RR*)-chxn} and H_2{3-MeOsal-(*RR*) or (*SS*)-chxn} denote *N,N'*-disalicylidene-(*R,R*)-1,2-cyclohexanediamine and *N,N'*-di-3-methoxysalicylidene-(*R,R*) or (*S,S*)-1,2-cyclohexanediamine, respectively.
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5 The reaction was too fast under pseudo-first-order reaction conditions to measure by the stopped-flow method. Therefore, the absorbance change was measured under second-order conditions. J. W. Moore and R. G. Pearson, "Kinetics and Mechanism" 3rd ed , John-Wiley, New York (1981), p. 305.
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