CHEMISTRY LETTERS, pp. 1593-1596, 1994.

Isomerization of a Diastereomeric Oxovanadium(IV) Complex Containing an Unsymmetrical Tetradentate Schiff Base Ligand Catalyzed by Oxovanadium(V) Species

Kiyohiko NAKAJIMA,* Masaaki KOJIMA,†,* Masanobu TSUCHIMOTO,††
Yuzo YOSHIKAWA,† and Junnosuke FUJITA†††
Department of Chemistry, Aichi University of Education, Igaya, Kariya 448
†Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700
††Department of Chemistry, Faculty of Science and Technology, Keio University,
Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223
†††Division of Natural Sciences, International Christian University, Osawa, Mitaka 181

The isomerization between the two diastereomers of [$V^{IV}O${3-MeOsal,sal-(*RR*)-chxn}] (H_2{3-MeOsal,sal-(*RR*)-chxn}=*N*-salicylidene-*N'*-3-methoxysalicylidene-(*RR*)-1,2-cyclohexanediamine) in acetonitrile-water(95:5 v/v) was observed under aerobic conditions. The reaction was accelerated by the addition of [$V^{V}O$(salen)]ClO_4 (H_2salen=*N*,*N'*-disalicylidene-1,2-ethanediamine), but the complex did not isomerize in dry acetonitrile. The mechanism of the isomerization was investigated.

Oxovanadium(IV) complexes containing an unsymmetrical tetradentate Schiff base ligand such as 3-Xsal,sal-(*RR*)-chxn (X=MeO, EtO) can have a pair of diastereomers (Fig. 1), which can isomerize to each other by changing the disposition of the oxo ligand. However, the V=O bond of oxovanadium(IV) complexes is said to be rather stable and inert.1) We have reported the preparation of the two isomers of [$V^{IV}O${3-EtOsal,sal-(*RR*)-chxn}] and their isomerization in the solid state.2) The stability of each isomer of these and related complexes in solution still remains unknown. In this letter we report the isomerization between the two diastereomers of [$V^{IV}O${3-MeOsal,sal-(*RR*)-chxn}] in acetonitrile-water(95:5 v/v).

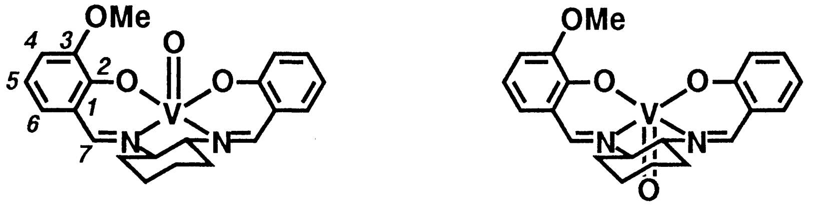


Fig. 1. Two isomers of [$V^{IV}O${3-MeOsal,sal-(*RR*)-chxn}]. 3)

The two isomers (I and II) of [$V^{IV}O${3-MeOsal,sal-(*RR*)-chxn}] (Fig. 1) were prepared according to the reported procedures.2-4) Found for isomer I :C, 57.53; H, 5.24; N, 6.31%. Calcd for [VO{3-MeOsal,sal-(*RR*)-chxn}]·H_2O=$C_{21}H_{24}N_2O_5V$: C, 57.93; H, 5.56; N, 6.43%. Found for isomer II :C, 56.41; H, 5.09; N, 6.18%. Calcd for [VO{3-MeOsal,sal-(*RR*)-chxn}]·1.5H_2O=$C_{21}H_{25}N_2O_{5.5}V$: C, 56.76; H, 5.67; N, 6.30%.

The progress of isomerization between isomers I and II was followed by a high-performance liquid chromatographic (HPLC) method. Each isomer of [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}] was dissolved in acetonitrile-water(95:5 v/v) and the solution was maintained at 40 °C in the air. Portions of the reaction mixture were withdrawn at intervals and chromatographed on a column (ø0.46 cm x 15 cm) of JASCO CrestPak C18S with CH_3CN-H_2O(44:56 v/v) as an eluent. The isomers I and II were detected at 250 nm where they have the same molar absorption coefficient. The reaction profile of isomerization of isomer I to II at 40 °C is given in Fig. 2(a). The isomerization reaction proceeded slowly to yield a ca. 1:1 mixture of isomers I and II in 8 hours. At room temperature it took more than a few days to attain equilibrium. In an atmosphere of nitrogen, the complex was stable and the isomerization did not take place. When isomer I was dissolved in dry acetonitrile in the air, formation of any amount of isomer II was not observed by the HPLC analysis in 8 hours.

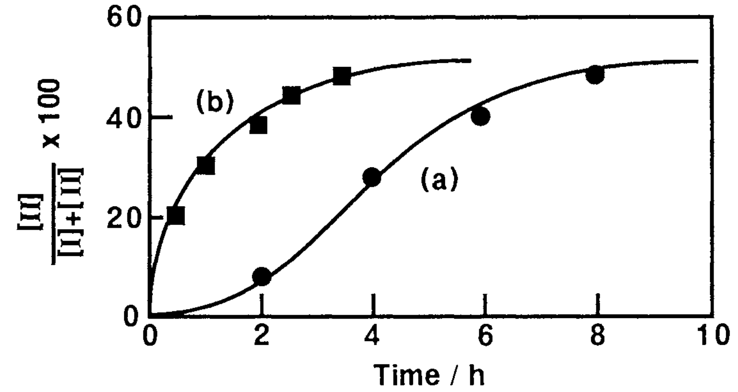
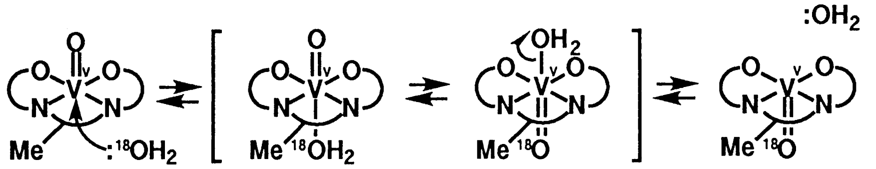


Fig. 2. Reaction profile of isomerization of isomer I to II of [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}]. (a) [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}]-I (1.2×10^{-3} mol dm^{-3}) in CH_3CN-H_2O(95:5 v/v) at 40 °C under aerobic conditions. (b) [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}]-I (1.2×10^{-3} mol dm^{-3}) in CH_3CN-H_2O(95:5 v/v) at 25 °C in the presence of [V^VO(salen)]ClO_4 (9.2×10^{-5} mol dm^{-3}) in an atmosphere of nitrogen.

[$V^{IV}O$(SB)] (SB=tetradentate Schiff base ligand) is oxidized to [V^VO(SB)]$^+$ by dioxygen.[5] Therefore, it is expected that a part of [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}] was oxidized in solution under aerobic conditions to the corresponding VO^{3+} species. The formation of the VO^{3+} species seems to be the first step of the isomerization reaction. Accordingly, a small portion of [V^VO(salen)]ClO_4 was added as an oxidizing agent to an acetonitrile-water (95:5 v/v) solution of isomer I ([V^VO(salen)]ClO_4 : [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}]-I = 0.08 : 1) in an atmosphere of nitrogen. The isomerization reaction proceeded fast (Fig. 2(b)). The redox reaction (1) between [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}]-I and [V^VO(salen)]ClO_4 took place immediately, and [$V^{IV}O$(salen)] was detected by the HPLC analysis. Thus the fast redox reaction occured prior to the isomerization, and the VO^{3+} species formed would catalyze the isomerization reaction.

$$[V^{IV}O\{\text{3-MeOsal,sal-}(RR)\text{-chxn}\}]\text{-I} + [V^{V}O(\text{salen})]^+$$
$$\rightleftharpoons [V^{V}O\{\text{3-MeOsal,sal-}(RR)\text{-chxn}\}]^+\text{-I} + [V^{IV}O(\text{salen})] \quad \cdots\cdots \ (1)$$

[V^VO\{3-MeOsal,sal-(*RR*)-chxn\}]$^+$ also has two isomers corresponding to isomers I and II. In order to investigate the isomerization rate of [V^VO\{3-MeOsal,sal-(*RR*)-chxn\}]$^+$ we tried to isolate these isomers by oxidizing I or II of [$V^{IV}O$\{3-MeOsal,sal-(*RR*)-chxn\}] with Ce(IV), but only a mixture of isomers was obtained. This result suggests a facile isomerization of [$V^{V}O$\{3-MeOsal,sal-(*RR*)-chxn\}]$^+$ in solution during oxidation and/or isolation. Fortunately, we could get one isomer of [$V^{V}O$\{sal-(*R*)-pn\}]NO_3,$^{6)}$ and studied its isomerization by ^1H NMR spectroscopy. The isomer of [$V^{V}O$\{sal-(*R*)-pn\}]NO_3 was dissolved in DMSO-d_6 containing a small amount of water at room temperature. The ^1H NMR spectra were measured at intervals. The intensity of the doublet (1.50 ppm) of CH_3 group of (*R*)-pn moiety decreased with time, and a new doublet attributable to the CH_3 group of the other isomer appeared at 1.39 ppm. The complex attained equilibrium within 1.5 hours. The relative abundance of the two isomers was ca. 2:1; the isomer showing the doublet at 1.50 ppm being more abundant than the other. Thus, [$V^{V}O$\{sal-(*R*)-pn\}]$^+$ easily isomerized in solution containing a small amount of water. In order to examine if the oxo ligand in a VO^{3+} complex is exchanged readily with water, we used oxygen-18 as an isotopic tracer. [$V^{V}O$\{sal-(*R*)-pn\}]NO_3 was dissolved in acetonitrile-$H_2{}^{18}O$ (95:5 v/v) and left for 2 hours at room temperature. The solvent was removed by evaporation at reduced pressure and the complex was collected. The IR spectrum of the collected complex showed the $V{=}^{18}O$ stretching at 922 cm^{-1} while $\nu_{(V=^{16}O)}$ of the original complex, [$V^{V}O$\{sal-(*R*)-pn\}]NO_3, was at 962 cm^{-1}, a complete exchange being indicated. Since VO^{3+} complexes prefer a six-coordinate structure, the coordination of water to the trans position of the oxo ligand was expected. The isomerization is supposed to occur by the following proton migration and elimination of the oxo ligand as water (Scheme 1).



Scheme 1.

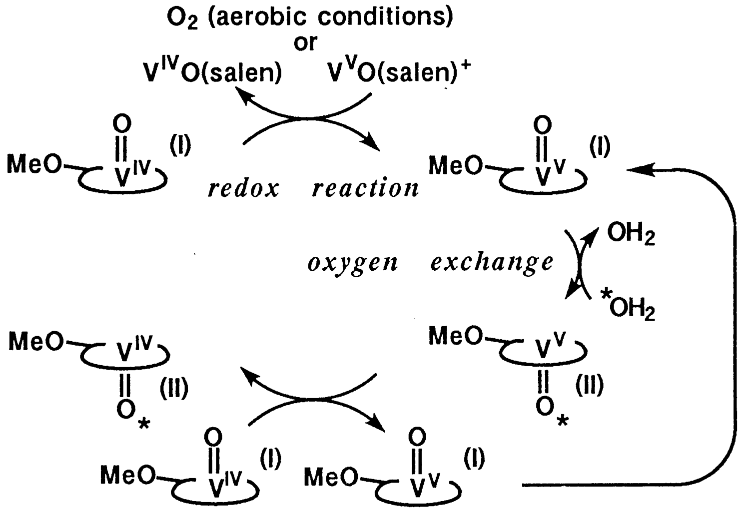


Fig. 3. A proposed mechanism of the isomerization of [VO\{3-MeOsal,sal-(*RR*)-chxn\}] in solution.

Figure 3 shows a proposed mechanism of the isomerization of [VO{3-MeOsal,sal-(*RR*)-chxn}]. [V^{IV}O{3-MeOsal,sal-(*RR*)-chxn}]-I is oxidized to [V^{V}O{3-MeOsal,sal-(*RR*)-chxn}]$^{+}$-I, and isomerizes to [V^{V}O{3-MeOsal,sal-(*RR*)-chxn}]$^{+}$-II in the course of oxo ligand exchange with oxygen of water. Then, [V^{V}O{3-MeOsal,sal-(*RR*)-chxn}]$^{+}$-II is reduced by an oxovanadium(IV) complex to yield the isomerized product of [V^{IV}O{3-MeOsal,sal-(*RR*)-chxn}]-II. In order to make the details of isomerization mechanism clear, we are now investigating the kinetics of the redox reaction between oxovanadium(IV) and oxovanadium(V) species (first step) and the oxo ligand exchange of oxovanadium(V) complexes (second step).

The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 05403009 and 06640720 from the Ministry of Education, Science and Culture.

References

1) R. K. Murmann, *Inorg. Chim. Acta*, **25**, L43 (1977).
2) M. Kojima, K. Nakajima, M. Tsuchimoto, M. Tanaka, T. Suzuta, Y. Yoshikawa, and J. Fujita, *Chem. Lett.*, **1994**, 949.
3) Two isomers (I and II) were separated by silica gel column chromatography (eluent: dichloromethane-ethyl acetate (93:7 v/v). The faster eluted isomer was named isomer I, and the slower one isomer II. Since we have not obtained crystals suitable for structure determination, we do not know which of the two isomers in Fig. 1 should be assigned to isomer I.
4) K. Nakajima, K. Kojima, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 2620 (1990).
5) The formation of a small amount of [VO(SB)]$^{+}$ in solution under aerobic conditions could be detected by the absorption spectrum.
6) [V^{V}O{sal-(*R*)-pn}]$^{+}$ (H_2{sal-(*R*)-pn} ; *N,N'*-disalicylidene-(*R*)-1,2-propanediamine) also has two diastereomers which differ from each other with respect to the disposition of the axial oxo ligand and the methyl substituent of the (*R*)-pn moiety. [V^{V}O{sal-(*R*)-pn}]NO_3 involving only one isomer was prepared by a similar method to that for the perchlorate,[4] 1 mol dm^{-3} HNO_3 being used instead of 1 mol dm^{-3} $HClO_4$.

(Received May 20, 1994)