

**Disproportionation Reaction of Seven-coordinate $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$
into $[\text{Re}^{\text{IV}}\text{O}(\text{tpen})]^{2+}$ and $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$
where tpen is *N,N,N',N'*-Tetrakis(2-pyridylmethyl)ethylenediamine**

Toshihiro Tabeya, Masaaki Abe,^{*,†} and Yoichi Sasaki^{*,††}

Division of Chemistry, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo 060-0810

(Received July 5, 2006; CL-060765; E-mail: mabetcm@mbox.nc.kyushu-u.ac.jp, yasaki@sci.hokudai.ac.jp)

UV-vis and ¹H NMR spectra provide unambiguous evidences for the disproportionation reactions of $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ to give $[\text{Re}^{\text{IV}}\text{O}(\text{tpen})]^{2+}$ and $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$ (tpen = *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine) in 2:1 ratio with the important participation of water molecules.

Rhenium provides stable complexes in various oxidation states ranging from -1 to $+7$.¹ Change in the oxidation states often occurs during the syntheses of rhenium complexes even if reduction or oxidation reagent was not used purposely. Disproportionation reactions may be possibly responsible for the change in the oxidation states, since facile disproportionations of some rhenium complexes have been reported.²⁻⁴ For example, a series of disproportionation reactions of the Re^{V} complex of 1,4,7-triazacyclononane (tacn), $[\text{Re}^{\text{V}}\text{O}(\text{tacn})(\text{O}_2\text{C}_2\text{H}_4)]^+$, has been reported.² When refluxed in 1.0 mol dm^{-3} HCl, it gave $[\text{Re}^{\text{IV}}_2(\mu\text{-O})_2\text{Cl}_2(\text{tacn})_2]_2$ and $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tacn})]_2$. Disproportionation reactions have been suggested for the reaction of $[\text{Re}^{\text{V}}(\text{O})_2(\text{pyridine})_4]^+$ with 2,2':6',2''-terpyridine (terpy) in ethanol/water medium to give $[\text{Re}^{\text{III}}(\text{terpy})_2(\text{OH})(\text{ReO}_4)_2]$.³ Disproportionation reaction has also been proposed in the preparation of the di- μ -oxo Re^{IV} dimers of tris(2-pyridylmethyl)amine from $[\text{Re}^{\text{V}}\text{OCl}_3(\text{PPh}_3)_2]$, since ReO_4^- was found as a counter anion.⁴ The ligand substitution and/or dimerization reactions are accompanied in all these cases, however, and the evidences for the disproportionation reactions are rather phenomenological.

We have shown that the reaction of $\text{Re}^{\text{V}}\text{OCl}_3(\text{PPh}_3)_2$ or $[\text{Re}^{\text{V}}\text{OCl}_3]^{2-}$ with tpen in aqueous ethanol (1/25, v/v) gives seven-coordinate Re^{IV} complex, $[\text{Re}^{\text{IV}}\text{O}(\text{tpen})]^{2+}$, occasionally together with small amount of Re^{V} analog, $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$.⁵ From the prolonged reaction mixture, a unique Re^{VII} complex ($[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$) with tridentate tpenH was isolated.⁶⁻⁸ We thought that the Re^{IV} and the Re^{VII} complexes could be formed through the disproportionation of $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$, and that it may be a good opportunity to study the disproportionation reaction in a quantitative way, since all these three complexes are mononuclear and the ligand tpen retains in the coordination sphere. In particular, the coordination spheres of the Re^{IV} and the Re^{V} complexes are practically the same (Chart 1).

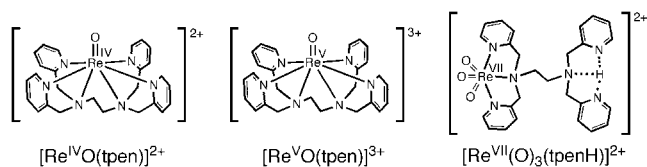


Chart 1. Re complexes dealt with in this study.

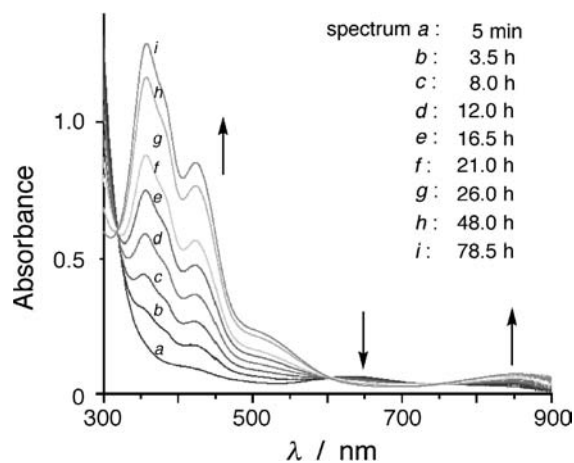


Figure 1. Change in the electronic absorption spectra of $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ ($1.6 \times 10^{-4} \text{ mol dm}^{-3}$) in H_2O (16.5 mol dm^{-3})/acetonitrile at 20°C .

All the following experiments were carried out under O_2 free conditions. The Re^{V} complex, $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$, was stable in anhydrous acetonitrile solution as the electronic absorption spectrum remained practically unchanged at least a week at room temperature. However, when water was added to the solution the spectral change was observed (Figure 1 for H_2O (16.5 mol dm^{-3})/acetonitrile solution). The original spectrum of the Re^{V} complex caused significant change with the isosbestic points at 320, 605, and 745 nm. The final spectrum has strong peaks at 360 and 423 nm and coincides with that of $[\text{Re}^{\text{IV}}\text{O}(\text{tpen})]^{2+}$ in acetonitrile.⁵ Quantitative analysis indicated that the amount of the Re^{IV} complex produced was 67% of the original Re^{V} complex. Thus, 33% of the Re^{V} complex must have converted to the species that has no absorption in the visible region. It should be noted that the known Re^{VII} -tpen species, $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$, has no significant absorption in the visible region.⁶ ¹H NMR spectra of the $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ solution of $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ also show significant change with time (Figure 2). The Re^{V} complex is diamagnetic and shows sharp signals (Figure 2a),⁵ which become broad and some new sharp signals appear simultaneously (Figures 2b and 2c). The broadening of the signals may be explained by considering the rapid electron exchange between the paramagnetic Re^{IV} species produced and original $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$. The sharp signals are coincide with those of $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$.⁶ The amount of the Re^{VII} species was evaluated from the integral intensity of the signals and was ca. 30% of that of the initial $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$. It was also observed that the pH of the solution becomes ca. 3 after the reaction. From these results, it is concluded that overall disproportionation reaction (eq 1) is a clean

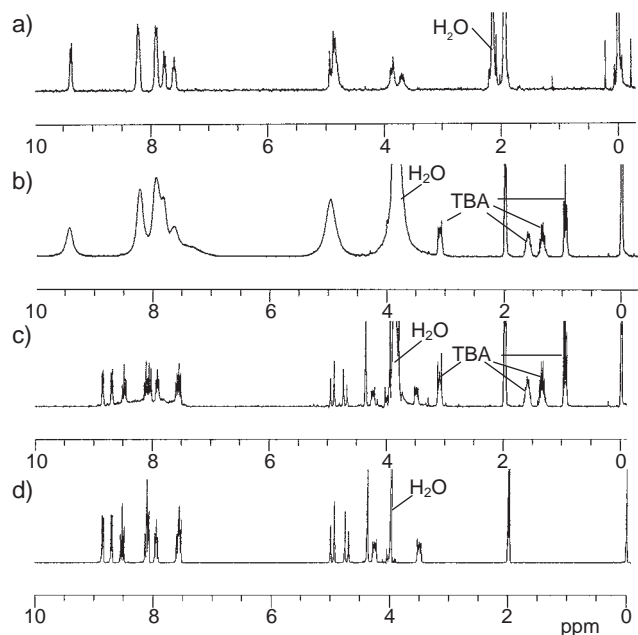
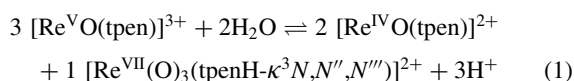


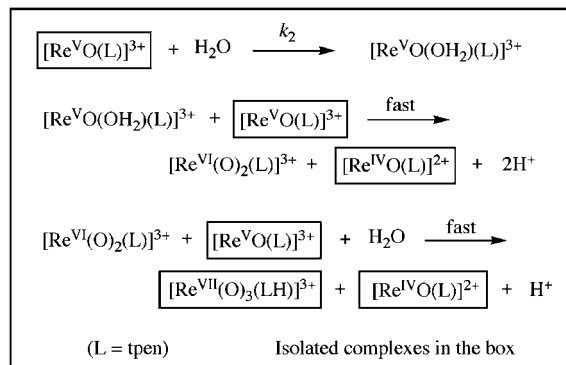
Figure 2. ^1H NMR spectra of $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ (1.8×10^{-2} mol dm $^{-3}$) (a) in CD_3CN at room temperature, (b) in D_2O (16.5 mol dm $^{-3}$)/ CD_3CN at 30°C , 16 min after dissolution (TBAPF $_6$ is included as a reference for the signal intensity; $[\text{TBAPF}_6] = 2.6 \times 10^{-3}$ mol dm $^{-3}$), (c) the same solution as (b) 29 h after dissolution, and (d) $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$ in D_2O (16.5 mol dm $^{-3}$)/ CD_3CN (0.5 mL of 70% DClO_4 was added) at room temperature.

reaction without appreciable side reactions.



A water molecule would attack the Re^{V} species to form “ $[\text{Re}^{\text{V}}\text{O}(\text{H}_2\text{O})(\text{tpen})]^{2+}$,” where coordination mode of tpen is unknown. The aqua complex would undergo proton-coupled oxidation to Re^{VI} species, as the deprotonated complex is much more favorable for oxidation. Thus, the proton-coupled oxidation of the Re^{V} aqua complex by original $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ would be a favorable reaction. Since the intermediate Re^{VI} complex is not spectroscopically detected, it would quickly react with additional $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ to form “ Re^{VII} species,” which would then be converted to the final product $[\text{Re}^{\text{VII}}(\text{O})_3(\text{tpenH-}\kappa^3\text{N,N'',N'''})]^{2+}$ with the aid of an additional water molecule. The proton release was confirmed by the pH decrease after the reaction. Overall reaction pathway is summarized in Scheme 1.

Time course of the disproportionation reaction was followed by the increase of the absorption peak of $[\text{Re}^{\text{IV}}\text{O}(\text{tpen})]^{2+}$ at 423 nm in acetonitrile at $I = 1.5 \times 10^{-2}$ (NaPF $_6$) containing different amount of water (2.75, 5.50, and 16.5 mol dm $^{-3}$) at 20–30 °C. In most cases, first-order plots, $\ln\{1/(A_\infty - A_t)\}$ vs. t , where A_∞ and A_t are absorbance at infinite time and at time t , gave good straight lines up to more than 75% of the total spectral change. From the slopes of the plots, k_1 values were evaluated. Similar plots obtained from the absorbance change at 630 nm also gave straight lines and gave similar k_1 values although they are less accurate because of smaller absorbance change. The fact that the reaction proceeds in the first-order manner with respect



Scheme 1. Reaction pathway of the disproportionation.

to the complex concentration indicates that the bimolecular disproportionation reaction is not the rate-determining step and the attack of water molecule to the original Re^{V} complex could be more likely. Although the quantitative comparison of k_1 values in different ratio of the mixed solvent $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ is not very appropriate, still it is seen that k_1 values roughly show linear dependence on $[\text{H}_2\text{O}]$; $1.56(\pm 0.02) \times 10^{-6}$, $4.09(\pm 0.03) \times 10^{-5}$, and $9.12(\pm 0.11) \times 10^{-5}$ s $^{-1}$ at $[\text{H}_2\text{O}] = 2.75$, 5.50, and 16.5 mol dm $^{-3}$, respectively (note that k_1 is practically 0 s $^{-1}$ without addition of H_2O ; bimolecular rate constant $k_2 = k_1[\text{H}_2\text{O}]$). All the subsequent reactions should be fast with regard to the aqua complex formation.

From the temperature dependence of k_1 at $[\text{H}_2\text{O}] = 16.5$ mol dm $^{-3}$ $\{2.02(\pm 0.27) \times 10^{-5}$ and $3.53(\pm 0.68) \times 10^{-5}$ s $^{-1}$ at 25 and 30 °C, respectively}, activation parameters were obtained: $\Delta H^\ddagger = 98 \pm 4$ kJ mol $^{-1}$ and $\Delta S^\ddagger = -7 \pm 14$ J K $^{-1}$ mol $^{-1}$, which may indicate that the coordination of H_2O to the Re^{V} complex would proceed by associative mode of activation.

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References and Notes

- † Present address: Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka 819-0395.
- †† Present address: Catalysis Research Center, Hokkaido University, Sapporo 001-0021.
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