Redox Behavior of New Ru–Dioxolene–Ammine Complexes and Catalytic Activity toward Electrochemical Oxidation of Alcohol under Mild Conditions

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The new Ru–dioxolene–ammine complexes, $[\mathrm{Ru^{II}(NH_3)(sq)(trpy)}](\mathrm{ClO_4})$ (**1**, sq = 3,5-di-*tert*-butyl-1,2-benzosemiquinone, trpy = 2,2′:6′,2″-terpyridine) and $[\mathrm{Ru^{III}(NH_3)(sq)(trpy)}](\mathrm{ClO_4})_2$ (**2**), were prepared. They have an ability to oxidize MeOH and *i*-PrOH catalytically under very mild conditions such as the electrolysis at 0 V (vs SCE) in $\mathrm{CH_2Cl_2}$.

Oxo-metal species are believed to work as active centers in various metal proteins that catalyze hydroxylation, epoxidation, and various oxidation of biological substrates.[1–3] Since Meyer et al. have found a versatile synthetic route of oxo-$\mathrm{Ru^{IV}}$ polypyridyl complexes by sequential proton and electron loss of the corresponding aqua-$\mathrm{Ru^{II}}$ ones, a variety of high-valent oxo-Ru polypyridyl complexes have been reported and their reactivity has also been extensively studied.[4] Recently, we have demonstrated that treatments of Ru-aqua-dioxolene complex, $[\mathrm{Ru(OH_2)(sq)(trpy)}]^{2+}$ (sq = 3,5-di-*tert*-butyl-1,2-benzosemiquinone, trpy = 2,2′:6′,2″-terpyridine), with bases produce the corresponding oxyl-radical complex without any oxidants (Eq 1).[5] We attribute this unprecedented radical complex formation to the acid–base equilibria among aqua, hydroxy, and oxo ligands coupling with the intramolecular electron transfer from negatively charged oxo ligand to Ru–dioxolene framework.[6] This view leads us to activate protic molecules on the Ru–dioxolene moiety under basic conditions to generate radical species aiming at catalytic oxidation of organic molecules. Along this line, we prepared new Ru–dioxolene complexes with an ammine ligand, $[\mathrm{Ru^{II}(NH_3)(sq)(trpy)}](\mathrm{ClO_4})$ (**1**) and $[\mathrm{Ru^{III}(NH_3)(sq)(trpy)}](\mathrm{ClO_4})_2$ (**2**). Here we report their syntheses, properties, and catalytic activities toward alcohol oxidation under basic conditions.

$$[\mathrm{Ru^{III}(OH_2)(sq)(trpy)}]^{2+} \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{Ru^{III}(OH)(sq)(trpy)}]^{+} \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{Ru^{II}(\dot{O})(sq)(trpy)}]^{0} \qquad (1)$$

The complex **1** was obtained by the reaction of $[\mathrm{Ru^{II}(OAc)(sq)(trpy)}]$[5,7] with an aqueous $\mathrm{HClO_4}$ solution in MeOH and then with an aqueous $\mathrm{NH_3}$ solution in THF. The complex **2** was prepared by one electron oxidation of **1** under the controlled potential electrolysis in a relatively high yield.[8] The EPR spectrum[9] of **1** displayed a broad isotropic signal ($g = 2.008$) at 298 K in $\mathrm{CH_2Cl_2}$ arising from the $\mathrm{Ru^{II}}$-sq framework, whereas **2** did not show any EPR signal because of antiferromagnetic interaction in the $\mathrm{Ru^{III}}$-sq one. The binding energies[10] for the Ru $3d_{5/2}$ of **1** and **2** were 280.4 and 281.2 eV, whose values well coincide with those of $\mathrm{Ru^{II}}$ and $\mathrm{Ru^{III}}$ complexes, respectively.[11,12] The complexes **1** and **2** naturally show the same cyclic voltammograms (CVs) in $\mathrm{CH_2Cl_2}$; two reversible redox waves at $E_{1/2} = -0.46$ V and $E_{1/2} = +0.34$ V (vs SCE) for the $[\mathrm{Ru^{II}(NH_3)(cat)}]^0/[\mathrm{Ru^{II}(NH_3)(sq)}]^+$ and $[\mathrm{Ru^{II}(NH_3)(sq)}]^+/[\mathrm{Ru^{III}(NH_3)(sq)}]^{2+}$ couples, respectively. Indeed, the rest potentials for **1** (+0.16 V) and **2** (+0.48 V) are located at the negative and the positive side of the redox potential of the $[\mathrm{Ru^{II}(NH_3)(sq)}]^+/[\mathrm{Ru^{III}(NH_3)(sq)}]^{2+}$ couple at +0.34 V. The electronic absorption spectra of **1** and **2** in $\mathrm{CH_2Cl_2}$ each show strong absorption bands at 854 nm (ε 13000 $\mathrm{M^{-1}cm^{-1}}$) and 615 nm (ε 13000 $\mathrm{M^{-1}cm^{-1}}$), assignable to the charge-transfer transition inside the $\mathrm{Ru^{II}}$-sq and the $\mathrm{Ru^{III}}$-sq frameworks, respectively. An addition of 1 equiv. of a methanolic solution of *t*-BuOK to **2** in $\mathrm{CH_2Cl_2}$ results in significant shift of the CT band from 615 to 854 nm (Figure 1). The resultant spectrum is consistent with that of **1** and remains unchanged even after addition of large excess *t*-BuOK to the solution. Thus, **2** is reduced stoichiometrically to **1** by the reaction with 1 equiv. of *t*-BuOK in MeOH.[13]

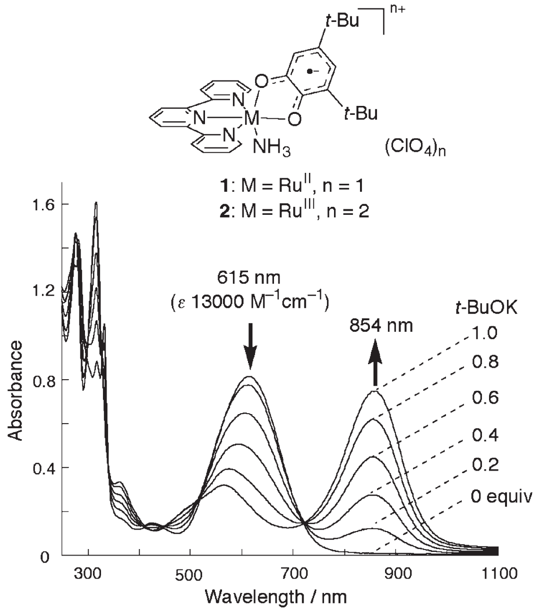

Figure 1. The change of the electronic absorption spectra of **2** in $\mathrm{CH_2Cl_2}$ containing various amounts of a methanolic solution of *t*-BuOK (8.2 mM).[13]

The CV of **1** in MeOH also shows two reversible redox waves as similar to that in $\mathrm{CH_2Cl_2}$ (Figure 2a), and exhibits strong catalytic anodic currents in the presence of excess *t*-BuOK at potentials more positive than the threshold potential of the redox couple at +0.34 V (Figure 2b). The observation that the $[\mathrm{Ru^{II}(NH_3)(cat)}]^0/[\mathrm{Ru^{II}(NH_3)(sq)}]^+$ redox couple at −0.39 V remains unchanged in the multi-scanning CV even in

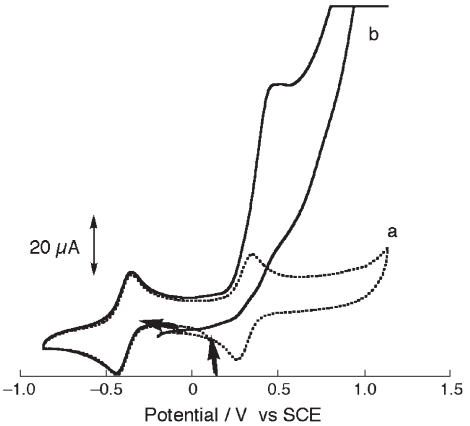

Figure 2. Cyclic voltammograms of **1** (1 mM) (a, dotted line) and in the presence of 20 equiv. of *t*-BuOK (b, solid line) in CH_3OH; TBAP was used as electrolyte (0.1 M). The arrow indicates the rest potential of the solution (a; +0.14 V, b; −0.083 V).

the presence of 20 equiv. of *t*-BuOK strongly suggests that **2** generated on the surface of the electrode works as a catalyst precursor for the catalytic oxidation of solvent molecules with the regeneration of **1** under basic conditions. In fact, 73 F/mole of electricity were consumed in the controlled potential electrolysis of **1** (1 mM) at +0.35 V in the presence of *t*-BuOK (100 equiv. for **1**) in MeOH.[14] The electron spray ionization mass spectra (ESIMS)[15] of the electrolyte solution revealed that **1** was completely converted to $[Ru^{III}(OCH_3)(sq)(trpy)]^+$, when the anodic currents came to rest. The fact that $[Ru^{II}(OCH_3)(sq)(trpy)]$ has no catalytic activity under the similar reaction conditions[16] indicates that **1** and **2** participate as catalyst precursors in the catalytic cycle of MeOH oxidation. Moreover, the analogous aqua complex $[Ru^{III}(OH_2)(sq)(trpy)]^{2+}$ affording $[Ru^{III}(OH)(sq)(trpy)]^+$ and $[Ru^{II}(O\bullet)(sq)(trpy)]$ under basic conditions (Eq 1) never shows such a strong irreversible anodic current in the CV experiments. The catalytic activity of **1** and **2** toward the MeOH oxidation increased in CH_2Cl_2 and the threshold potential of the irreversible catalytic currents moved to 0 V in MeOH/CH_2Cl_2 (1:99 v/v). Electrochemical oxidation of *i*-PrOH in CH_2Cl_2 was conducted under the electrolysis of **1** (1 mM) at 0 V in the presence of *i*-PrOH and *t*-BuOK (30 equiv. and 2 equiv. for **1**, respectively). Even such mild conditions, the oxidation of *i*-PrOH proceeded and acetone was confirmed by GC–MS of the electrolyte solution after 1.0 C passed in the electrolysis.

It is worth noting that the analogous aqua Ru^{III} complex is converted to the oxyl-radical Ru^{II} one upon dissociation of two protons of the aqua ligand (Eq 1), whereas **2** is reduced to **1** in the reaction with a stoichiometric amount of base in CH_3OH. Based on these facts, the catalytic cycle of MeOH oxidation may be explained as follows: treatment of **2** with a base probably produces $[Ru^{III}(NH_2{}^-)(sq)(trpy)]^+$ and the subsequent electron transfer from $NH_2{}^-$ to Ru^{III} will give $[Ru^{II}(NH_2\bullet)(sq)(trpy)]^+$. The resultant amino-radical complex may work as the active species for the abstraction of hydrogen from CH_3OH with the regeneration of **1**.

In summary, the present study demonstrates that new Ru–dioxolene–ammine complexes **1** and **2** have an ability to oxidize alcohols catalytically under very mild conditions such as the electrolysis at +0.35 and 0 V (vs SCE) in MeOH and MeOH/CH_2Cl_2 (v/v 1:99), respectively. The elucidation about reaction mechanisms in the alcohol oxidation is underway.

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8 Aqueous $HClO_4$ solution (70%, 2 mL) was added to a methanol solution (6 mL) of $[Ru^{II}(OAc)(sq)(trpy)]^{5,7}$ (202 mg). After stirring overnight, the crude products were extracted with CH_2Cl_2, dried with Na_2SO_4 and evaporated. To the residue was added THF (20 mL) and aqueous NH_3 solution (28%, 2 mL). After stirring overnight, the reaction mixture was extracted with CH_2Cl_2, dried, evaporated, and purified on neutral aluminum column using acetone/MeOH as an eluent. Dark purple needles of **1** crystallized from acetone/$NaClO_4$ aqueous solution; yield 52.8 mg (24%). Anal. Calcd for $C_{29}H_{34}ClN_4O_6Ru$: C, 51.90; H, 5.11; N, 8.35%. Found: C, 52.09; H, 5.27; N, 8.09%. The complex **2** was prepared under the controlled-potential electrolysis of **1** (50 mg) at +0.64 V in MeOH containing $LiBF_4$ (0.05 M) as an electrolyte with using a glassy carbon plate and a platinum foil as working and counter electrodes, respectively. After 8.2 coulombs passed in the electrolysis, the crude products were extracted with CH_2Cl_2, dried and evaporated. The residue was washed with ethyl acetate and diethyl ether several times. Deep blue needles of **2** crystallized from acetone/NH_4ClO_4 aqueous solution; yield 28 mg (48%). Anal. Calcd for $C_{29}H_{34}Cl_2N_4O_{10}Ru$: C, 45.20; H, 4.45; N, 7.27%. Found: C, 44.98; H, 4.53; N, 6.99%.
9 EPR spectrum was measured with JEOL X-band spectrometer (JES-RE1XE). The *g* value was calibrated precisely with an Mn^{2+} marker.
10 X-ray photoelectron spectrum was recorded on a VG Scientific Ltd. ESCA LAB MK II. Mg Kα radiation (1253.6 eV) operated at 14.5 kV and 20 mA was used as an X-ray excitation source. The samples were deposited on gold foil from CH_2Cl_2 solutions. The C 1s peak was assigned as the value of 284.6 eV and used as the internal reference.
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13 Oxidation products of MeOH were not identified in the stoichiometric reaction of Figure 1.
14 The controlled potential electrolysis was performed under the similar conditions as the preparation of **2**.[8] The occurrence of oxidation of methanol but not *t*-BuOH was demonstrated by the fact that anodic currents also smoothly flowed in the presence of MeOLi in place of *t*-BuOK in MeOH. Formaldehyde and methyl formate (as two and four electron oxidation products of MeOH) were identified in the GC–MS analysis of the final electrolyte solution.
15 ESIMS spectra were obtained on a PE SCIEX API300.
16 $[Ru^{II}(OCH_3)(sq)(trpy)]$ synthesized from $[Ru^{II}Cl(sq)(trpy)]$ by the reaction with NaOMe in MeOH.

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