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Reversible Conversion Between Chemical and Electrical Energies Catalyzed by Ru Complexes Aimed to Construct Sustainable Society

Koji Tanaka,[1] Tohru Wada,[1] Etsuko Fujita,[2] and James Muckerman[2]

[1]Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan
[2]Brookhaven National Laboratory, Upton, NY. 11973-5000, USA

Chemistry Department

Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

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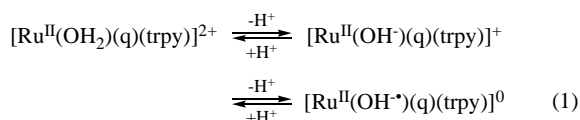*Koji Tanaka,[1] Tohru Wada,[1] Etsuko Fujita,[2] and James Muckerman[2]*

[1]Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan
[2]Brookhaven National Laboratory, Upton, NY. 11973-5000, USA

Introduction

Reversible conversion between CO_2 and MeOH through six-electron redox reactions is a feasible pathway to construct sustainable societies. Metal-oxo species involved in metal proteins work as active centers to catalyze hydroxylation, epoxidation and oxidation of various biological molecules under mild conditions.[1-3] Metal-oxo complexes, therefore, would be reasonable candidates for electrode materials in methanol fuel cells. A variety of high valent Ru-oxo polypyridyl complexes have been prepared by sequential electron and proton loss from Ru^{II}-aqua ones,[4] though redox potentials of the complexes thus obtained are too positive for use as energy converters. On the other hand, introduction of a quinone ligand into Ru-aqua complexes allows smooth double deprotonation without using any oxidants. For example, the pK_a value of $[Ru^{II}(OH_2)(q)(trpy)]^{2+}$ (q = 3,5-di-*tert*-butyl-1,2-benzoquinone) is 5.5. The resultant $[Ru^{II}(OH)(q)(trpy)]^+$ dissociates the hydroxy proton in a pH range over 10 to form the first oxyl radical complex, $[Ru^{II}(O^{-\cdot})(sq)(trpy)]^0$ (eq 1) due to intramolecular electron transfer from the negatively charged oxo ligand to quinone (eq 1).[5] However, the Ru-oxyl radical complex thus formed did not show distinct reactivity toward the

$$[Ru^{II}(OH_2)(q)(trpy)]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Ru^{II}(OH^-)(q)(trpy)]^+$$

$$\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Ru^{II}(OH^{\cdot})(q)(trpy)]^0 \qquad (1)$$

oxidation of MeOH. So, we prepared $[Ru^{II}(NH_3)(sq)(trpy)](ClO_4)$ ($[1](ClO_4)$) in place of Ru-aqua complexes to examine the reactivity of the Ru-aminyl radical toward the oxidation of alcohol under basic conditions.

Experimental

An aqueous $HClO_4$ solution (70%, 2 ml) was added to a methanol solution (6 ml) of $[Ru^{II}(OAc)(sq)(trpy)]$ [6,7] (202 mg), stirred 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 an aqueous NH_3 solution (28%, 2 ml), and stirred overnight. The mixture was extracted with CH_2Cl_2, dried, evaporated, and purified on neutral aluminum oxide column using acetone/MeOH as an eluent. Dark purple needles of $[Ru^{II}(NH_3)(sq)(trpy)](ClO_4)$ ($[1](ClO_4)$) were crystallized from an 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 oxidized form of $[1]^+$ was prepared under the controlled-potential electrolysis of $[1](ClO_4)$ (50 mg) at +0.64 V in MeOH containing $LiBF_4$ 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 solution was extracted with CH_2Cl_2, dried and evaporated. The residue was washed with ethyl acetate and diethyl ether several times. Deep blue needles of $[1](ClO_4)_2$ were 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%.

Cyclic voltammetric experiments were carried out in a one-compartment cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an $Ag/Ag(NO_3)$ (0.01 M) reference electrode. All solutions were deoxygenated with a stream of Ar. Cyclic voltammograms of the complexes under basic conditions were obtained by an addition of various amounts of a methanolic solution of CH_3ONa (0.45 M) to the solution. Bu_4NClO_4 (0.10 M) was used as an electrolyte. An ALS/Chi model 660 electrochemical analyzer was used to collect the cyclic voltammetric data. All potentials are quoted vs. SCE. ESI-MS were obtained on a PE SCIEX API300. EPR spectrum was measured with JEOL X-band spectrometer (JES-REIXE). The g value was calibrated precisely with an Mn^{2+} marker.

Results and Discussion

The addition of an aqueous $HClO_4$ solution to $[Ru^{II}(OAc)(sq)(terpy)]$ in MeOH gave $[Ru^{II}\{O(H)Me\}(sq)(terpy)]^+$. Treatment of the MeOH adduct with NH_3 in THF produced $[Ru^{II}(NH_3)(sq)(terpy)]^+$ ($[1]^+$), which was isolated as a ClO_4^- salt ($[1](ClO_4)$). Electrochemical oxidation of purple $[1](ClO_4)$ at +0.64 V in dry MeOH afforded blue $[Ru^{II}(NH_3)(q)(terpy)](ClO_4)_2$ ($[1](ClO_4)_2$). A broad isotropic EPR signal (g = 2.008) of $[1]^+$ at 298 K in CH_2Cl_2 and the absence of any EPR signals of $[1]^{2+}$ reflect the electronic structures of the $Ru^{II}(sq)$ and $Ru^{II}(q)$ frameworks, respectively, The electronic absorption spectra of $[1]^+$ and $[1]^{2+}$ in CH_3OH displayed a strong absorption band at 853 nm (ε 13 000 $M^{-1}cm^{-1}$) and 615 nm (ε 13 000 $M^{-1}cm^{-1}$), respectively, assignable to the charge-transfer transition within the Ru^{II}-sq and Ru^{II}-q frameworks. It is worthy of note that $[1]^{2+}$ is quantitatively reduced to $[1]^+$ by an addition of 1 equiv of CH_3ONa or *t*-BuOK in CH_2Cl_2 (Figure 1).
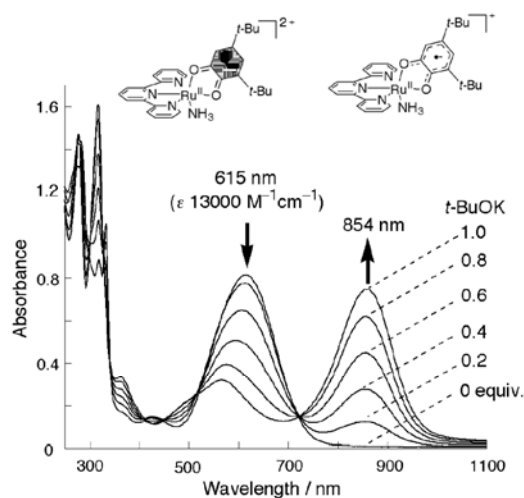

Figure 1. The electron absorption spectra of $[1]^{2+}$ in the presence of various amounts of *t*-BuOK in CH_2Cl_2

The cyclic voltammogram (CV) of $[1]^{2+}$ showed two reversible redox waves at $E_{1/2}$ = –0.46 V and $E_{1/2}$ = +0.34 V (vs. SCE) assignable to the $[Ru^{II}(NH_3)(cat)]^0$ / $[Ru^{II}(NH_3)(sq)]^+$ and $[Ru^{II}(NH_3)(sq)]^+$ / $[Ru^{II}(NH_3)(q)]^{2+}$ couples, respectively, in CH_3OH. The addition of excess amounts of CH_3ONa to $[1]^{2+}$ results in the appearance of strong catalytic currents at potentials more positive than the redox couple at +0.34 V (Figure 2). Furthermore, the $[Ru^{II}(NH_3)(cat)]^0$ / $[Ru^{II}(NH_3)(sq)]^+$ redox couple at $E_{1/2}$ = –0.39 V remained unchanged even in multi-scanning CV in the presence of

excess of CH_3ONa, indicating smooth regeneration of $[\mathbf{1}]^+$ after the oxidation of MeOH by the oxidized form of $[\mathbf{1}]^{2+}$. Indeed, 73 F / mole of electricity were consumed in the controlled potential electrolysis of $[\mathbf{1}]^+$ (1 mM) at +0.35 V in the presence of CH_3ONa (100 equivs based on $[\mathbf{1}]^+$) in MeOH,[8] and then the electrolysis completely stopped. Electron spray ionization mass spectra of the final electrolyte solution revealed the complete conversion from $[\mathbf{1}]^+$ to $[Ru^{II}(OCH_3)(q)(trpy)]^+$ during the electrolysis.[9] In fact, $[Ru^{II}(OCH_3)(sq)(trpy)]$ did not show any catalytic activity toward the oxidation of MeOH under similar reaction conditions.
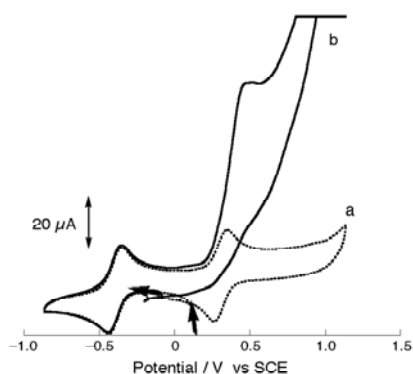

Figure 2. The CVs of $[\mathbf{1}]^+$ in the absence (a) and the presence of *t*-BuOK (100 equiv) (b) in MeOH

In contrast to $[\mathbf{1}]^+$, treatment of $[Ru^{II}(NHPh\text{-}bpa)(q)]^+$ (NH$_2$Ph-bpa = 2-[Bis(2-pyridylmethyl)aminomethyl]aniline) with BuOLi in DMF did not cause the reduction of the quinone ligand, but selectively gave $[Ru^{II}(\cdot NPh\text{-}bpa)(sq)]$ with semiquinone and anilido radicals, because the complex showed a triplet state in the EPR spectrum composed of $g_{xx} = g_{yy} = 2.060$, $g_{zz} = 2.025$, and $|D| = 0.018$ cm^{-1} in CH_2Cl_2 at 5 K.[9] Furthermore, electrochemical reduction of $[Ru^{II}(\cdot NPh\text{-}bpa)(sq)]$ at -1.5 V (*vs.* SCE) in DMF resulted in the reduction of sq. The resultant $[Ru^{II}(\cdot NPh\text{-}bpa)(cat)]^-$ displayed a rhombic pattern EPR spectrum with $g_1 = 2.175$, $g_2 = 2.105$, and $g_3 = 1.950$, and the g_3 component was split into three signals due to the hyperfine coupling with the N atom (I = 1) on the anilino radical with a hyperfine coupling constant, $A_{(N)}$ of 8.2 mT in DME at 20 K.[10] Thus, deprotonation of $[Ru^{II}(NHPhbpa)(q)]^+$ is followed by the intramolecular electron transfer from $(N\text{-}Phbpa)^{2-}$ to q to generate $[Ru^{II}(\cdot NPh\text{-}bpa)(sq)]$ (eq 2), similar to the equilibrium of eq 1.

$$ \text{(2)} $$
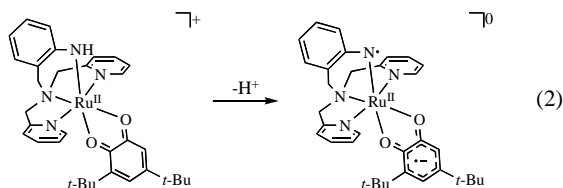
Electrochemical oxidation of $[Ru^{III}(NH_3)(bpy)(trpy)]^{2+}$ at +0.8 V (vs. SCE) in H_2O has been shown to produce $[Ru^{II}(NO_2)(bpy)(trpy)]^+$ through $[Ru^{II}(NH_3)(bpy)(trpy)]^+$ and $[Ru^{IV}(=NH)(bpy)(trpy)]^{2+}$ due to successive electron and proton loss of the central Ru and the NH_3 ligand.[11] On the other hand, the ligand based of the [sq]/[q] redox couple plays the main role in the oxidative activation of $[\mathbf{1}]^+$ toward the oxidation of MeOH. The catalytic cycle of MeOH oxidation would be initiated by the dissociation of the amino proton of $[Ru^{II}(NH_3)(q)(trpy)]^{2+}$ followed by intramolecular electron transfer from the negatively charged NH_2^- to the $Ru^{II}(q)$ framework. Such an electron transfer generates radical character on the nitrogen atom.

The reactivity of the radical formed through the acid-base equilibrium of amino protons is largely dependent on the substituent on the nitrogen atom. The anilido radical complexes of both $[Ru^{II}(\cdot NPh\text{-}bpa)(Bu_2sq)]$ and $[Ru^{II}(\cdot NPh\text{-}bpa)(Bu_2cat)]^-$ were definitely identified by EPR and resonance Raman spectra. On the other hand, the amino radical complexes of neither $[Ru^{II}(\cdot NH_2)(sq)]^+$ nor $[Ru^{II}(\cdot NH_2)(q)]^{2+}$ were detected by spectroscopic measurements due to the high reactivity of the complexes. The distinct difference of the reactivity between the $Ru^{II}(\cdot NPh\text{-}bpa)$ and $Ru^{II}(\cdot NH_2)$ groups is ascribed to the large π-electron distribution over the NPh-bpa group of the former, and the large spin density of the nitrogen atom of the latter due to the localization on the nitrogen atom. The catalytic oxidation of MeOH, therefore, is explained by hydrogen abstraction from MeOH by the $Ru^{II}(NH_2)$ group.

Conclusions

The present study demonstrates that $[Ru^{II}(NH_3)(q)(trpy)]^+$ has an ability to oxidize alcohols catalytically under very mild conditions under electrolysis at +0.35 V in MeOH. The elucidation of the reaction mechanisms in the alcohol-oxidation is underway.

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