

Metal Complexes Aiming Conversion between Chemical and Electrical Energies

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Metal ions involved in various metal proteins play key roles to generate metabolic energies through oxidation of organic molecules. Metal complexes having an ability to oxidize organic molecules at potentials more negative than that of reduction of dioxygen, therefore, are feasible catalysts to convert chemical energy to electrical one when combined with dioxygen reduction. Aqua-Ru complexes can be converted to high valent Ru=O ones by sequential proton and electron loss, and some of the latter can oxidize organic molecules. However, the redox potentials to generate high valent Ru=O complexes are too positive to use as energy converters. We have succeeded smooth conversion from aqua to oxo ligands on Ru-dioxolene framework through proton coupled intramolecular electron transfer from the deprotonated form of Ru–OH species to dioxolene ligand. The aqua-oxo conversion using the unique redox behavior of Ru-dioxolene frameworks enabled to isolate unprecedented metal–oxo and –amino radical complexes. We are elucidating the reactivity of those complexes as electrocatalysts toward the oxidation of hydrocarbons.

1. Experimental and Theoretical Evaluation of the Charge Distribution over Ruthenium and Dioxolene Framework of [Ru(OAc)-(dioxolene)(terpy)] (terpy = 2,2':6',2''-terpyridine) Depending on Substituents¹⁾

Ru complexes [Ru(OAc)(dioxolene)(terpy)] having various substituents on the dioxolene ligand (dioxolene = 3,5-*t*-BuC₆H₂O₂ (**1**), 4-*t*-BuC₆H₃O₂ (**2**), 4-ClC₆H₃O₂ (**3**), 3,5-Cl₂C₆H₂O₂ (**4**), Cl₄C₆O₂ (**5**); terpy = 2,2':6',2''-terpyridine) were prepared. EPR spectra of these complexes in glassy frozen solutions (CH₂Cl₂:MeOH = 95:5, vol./vol.) at 20 K showed anisotropic signals with *g* tensor components 2.242 > *g*₁ > 2.104, 2.097 > *g*₂ > 2.042, and 1.951 > *g*₃ > 1.846. An anisotropic value, Δ*g* = *g*₁ – *g*₃, and an isotropic *g* value, <*g*> =

$[(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$, increase in the order **1** < **2** < **3** < **4** < **5**. The resonance between the Ru^{II}(sq) (sq = semiquinone) and Ru^{III}(cat) (cat = catecholato) frameworks shifts to the latter with an increase of the number of electron-withdrawing substituents on the dioxolene ligand. DFT calculations of **1**, **2**, **3**, and **5** also support the increase of the Ru spin density (Ru^{III} character) with an increase of the number of Cl atoms on the dioxolene ligand. The singly occupied MOs (SOMOs) of **1** and **5** are very similar to each other and stretch out the Ru–dioxolene frameworks, whereas the LUMO of **5** is localized on Ru and two O atoms of dioxolene in comparison with that of **1**. Electron-withdrawing groups decrease the energy levels of both the SOMO and LUMO. An increase in the number of Cl atoms in the dioxolene ligand results in an increase of the positive charge on Ru. Successive shifts in the electronic structure between the Ru^{II}(sq) and Ru^{III}(cat) frameworks caused by the variation of the substituents are compatible with the experimental data (Figure 1).

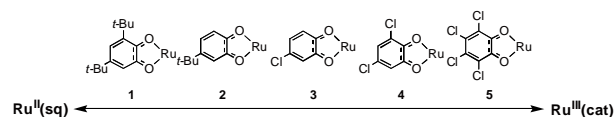


Figure 1. Charge distribution on the Ru–dioxolene framework depending on substituents.

2. Generation of Ru^{II}–Semiquinone–Anilino Radical through Deprotonation of Ru^{III}–Semiquinone–Anilido Complex²⁾

Aminyl radicals are thermodynamically unstable and have an ability to oxidize organic substrates through H-atom abstraction. Metal complexes bearing an aminyl radical may, therefore, have potential uses as new oxidation catalysts in organic synthesis. Actual electronic states of aminyl radical metal

complexes would lie somewhere between two limiting resonance structures such as the amido state $\{M^{(n+1)+}-NR_2\}$ and the aminyl radical $\{M^{n+}-\cdot NR_2\}$ and would usually be shifted toward the former. Recently, metal complexes having aminyl radicals were isolated by means of chemical and electrochemical oxidation of the corresponding metal amido complexes. On the other hand, a Ru^{II} -semiquinone-oxy radical complex, $[Ru^{II}(terpy)(Bu_2sq)(O^{\cdot-})]$ ($terpy = 2,2':6',2''$ -terpyridine, $Bu_2sq^- = 3,5$ -di-*tert*-butylsemi-quinonate), was isolated through deprotonation of $[Ru^{III}(terpy)(Bu_2sq)(OH)]^+$ under basic conditions without using any oxidants. Furthermore, the deprotonated species of $[Ru^{III}(terpy)(Bu_2sq)(NH_3)]^{2+}$ and $[Ru^{III}(NH_2-bpa)(Bu_2sq)]^{2+}$ ($NH_2-bpa =$ bis(2-pyridylmethyl)-2-aminoethylamine) were proved to oxidize alcohols to aldehydes or ketones with the generation of $[Ru^{II}(terpy)(Bu_2sq)(NH_3)]^+$ and $[Ru^{II}(NH_2-bpa)(Bu_2sq)]^+$, respectively. The most plausible active species for the oxidation of alcohols is a Ru^{II} -semiquinone-aminyl radical that is a limiting resonance structure of an Ru^{III} -semiquinone-amido complex. Although the Ru^{II} -semiquinone-aminyl radical intermediate was too labile to identify its existence in oxidation reactions, an analogous Ru^{III} -semiquinone-anilino radical complex that also would be formed from the corresponding Ru^{III} -semiquinone-aniline complexes may be stabilized due to the π -conjugated system of aniline group. We successfully isolated the Ru^{II} -semiquinone-anilino radical, $[Ru^{II}(\cdot NPh-bpa)(Bu_2sq)]-2H_2O$ (**2**), and its one-electron reduced species, *i.e.*, the Ru^{II} -catechol-anilino radical, $[Ru^{II}(\cdot NPh-bpa)(Bu_2cat)]^-$ (**3**), complexes bearing the 2-[Bis(2-pyridylmethyl)aminomethyl]-anilido ligand ($NPh-bpa^{2-}$). The anilino radical characters of **2** and **3** are proved by EPR spectroscopy, resonance Raman spectroscopy, and DFT calculations (Figure 2).

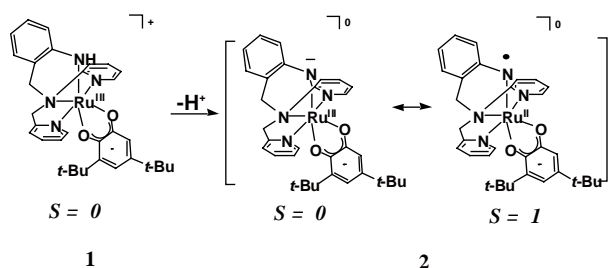
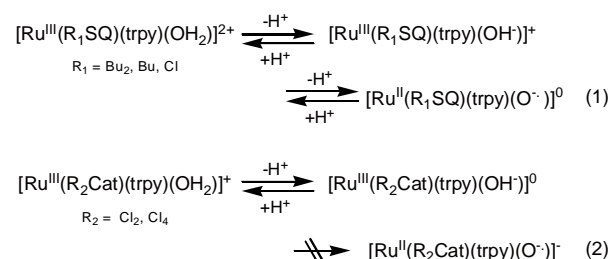


Figure 2. The formation of anilino radical complex.

3. Proton Coupled Electron Transfer Driven by the Acid-Base Equilibrium of Aqua-Ruthenium-Dioxolene Complexes

Ruthenium-dioxolene complexes with an aqua ligand, $[Ru^{III}(trpy)(R_1\text{-dioxolene})(OH_2)](ClO_4)_2$ ($R_1 = Bu_2$ (**6**)

(ClO_4)₂, Bu (**7**)(ClO_4)₂, Cl (**8**)(ClO_4)₂, and $[Ru^{III}(trpy)(R_2\text{-dioxolene})(OH_2)](BF_4)_2$ ($R_2 = Cl_2$ (**9**) and Cl_4 (**10**)) were prepared by the hydrolysis of the correspondent acetato complexes, $[Ru^{III}(trpy)(R_3\text{-dioxolene})(OAc)]$ ($R_3 = Bu_2$ (**1**), Bu (**2**), Cl (**3**), Cl_2 (**4**) and Cl_4 (**5**)). The EPR spectra of ruthenium-acetato complexes, suggest that the $Ru^{III}(SQ)$ framework is the principal contribution to the electronic structure of the complexes, **1–3**, whereas the $Ru^{III}(Cat)$ one became the main contribution to the complexes **4** and **5**. The electronic structures of the analogous aqua complexes are also largely influenced by the substituents of the dioxolene ligand. The dicationic complexes **6**(ClO_4)₂, **7**(ClO_4)₂, and **8**(ClO_4)₂ have the $Ru^{III}(SQ)$ frameworks. The acid-base reaction of the aqua ligand of **7**²⁺, whose redox potentials lied between those of **6**²⁺ and **8**²⁺, proceeds *via* two subsequent proton dissociations. The CVs of those complexes also indicate the formation of oxy radical complexes $[Ru^{II}(trpy)(SQ)(O^{\cdot-})]^0$, because addition of two equivs of BuOK to $[Ru^{III}(trpy)(SQ)(OH_2)]^{2+}$ resulted in shift of the rest potential of the solution to negative directions across the $Ru^{III}(SQ)/Ru^{II}(SQ)$ redox potential. On the other hand, the aqua complexes **9**⁺ and **10**⁺ that have mainly the $Ru^{III}(Cat)$ character due to more electron-withdrawing dioxolene ligands dissociate only one proton in the experimental conditions. The CV did not show the formation of the $Ru^{II}(Cat)$ core by an addition of large excess of BuOK to $[Ru^{III}(SQ)(trpy)(OH_2)]^{2+}$. It is, therefore, concluded that the conversion from $[Ru^{III}(SQ)(trpy)(OH^-)]^+$ to $[Ru^{II}(SQ)(trpy)(O^{\cdot-})]^0$ through $[Ru^{III}(SQ)(trpy)(O^{2-})]^0$ is achieved by the neutralization energy generated by treatment of the Ru-OH bond with BuOK, whereas it is not enough to convert from $[Ru^{III}(SQ)(trpy)(OH^-)]^+$ to $[Ru^{II}(Cat)(O^{\cdot-})]^0$ *via* $[Ru^{III}(SQ)(trpy)(O^{2-})]$ $[Ru^{III}(SQ)(trpy)(O^{2-})]^0$.



References

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- 2) Y. Miyazato, T. Wada, K. Tanaka, E. Fuhita and J. T. Muckerman, *Angew. Chem., Int. Ed.* **46**, 5728–5730 (2007).