

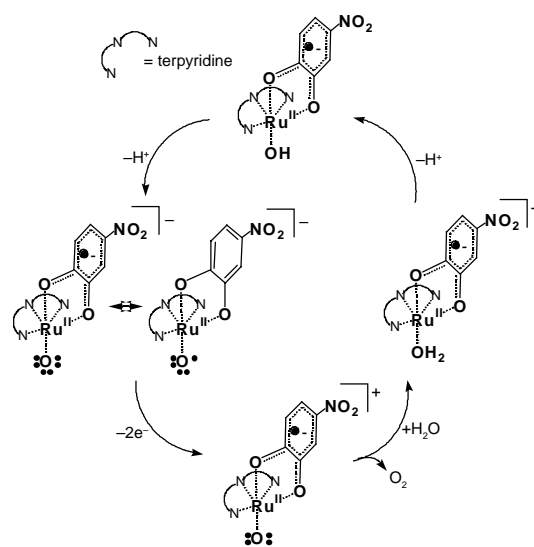
VIII-I Development of Metal-Cojugated Redox Systems in Metal-Dioxolene Complexes and Electrochemical Activation of Water Ligand

Dioxolenes function as a versatile electron-acceptor and electron-donor through the reversible two-electron redox reactions among the three oxidation states of catechol (Cat), semiquinone (SQ), and quinone (Q). A variety of metal-dioxolene complexes has appeared and the unique metal-conjugated electronic interaction has been extensively investigated. The ruthenium-terpyridine-dioxolene complexes exhibit the reversible two-electron redox behavior derived from a resonance hybrid between the metal center and the dioxolene ligand. In the ruthenium-dioxolene complex, its aqua ligand undergoes the electrochemical activation to generate a novel ruthenium-oxo bond. Fabrication of a water-soluble ruthenium-terpyridine complex having a strongly electron-withdrawing dioxolene is a particularly urgent target for the future applications as an electrochemical catalyst utilizing water molecules.

VIII-I-1 Synthesis of a Water-Soluble Ruthenium-Terpyridine-Dioxolene and the Electrochemical Activation of Water Molecules

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A ruthenium-terpyridine-dioxolene complex having a chloro ligand was synthesized using 4-nitrocatechol. The dioxolene complex, $[\text{Ru}^{\text{II}}\text{Cl}(\text{NO}_2\text{-SQ})(\text{terpy})]$ was transformed to a hydroxo complex, $[\text{Ru}^{\text{II}}(\text{OH})(\text{NO}_2\text{-SQ})(\text{terpy})]$ (**1**) by elimination of the chloro ligand with Ag^+ in acetone/water, where terpy and $\text{NO}_2\text{-SQ}$ are 2,2':6',2''-terpyridine and 4-nitrobenzosemiquinone, respectively. The hydroxo complex, **1** is soluble in water, unlike the chloro complex. The intense near-IR absorption band of **1** is ascribable to the $\text{Ru}(\text{II}) \rightarrow \text{NO}_2\text{-SQ}$ charge transfer. Both of the complexes show two-reversible redox waves of the cyclic voltammograms (CV) in the organic solvents. Based on the electrochemical measurement, the two-redox reactions correspond to $\text{Ru}(\text{II})\text{-NO}_2\text{-Cat} \leftrightarrow \text{Ru}(\text{II})\text{-NO}_2\text{-SQ} \leftrightarrow \text{Ru}(\text{III})\text{-NO}_2\text{-SQ}$ ($\text{Ru}(\text{II})\text{-NO}_2\text{-Q}$). The UV-Vis-near-IR absorption spectrum and CV of **1** are significantly changed depending on pH in water. In pH 12, a catalytic current is observed around 0.7 V vs. Ag/AgCl . When we suppose that oxygen molecules are evolved catalytically at the oxidation potential, an electrocatalytic cycle can be proposed, as shown in Scheme 1.



Scheme 1. The electrocatalytic cycle.