Redox Regulation Based on the pH-Dependent Hydrolysis of 2-Pyridinecarboxaldehyde Coordinated to Ruthenium(II)

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Aqueous redox processes often occur with the concomitant transfer of protons (acidic conditions) or hydroxide ions (basic conditions), resulting in pH-dependent redox potentials.[1] Transition-metal aqua complexes typically exhibit pH-dependent redox potentials stemming from the increased acidity of the aqua ligand accompanying oxidation of the metal center, as illustrated in eq 1 for the oxidation of $V^{II}(H_2O)_6^{2+}$.[2-4] Since subsequent oxidations are not subjected to systematically increasing electrostatic barriers (e.g., eq 2), multiple electron transfer and proton transfer reactions can occur within a relatively narrow potential range, and the overall pH dependence of the redox mechanism can be quite complex.[5] The number of pH-dependent redox

$$V^{II}(OH_2)_6^{2+} \xrightarrow{-e^-} V^{III}(OH)(OH_2)_5^{2+} + H^+ \quad (1)$$

$$V^{III}(OH)(OH_2)_5^{2+} \xrightarrow{-e^-} V^{IV}O(OH_2)_5^{2+} + H^+ \quad (2a)$$

$$V^{III}(OH)(OH_2)_5^{2+} \xrightarrow{-e^-} V^{IV}O(OH)(OH_2)_4^{+} + 2H^+ \quad (2b)$$

reactions can be reduced by limiting the inner coordination sphere to one aqua ligand; however, multiple redox reactions can still occur within a narrow potential range due to sequential deprotonations of the aqua ligand. For example, at pH 7 the monoaqua complex $[Ru(bpy)_2(py)(OH_2)]^{2+}$ (py is pyridine; bpy is 2,2'-bipyridine) exhibits two closely spaced one-electron couples at 0.42 and 0.53 V vs SCE, corresponding to the $Ru^{III/II}$ (eq 3) and $Ru^{IV/III}$ (eq 4) couples, respectively.[6]

$$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+} \xrightarrow{-e^-} [Ru^{III}(bpy)_2(py)(OH)]^{2+} + H^+ \quad (3)$$

$$[Ru^{III}(bpy)_2(py)(OH)]^{2+} \xrightarrow{-e^-} [Ru^{IV}(bpy)_2(py)(O)]^{2+} + H^+ \quad (4)$$

We are interested in designing transition-metal complexes that exhibit a *single pH-dependent one-electron couple over a relatively broad potential range.* In addition to serving as models for simple pH-dependent electron-transfer reactions, these complexes would permit one to "tune" an isolated one-electron redox couple via pH, which may be important with respect to the development of molecular switches[7] and molecular electronic devices.[8] Our approach is based on the design and synthesis of coordinatively saturated, substitutionally inert transition-metal complexes for which oxidation of the metal is coupled to a proton- or hydroxide-transfer reaction at a remote site on one of the coordinated ligands. By limiting the inner coordination sphere to one pH-dependent reaction and eliminating coordinated water molecules, we reasoned that it should be possible to obtain complexes that give a *single* pH-dependent couple over a broad potential range. Toward this end, we report here the pH-dependent electron-transfer reaction of $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ based on the reversible hydrolysis of 2-pyridinecarboxaldehyde (I) coordinated to ruthenium(II).

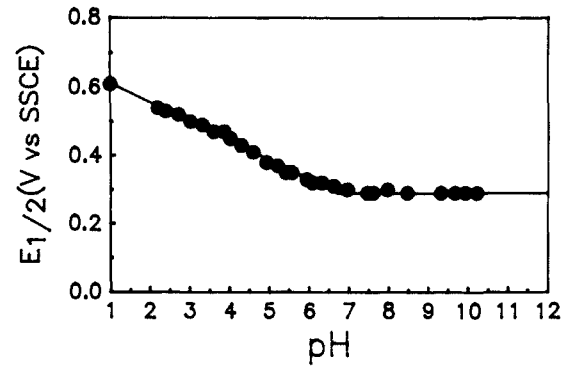
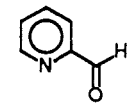
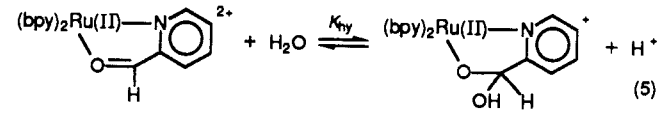


Figure 1. Pourbaix diagram showing $E_{1/2}$ for the $Ru^{III/II}$ couple of $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ as a function of pH. The $E_{1/2}$ potentials were measured by cyclic voltammetry ($E_{1/2} = (E_{p,c} + E_{p,a})/2$) in aqueous buffers at a glassy carbon electrode with a scan rate of 100 mV s^{-1}.



I: 2-CHOpy

The complex $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ was prepared in an inert atmosphere box[9] by heating 200 mg of $Ru(bpy)_2Cl_2 \cdot 2H_2O$[10] and a 5-fold excess of 2-pyridinecarboxaldehyde (Aldrich) in 40 mL of methanol for 3 h. Addition of excess NH_4PF_6(aqueous) and evaporation of methanol precipitated the complex, which was isolated by suction filtration and dried under vacuum (90% yield). The complex was characterized by elemental analysis, mass spectrometry, and ^1H NMR spectroscopy.[11] A ^1H NMR spectrum of the complex in 0.1 M D_2SO_4 showed the aldehyde proton resonance at 10.2 ppm; however, in 0.1 M NaOD, the aldehyde-proton resonance was not observed. The addition of D_2SO_4 regenerated the aldehyde-proton resonance, consistent with reversible hydration of the coordinated aldehyde as shown in eq 5. Ford has demonstrated a similar hydrolysis equilibrium for the analogous tetraamine complex $[Ru(NH_3)_4(2\text{-}CHOpy)]^{2+}$.[12]



(5)

The cyclic voltammogram of $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ in acetonitrile[13] showed an irreversible oxidation wave at approximately 1.3 V vs SSCE (saturated sodium calomel electrode). In water, however, the complex exhibited a single, reversible one-electron oxidation wave over a wide range of pH values.[14] No

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(9) Syntheses were carried out in an inert atmosphere box in order to avoid oxidation of 2-pyridinecarboxaldehyde to picolinic acid. When this reaction was carried out in nondegassed solvents, significant yields of $[Ru(bpy)_2(picolinate)]^{2+}$ were obtained.
(10) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(11) For $[Ru(bpy)_2(2\text{-}CHOpy)](PF_6)_2$: mass spectrum (FAB positive ionization) [M] = 521, [M + F] = 540; ^1H NMR (CD_3CN) δ 10.2 (s, CHO), 7.3-8.2 (m, Ar H). Anal. Calcd: C, 38.53; H, 2.61; N, 8.64. Found: C, 38.28; H, 2.70; N, 8.66.
(12) Alvarez, V. E.; Allen, R. J.; Matsubara, T.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 7686.
(13) Cyclic voltammograms were measured in 0.1 M $n\text{-}Bu_4NPF_6/CH_3CN$ at a platinum disk electrode or in aqueous buffers[14] at a glassy carbon electrode. In all cases, the scan rate was 100 mV s^{-1}.

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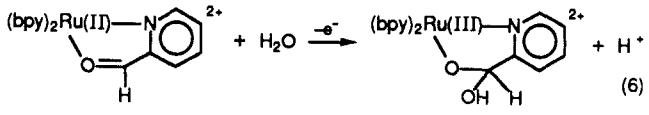
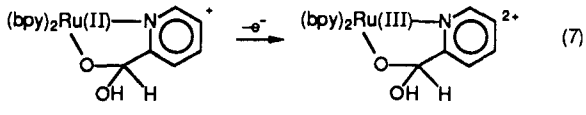
additional oxidations were observed out to the solvent window at the various pHs investigated. A plot of $E_{1/2}$ vs pH (i.e., a Pourbaix diagram)[3] for $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ is shown in Figure 1. The pH dependence observed for the $Ru^{III/II}$ couple in the acidic region of the Pourbaix diagram is due to the redox reaction shown in eq 6, where oxidation of Ru^{II} is coupled to hydrolysis of the coordinated aldehyde. The slope in the acidic region is -60 mV/pH unit, as expected from the Nernst equation.[1] The sta-



(6)

bilization of Ru^{III} associated with hydrolysis of the aldehyde ligand can be understood in terms of the lost back-bonding to Ru^{II} upon disruption of the aldehyde π^* system and the enhanced electron-donating ability of the resulting anionic oxygen. At more basic pHs, the Ru^{II} complex undergoes hydrolysis, and the oxidation reaction consists of a simple electron transfer (eq 7).



(7)

Therefore, no pH dependence is expected at higher pHs, in agreement with Figure 1. The pH at which the two linear portions of the Pourbaix diagram meet corresponds to the pH at which the concentrations of $[Ru^{II}(bpy)_2(2\text{-}CHOpy)]^{2+}$ and $[Ru^{II}(bpy)_2(2\text{-}CO(OH)Hpy)]^{+}$ are equal, and hence pH = pK_{hy} for eq 5. The data in Figure 1 yielded a pK_{hy} of 6.7 for the Ru^{II} complex.

The hydrolysis constant was also determined by following the electronic spectrum of $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ as a function of pH. At low pH, the lowest energy metal-to-ligand charge transfer (MLCT) band occurs at 430 nm (7.4×10^3 M^{-1} cm^{-1}), while at high pH, the MLCT band is shifted to 500 nm (7.7×10^3 M^{-1} cm^{-1}). At intermediate pHs both bands are observed, and the relative intensities reflect the relative concentrations of $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ and $[Ru(bpy)_2(2\text{-}CO(OH)Hpy)]^{+}$. Analysis of the pH-dependent spectral data by the method of Clarke and Ford[15] yielded a pK_{hy} value of 6.5, in good agreement with the value obtained from the Pourbaix diagram. The hydrolysis constant for $[Ru(NH_3)_4(2\text{-}CHOpy)]^{2+}$ was determined spectrophotometrically by Ford to be 11.8.[12] The decrease in K_{hy} of 5 orders of magnitude upon going from the tetraammine system to the bis(2,2'-bipyridine) system can be understood in terms of π-back-bonding. The aldehyde form of the ligand is stabilized in $[Ru(NH_3)_4(2\text{-}CHOpy)]^{2+}$ by π-back-bonding with Ru^{II}. When the ammine ligands are replaced by 2,2'-bipyridine ligands, 2-CHOpy must compete with the bpy ligands for the available $d\pi$ electron density on Ru^{II}. The combined effect of the decreased back-bonding to 2-CHOpy and the enhanced Lewis acidity of the Ru^{II} site is to increase the electrophilicity of the aldehyde carbon,[16] resulting in an increase in the hydrolysis constant. This result suggests that it may be possible to "tune" the hydrolysis constant (and hence the break point in the Pourbaix diagram) by regulating the π-acidity of the spectator ligands.

In summary, the reversible hydrolysis of 2-pyridinecarboxaldehyde coordinated to ruthenium(II) has been used to design a reversible pH-dependent one-electron redox couple such that only one electron-transfer reaction is observed over a relatively large potential region. In addition to providing a chemical means of tuning redox potentials, the coupling of a chemical reaction to an electron-transfer reaction in $[Ru(bpy)_2(2\text{-}CHOpy)]^{2+}$ illustrates the possibility of regulating chemical reactivity (in this case, carbon-oxygen bond formation) of an organic ligand by controlling the oxidation state of the coordinate metal.

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Oxidation Chemistry of d^0 Organometallic Complexes

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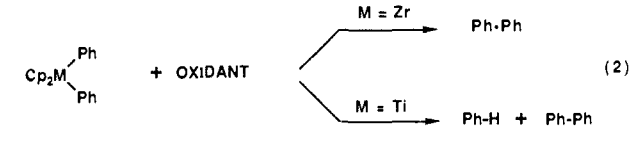
Electron-transfer processes can play an important role in organometallic chemistry.[1,2] Herein, we demonstrate that even d^0 organometallic complexes exhibit a rich redox chemistry and present electrochemical, kinetics, and stereochemical studies that establish a general outer-sphere oxidation process for d^0 group 4 metallocene complexes. This oxidation chemistry closely parallels the reported LMCT photochemistry of these complexes.[3]

Recent observations in our laboratory[4] and others[5,6] indicate that d^0 bis(cyclopentadienyl) dialkyl complexes of Ti and Zr react readily with one-electron oxidants to give products arising from either alkyl radical expulsion or formal reductive elimination. We have observed that the titanacyclobutanes[7] **1** react with one-electron oxidants such as tetrakis(trifluoromethyl)cyclopentadienone (TTFC), Ag^+, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), or $[Cp_2Fe]^+$ (Cp = η^5-cyclopentadienyl) in methylene chloride or acetonitrile, resulting in the quantitative production (by NMR) of the corresponding cyclopropanes (eq 1).[8] Di-

(1)

1a: R=t-Bu; R'=H
1b: R=CH_3; R'=CH_3
1c: R=i-Pr; R'=H



(2)

OXIDANT = TTFC, Ag^+, TCNQ, $[Cp_2Fe]^+$

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