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Contrasting effects of redox potentials on the rate constants of oxidation and hydrolysis reactions in ruthenium complexes

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We report in this work the rate constant of oxidation by peroxydisulfate of the ammine ruthenium center in $[(bpy)_2Ru(\mu-5-CNphen)Ru(NH_3)_5]^{4+}$ ($bpy = 2,2'$ -bipyridine and $5-CNphen = 5$ -cyano-1,10-phenanthroline) and the rate constant of hydrolysis of coordinated acetonitrile in $[Ru(TPTZ)(bpy)(CH_3CN)]^{2+}$ ($TPTZ = 2,4,6$ -tris(2-pyridil)-1,3,5-triazine). With these data and literature values of related reactions, we establish the existence of contrasting effects of redox potentials of $Ru^{3+/2+}$ couples on the rates of both processes.

Keywords: Linear free energy relationships; Redox reactions; Nitrile hydrolysis

1. Introduction

The metal redox potentials of coordination compounds are relevant parameters in the prediction of rates of various chemical processes. Thus, the determination of oxidation rate constants of metal centers is necessary for the construction of linear free energy relationships (LFERs) based on the Marcus equation; these expressions are particularly useful for predicting the velocity of intramolecular electron-transfer processes relevant to artificial photosynthesis [1]. Although hydrolysis of coordinated ligands occur by completely different reaction paths, LFER can also be used to predict the rate constants of hydrolysis of metal-coordinated nitrile groups, a subject of industrial and pharmaceutical relevance [2].

In this communication, we report for the first time the rate constant of oxidation of a dinuclear ruthenium complex, previously prepared in our laboratory [3], by potassium peroxydisulfate and the rate constant of basic hydrolysis of coordinated acetonitrile in a newly synthesized mononuclear ruthenium complex [4]. With these and previously reported data [1, 5], we attempt to elucidate the effect of redox potentials of $Ru^{3+/2+}$ couples on the rates of both processes.

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2. Results and discussion

$[(\text{bpy})_2\text{Ru}(\mu\text{-5-CNphen})\text{Ru}(\text{NH}_3)_5]^{4+}$, **1** (bpy = 2,2'-bipyridine; 5-CNphen = 5-cyano-1,10-phenanthroline), was prepared as a PF_6^- salt according to our previous work [3]. Its structure is shown schematically in figure 1.

The IR spectrum of this complex showed an intense band for $\nu(\text{C}\equiv\text{N})$ at 2182 cm^{-1} , a value significantly lower ($\Delta\nu = -40\text{ cm}^{-1}$) than that of the free ligand. This result could be attributed to the strong π -back-bonding effect of the pentaammineruthenium(II) group. Visible bands were detected (in CH_3CN solutions) at $\lambda_{\text{max}} = 500, 454,$ and 418 nm assigned to $d_\pi(\text{Ru}_a) \rightarrow \pi^*(5\text{-CNphen})$, $d_\pi(\text{Ru}_b) \rightarrow \pi^*(\text{bpy})$, and $d_\pi(\text{Ru}_b) \rightarrow \pi^*(5\text{-CNphen})$ metal-to-ligand charge transfer (MLCT) transitions, respectively, where $\text{Ru}_a = \text{Ru}$ bonded to NH_3 and $\text{Ru}_b = \text{Ru}$ bonded to bpy. Oxidation of **1** by Br_2 caused the disappearance of the band at 500 nm and generation of a new weak band at $\lambda_{\text{max}} = 664\text{ nm}$, which could be readily assigned to a metal-to-metal charge transfer (MMCT) transition, $\text{Ru}_b^{\text{II}} \rightarrow \text{Ru}_a^{\text{III}}$, which is typical in mixed-valent systems [6]. The electrochemical properties of **1** were studied by cyclic voltammetry (CV), in acetonitrile, with 0.1 mol L^{-1} tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Two reversible waves appeared, one at $E_{1/2} = 1.38\text{ V}$, assigned to the $\text{Ru}_b^{\text{III}}/\text{Ru}_b^{\text{II}}$ couple, and a second one at $E_{1/2} = 0.68\text{ V}$, corresponding to the $\text{Ru}_a^{\text{III}}/\text{Ru}_a^{\text{II}}$ couple. The crystal structure of **1** consisted of dinuclear $[(\text{bpy})_2\text{Ru}(\mu\text{-5-CNphen})\text{Ru}(\text{NH}_3)_5]^{4+}$ centers counterbalanced by four highly disordered PF_6^- anions. The bond involving Ru_a and the cyano nitrogen ($1.932(8)\text{ \AA}$) was shorter than the other metal–nitrogen coordination distances around Ru_a or Ru_b , due to strong π -back-bonding from Ru_a to nitrile [3].

The rate constants for oxidation of **1** by $\text{S}_2\text{O}_8^{2-}$ were measured at different complex concentrations, at 25°C , under pseudo-first order in aqueous solutions of $\text{pH} = 4.7$ (HAc/Ac^- buffer) and $I = 0.1\text{ mol L}^{-1}$ (controlled by adding enough KNO_3 to complete the buffer contributions). A UV/Visible Varian Cary-50 spectrophotometer connected to a “stopped-flow” accessory of Applied photophysics was used. Oxidation reactions

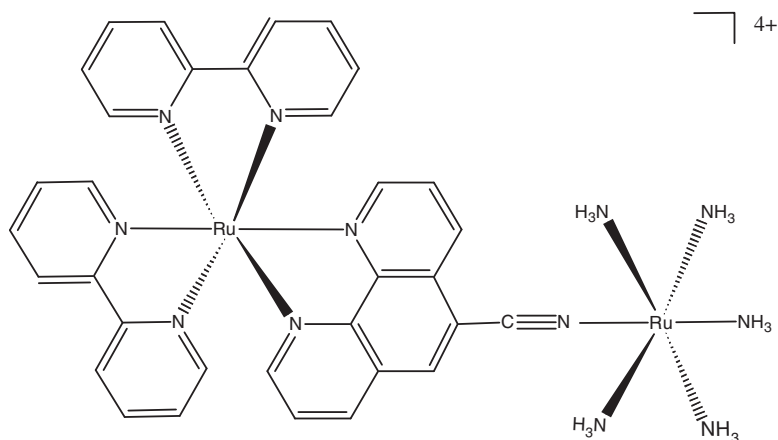
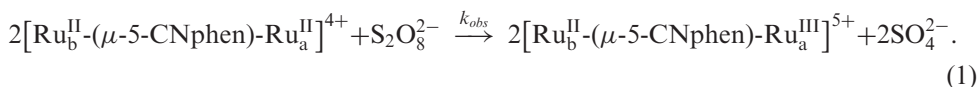


Figure 1. Structure of $[(\text{bpy})_2\text{Ru}(\mu\text{-5-CNphen})\text{Ru}(\text{NH}_3)_5]^{4+}$.

were monitored by measuring the decrease in absorbance of the $d_{\pi}(\text{Ru}_a) \rightarrow \pi^*(5\text{-CNphen})$ band at 500 nm.

Peroxydisulfate is a strong two-electron oxidant which can oxidize many organic and inorganic compounds; however, in many cases, the rate appears to be very slow [7], a fact that can be ascribed to the low potential for the $\text{S}_2\text{O}_8^{2-}/\text{S}_2\text{O}_8^{3-}$ couple. It is well known [1] that the reactions of the one-electron reduction product $\text{SO}_4 \cdot$ are very fast. The reaction of $\text{S}_2\text{O}_8^{2-}$ with a dinuclear complex such as **1** occurs in two, well-defined steps. The product of the first fast reaction (stopped-flow time scale) is the mixed-valent complex with oxidation at the pentaammine ruthenium center, according to the following equation:



In spite of the fact that $\text{S}_2\text{O}_8^{2-}$ is a two-electron reactant, no oxidation is observed at the Ru_b^{II} center in this step, because the redox potential at the Ru_a^{II} center is much lower than that at the Ru_b^{II} center (by 0.70 V, see above). The preferential attack on Ru_a^{II} may be anticipated both on thermodynamic and kinetic grounds.

The rate law for reaction (1) was $-\text{d}[\text{Ru}_b^{\text{II}}\text{-L-Ru}_a^{\text{II}}]/\text{d}t = k_{\text{obs}}[\text{Ru}_b^{\text{II}}\text{-L-Ru}_a^{\text{II}}]$. As in reference [1], we found a linear dependence of k_{obs} with $[\text{S}_2\text{O}_8^{2-}]$. The second order rate constant was $k_{\text{ox}} = (6.1 \pm 0.1) \times 10^3 (\text{mol L}^{-1})^{-1} \text{s}^{-1}$. Kinetic data are consistent with an outer-sphere electron-transfer process, similar to that occurring in oxidation of $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ (edta^{4-} = ethylenediaminetetraacetate) with $\text{S}_2\text{O}_8^{2-}$ [8].

Data of $\ln k_{\text{ox}}$ against $E_{1/2}(\text{Ru}_a^{3+/2+})$ for **1** and corresponding values obtained for similar complexes [1] were fitted to a straight line with a slope of -19 V^{-1} , a value close to that obtained before [1]. In our previous work, the plot covered *ca* 1.5 V in the correlation comprising the oxidation at both metal centers, with a range of rate values of 24 logarithmic units [1]. In table 1, we have collected the redox potentials and oxidation rate constants for **1** and related species; although the span of logarithmic units in rate constants in this particular case is only 4, it is representative of the general LFER predicted by Marcus. This relationship is illustrated in figure 2: increasing the redox potential of the $\text{Ru}_a^{3+/2+}$ couple causes the expected *decrease* in k_{ox} , since the magnitude of the thermodynamic driving force of the reaction is lowered. In electron-transfer reactions, free energy changes are directly proportional to redox potentials [9].

Although nitrile hydrolysis in ruthenium complexes occurs by a completely different mechanism than that of metal oxidations, we attempted to compare the effect of changing the $\text{Ru}^{3+/2+}$ redox potentials on the rates of hydrolysis of coordinated nitriles.

Table 1. $\text{Ru}_a^{3+/2+}$ redox potentials and rate constants for the oxidation of $[\text{Ru}_b^{\text{II}}\text{-L-Ru}_a^{\text{II}}]^{4+}$ with peroxydisulfate (L = trpy (= 2,2':6',2''-terpyridine); 4,4'-bpy (= 4,4'-bipyridine); pz (= pyrazine); 4-CNpy (= 4-cyanopyridine)).

Complex	$E_{1/2}(\text{Ru}_a^{3+/2+})$, V ^a	$\ln k_{\text{ox}}$	Ref.
$[(\text{trpy})(\text{bpy})\text{Ru}_b^{\text{II}}-(4,4'\text{-bpy})\text{-Ru}_a^{\text{III,II}}(\text{NH}_3)_5]^{4+/5+}$	0.40	11.8	[1]
$[(\text{trpy})(\text{bpy})\text{Ru}_b^{\text{II}}\text{-pz-Ru}_a^{\text{III,II}}(\text{NH}_3)_5]^{4+/5+}$	0.60	9.98	[1]
$[(\text{bpy})_2\text{Ru}_b^{\text{II}}-(5\text{-CNphen})\text{-Ru}_a^{\text{III,II}}(\text{NH}_3)_5]^{4+/5+}$	0.62	8.70	This work
$[(\text{trpy})(\text{bpy})\text{Ru}_b^{\text{II}}-(4\text{-CNpy})\text{-Ru}_a^{\text{III,II}}(\text{NH}_3)_5]^{4+/5+}$	0.64	8.10	[1]

^aIn H_2O , 0.1 mol L^{-1} KNO_3 , vs. NHE.

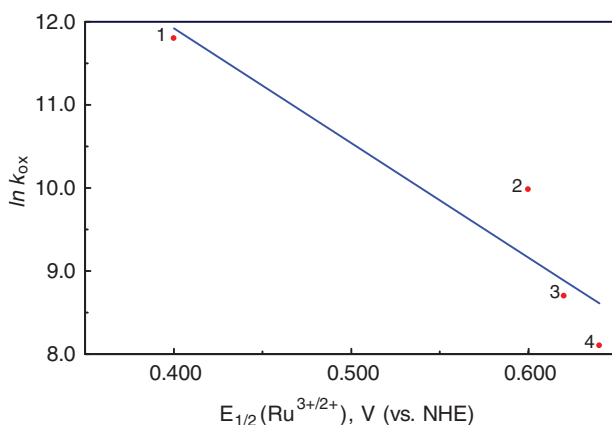


Figure 2. LFER obtained for the oxidation of ruthenium complexes by $\text{S}_2\text{O}_8^{2-}$. 1: $[(\text{trpy})(\text{bpy})\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{4+}$; 2: $[(\text{trpy})(\text{bpy})\text{Ru}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{4+}$; 3: $[(\text{bpy})_2\text{Ru}(5\text{-CNphen})\text{Ru}(\text{NH}_3)_5]^{4+}$; 4: $[(\text{trpy})(\text{bpy})\text{Ru}(4\text{-CNpy})\text{Ru}(\text{NH}_3)_5]^{4+}$.

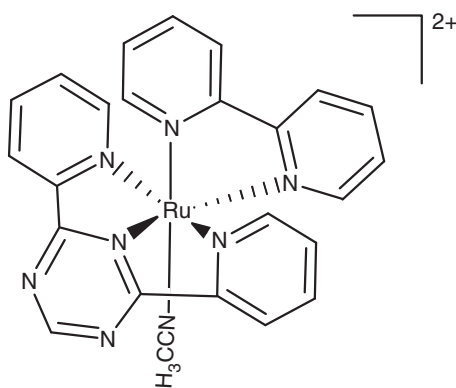


Figure 3. Structure of $[(\text{Ru}(\text{TPTZ})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}$.

For this purpose, the new complex $[(\text{Ru}(\text{TPTZ})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}$, **2** (TPTZ = 2,4,6-tris(2-pyridyl)-1,3,5-triazine), was synthesized as the PF_6^- salt, following procedures well known for similar complexes [5(b)]. Its structure is shown schematically in figure 3.

The rate constant of acetonitrile basic hydrolysis in **2** was determined at 25°C , $I=0.1 \text{ mol L}^{-1}$ and $\text{pH}=13.0$ (NaOH) using a UV/Visible Shimadzu UV-160 A spectrophotometer. We determined a value of $k_{\text{OH}} = (6.7 \pm 0.1) \times 10^{-3} (\text{mol L}^{-1})^{-1} \text{ s}^{-1}$. The spectroscopic changes can be associated to the hydrolysis of a bonded nitrile followed by a ligand substitution reaction, as confirmed by experimental evidence [5].

This mechanism is supported by the fact that amides are rapidly released from the coordination sphere of the metal center since they behave as poor π -acceptor ligands. The value of k_{OH} obtained in this work for **2** is several orders of magnitude higher than that expected for a simple substitution of CH_3CN and *ca* 1.5 times higher than that obtained for the related complex $[(\text{Ru}(\text{trpy})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}$ ($k_{\text{OH}} = 4.6 \times 10^{-3} (\text{mol L}^{-1})^{-1} \text{ s}^{-1}$)

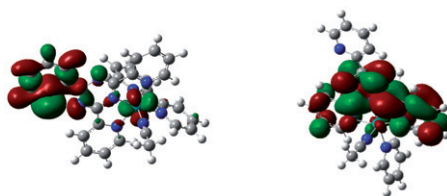


Figure 4. The LUMO (right) and HOMO (left) orbitals of $[(\text{Ru}(\text{TPTZ})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}]$ in the ground state.

[5a], an increase that can be ascribed to a higher π -backbonding effect from the metal to TPTZ as compared to trpy, making the Ru^{II} center more electropositive in **2**. These explanations can be reinforced by quantum mechanical calculations. We have performed geometry optimizations in the gas phase by using a DFT method in Gaussian'03 [10]. The molecules were optimized using Becke's three-parameter hybrid functional B3LYP, with the local term of Lee, Yang, and Parr. The basis set LanL2DZ was chosen for all atoms. As shown in figure 4, the highest occupied molecular orbital (HOMO) is mainly $\text{Ru}(\text{d}\pi)$ in character, with some ligand contributions, while the lowest unoccupied molecular orbital (LUMO) is mostly TPTZ (π^*) in character, in agreement with its spectroscopic and electrochemical properties [4]. In **2**, the value of the Mulliken charge is -0.056 for the nitrile C of coordinated CH_3CN , while in $[(\text{Ru}(\text{trpy})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}]$ this value for the same C is -0.14 ; therefore, the nitrile carbon in **2** is more susceptible to nucleophilic attack of OH^- than the same C in the related trpy complex. As a result, the hydrolysis rate constant is larger by a factor of 1.5. Mulliken charge values for the nitrile carbons of $[(\text{Ru}(\text{bpea})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}]$ and $[(\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}]$, with bpea = *N,N*-bis(2-pyridylmethyl)ethylamine) and tpm = tris(1-pyrazolyl) methane), are -0.064 and -0.063 , respectively; as expected, the hydrolysis rate constants of coordinated CH_3CN become lower in these complexes than that of **2** [5]. However, no defined correlation between the hydrolysis rate constants and Mulliken charges was found, maybe because these charges are very sensitive to steric effects induced by changing meridional coordination (in TPTZ and trpy) to a facial one (tpm and bpea). Instead, a good correlation has been found between these rate constants and $\text{Ru}^{3+}/\text{Ru}^{2+}$ redox potentials, as discussed below.

In this work, the activation parameters for nitrile hydrolysis in $[(\text{Ru}(\text{TPTZ})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}]$ were not determined, but they are expected to be very similar to other nitrile hydrolysis activation parameters already determined. For example, values of $\Delta H^* = (74 \pm 4) \text{ kJ mol}^{-1}$ and $\Delta S^* = (-42 \pm 12) \text{ J mol}^{-1} \text{ K}^{-1}$ have been obtained for base hydrolysis of coordinated acetonitrile in $[(\text{Ru}(\text{L})(\text{bpy})(\text{CH}_3\text{CN}))^{2+}]$, where L = trpy, tpm, and bpea [5], and they all indicate the operation of an associative process.

Figure 5 shows the relationship between the $\text{Ru}^{3+}/\text{Ru}^{2+}$ reduction potentials and the rate constant for the basic hydrolysis in **2** and similar data from the literature [5]. We could establish a correlation opposite to that shown in figure 2.

Increasing the redox potential of the $\text{Ru}^{3+}/\text{Ru}^{2+}$ couple causes an *increase* in the hydrolysis rate constant of coordinated acetonitrile. This effect can be explained on the basis of competition existing between polypyridines and CH_3CN for the π -electron density of the metal center. Thus, ligands that remove electron density from the Ru^{II} also reduce the electron density in the $\text{C}\equiv\text{N}$ bond of coordinated CH_3CN and therefore

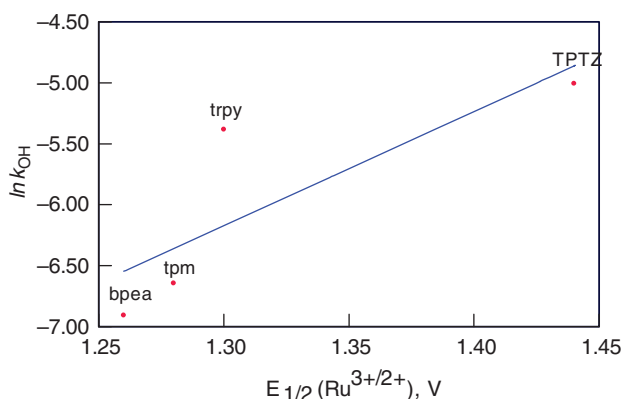


Figure 5. \ln of the rate constants of basic hydrolysis of coordinated CH_3CN in mononuclear complexes of the type $[\text{Ru}(\text{L})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ ($\text{L} = \text{bpea}, \text{tpm}, \text{trpy}, \text{and TPTZ}$) vs. redox potentials of the $\text{Ru}^{3+/2+}$ couple (vs. SCE).

make the carbon more susceptible for OH^- attack. The slope of figure 5 is *ca* 10 V^{-1} , evidencing high sensitivity to redox potential changes.

To summarize, increasing the metal redox potential can either inhibit or promote a process, depending on its mechanism. For example, when the $\text{Ru}^{3+/2+}$ redox potential increases, the oxidation of pentaammine ruthenium complexes is slowed (figure 2), while the basic hydrolysis of coordinated nitrile groups in polypyridinic ruthenium complexes is accelerated (figure 5). These contrasting effects emphasize the fact that modifying metal redox potentials along a series of compounds can lead to completely different LFERs for reactions of that series if the reactions under scrutiny are governed by different reaction mechanisms. Furthermore, we have proved here that calculation of simple Mulliken charges can help in explaining the sign changes in experimental LFER slopes in those cases where the main controlling factor in rate variations changes from the thermodynamic driving force (linearly related to the $E_{1/2}$ axes used in figure 2) to the electrostatic potential effects on the rates of hydrolysis of coordinated ligands (related to the $E_{1/2}$ axes used in figure 5).

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