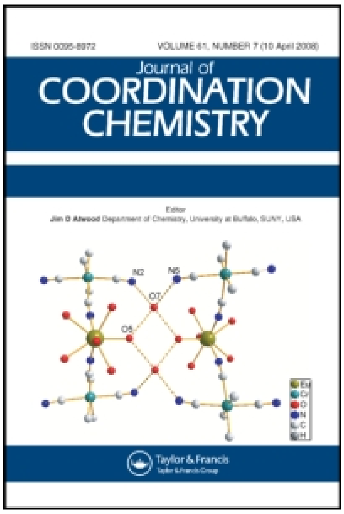

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Fagalde, Florencia , Mellace, María Gabriela , de Katz, Noemí D. Lis and Katz, Néstor E.(2004) 'Nitrile hydrolysis in a rhenium(I)-ruthenium(III) dinuclear complex', Journal of Coordination Chemistry, 57: 8, 635 — 639
To link to this Article: DOI: 10.1080/00958970410001689111
URL: http://dx.doi.org/10.1080/00958970410001689111

J. Coord. Chem., Vol. 57, No. 8, 20 May 2004, pp. 635–639

NITRILE HYDROLYSIS IN A RHENIUM(I)–RUTHENIUM(III) DINUCLEAR COMPLEX

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(Received 23 January 2003; Revised 6 October 2003; In final form 27 February 2004)

Kinetic data for the hydrolysis reaction: $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{4+} + H_2O \rightarrow [(CO)_3(bpy)Re^I(4\text{-}C(O)NHpy)Ru^{III}(NH_3)_5]^{3+} + H^+$ (bpy = 2,2′-bipyridine, 4-CNpy = 4-cyanopyridine and 4-C(O)NHpy = isonicotinamido), that occurs after oxidation with $S_2O_8^{2-}$ of the dinuclear species $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{II}(NH_3)_5]^{3+}$, have been obtained in aqueous solutions by spectrophotometric techniques. The observed rate constant, $k_h = (8.6 \pm 0.5) \times 10^{-3}\,s^{-1}$, at 25°C, pH = 3.0 ($CF_3COOH$) and $I = 0.1$ M (KCl), is *ca.* three times higher than the corresponding one for the mononuclear complex $[(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{3+}$, indicating that the catalytic effect of the $Ru^{III}(NH_3)_5$ moiety is enhanced by coordination of the free N of 4-CNpy to the $Re^I(CO)_3(bpy)$ moiety. The value of k_h is even higher than that of the dinuclear complex $[(trpy)(bpy)Ru^{II}(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{5+}$ (trpy = 2,2′:6′,2″-terpyridine), reflecting the fact that carbonyls are much stronger π-acceptors than polypyridines.

Keywords: Nitrile hydrolysis; Mixed-valent complexes; 4-cyanopyridine; Catalysis; Dinuclear complexes

INTRODUCTION

The hydrolysis of nitriles to amides catalyzed by transition metals is a subject of considerable interest [1,2]. For some coordinated nitriles, selective hydrolysis is possible, so catalytic hydrolytic systems can be designed. Since the pioneering work by Zanella and Ford [3], ruthenium-catalyzed nitrile hydrolysis reactions have been extensively investigated. Tfouni *et al.* [2] have reviewed the chemistry of Ru(II) and Ru(III) ammine complexes with coordinated nitriles.

Recently we studied [4] the preparation and characterization of a new dinuclear complex, of formula $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{II}(NH_3)_5]^{3+}$, (**I**), (with bpy = 2,2′-bipyridine and 4-CNpy = 4-cyanopyridine, coordinated to Ru through the nitrile N). The asymmetric mixed-valent species, $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{4+}$, (**II**),

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00958970410001689111

was obtained "*in situ*" by oxidation of (**I**) with *p*-fluorobenzene-diazonium hexafluorophosphate in CH_3CN. In order to extend our knowledge of the catalytic effect of remote metallic sites, we report in this work the hydrolysis reaction that occurs after formation of the mixed-valent complex (**II**) by oxidizing (**I**) with $S_2O_8^{2-}$ in aqueous solutions.

EXPERIMENTAL

Syntheses

The Br^- salt of (**I**) was obtained by dissolving 50 mg of the PF_6^- salt, prepared as in reference [4], in 2 mL of acetone and adding 1 g of $Bu^n{}_4NBr$, previously dissolved in 2 mL of acetone. The precipitate was collected by filtration, washed with cold acetone and dried *in vacuo* over P_4O_{10}. Yield: 67%. (Anal. Calcd. for $ReRuC_{19}H_{27}N_9O_3P_3F_{18}$: C, 19.8; H, 2.4; N, 10.9%. Found: C, 19.7; H, 2.7; N, 9.7%).

The mixed-valent complex (**II**) was obtained "*in situ*" by oxidation of (**I**) with $S_2O_8^{2-}$ in aqueous solutions.

The hydrolysis product, $[(CO)_3(bpy)Re^I(4\text{-}C(O)NHpy)Ru^{III}(NH_3)_5]^{3+}$, (**III**), (4-C(O)NHpy = isonicotinamido), was obtained as a PF_6^- salt by adding ten-fold excess of $K_2S_2O_8$ to (**I**), previously dissolved in 6 mL of 10^{-3} M CF_3COOH. After 30 min of reaction, NH_4PF_6 was added to precipitate the complex. The solid was filtered off, washed with water and dried *in vacuo* over P_4O_{10}. (Anal. Calcd. for $ReRuC_{19}H_{28}N_9O_4P_3F_{18} \cdot 9NH_4KS_2O_8$: C, 6.2; N, 7.3%. Found C, 6.2; N, 7.5%).

Materials, Instrumentation and Techniques

All chemicals were reagent grade and used as received. Double distilled water was used for all kinetic determinations. pH measurements were carried out with a precision of ±0.05 pH units, using a Mehtrom 744 pHmeter. UV-visible spectra were recorded with a Shimadzu UV-160A spectrophotometer, equipped with a thermostatted cell compartment. IR spectra were measured (as KBr pellets) using a double-beam Perkin-Elmer 983G spectrophotometer. Chemical analyses were done at INQUIMAE, University of Buenos Aires, Argentina.

The hydrolysis reactions were studied under *pseudo*-first-order conditions, at temperatures between 15 and 30°C, pH = 3 (CF_3COOH) and pH = 5 (buffer acetic acid/acetate) and $I = 0.1$ M (KCl). Absorbance (A) *vs.* time (t) data were recorded at $\lambda = 470$ nm. Duplicate or triplicate runs were made at each temperature and pH. Rate constants were obtained from least-squares fits of $\ln(A_t - A_\infty)$ *vs.* t, which were linear up to three half-lives. The errors in rate constants were estimated to be ±2–5%.

RESULTS AND DISCUSSION

In previous work [4], we demonstrated that 4-CNpy can act as a bridging ligand in the dinuclear species $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{II}(NH_3)_5]^{3+}$ (**I**), where the pyridine N (of 4-CNpy) is coordinated to a $Re^I(CO)_3(bpy)$ group and the nitrile N (of 4-CNpy) to a $Ru^{II}(NH_3)_5$ moiety. In aqueous solutions, $S_2O_8^{2-}$ rapidly oxidizes the ammine ruthenium, as studied previously [5–7]. In this work we have investigated the hydrolysis of the oxidized cyanopyridine complex $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{4+}$ (**II**) by conventional spectrophotometric techniques, to give $[(CO)_3(bpy)Re^I(4\text{-}C(O)NHpy)Ru^{III}(NH_3)_5]^{3+}$, (**III**), according to equation (1):

$$[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{4+} + H_2O \xrightarrow{k_h} [(CO)_3(bpy)Re^I(4\text{-}C(O)NHpy)Ru^{III}(NH_3)_5]^{3+} + H^+. \tag{1}$$

The identity of the product is confirmed by comparing the IR spectra of the PF_6^- salts of (**I**) and (**III**). The nitrile stretching band, which appears at 2177 cm^{-1} in (**I**), disappears completely in (**III**), while the ammonia symmetric deformation frequency, $\delta_{sym}(NH_3)$, shifts from 1282 cm^{-1} in (**I**) to 1312 cm^{-1} in (**III**), a clear indication of the oxidation state for the ammine Ru(III) center [4]. A new and intense band appears at 1405 cm^{-1}, which can be assigned to stretching vibrations of an amide (–C(O)NH–) group.

Figure 1 shows the consecutive spectra obtained at $pH = 3.0$ (CF_3COOH), $I = 0.1$ M (KCl) and 25°C upon mixing aqueous solutions of (**I**) ($C = 1.1 \times 10^{-4}$ M) and $S_2O_8^{2-}$ ($C = 1.1 \times 10^{-3}$ M). During a time scale of 30 min, the oxidized cyanopyridine complex (**II**), with a shoulder at λ *ca.* 470 nm (deconvoluted band maximum of the metal-to-metal charge transfer (MMCT) transition Re(I) → Ru(III)) [4], evolved exponentially into that of amido complex (**III**) (shoulder at λ *ca.* 440 nm); an isosbestic point at 425 nm being obtained. The spectrum of the final product is coincident with that obtained when dissolving the solid salt (**III**) in CF_3COOH (10^{-3}M).

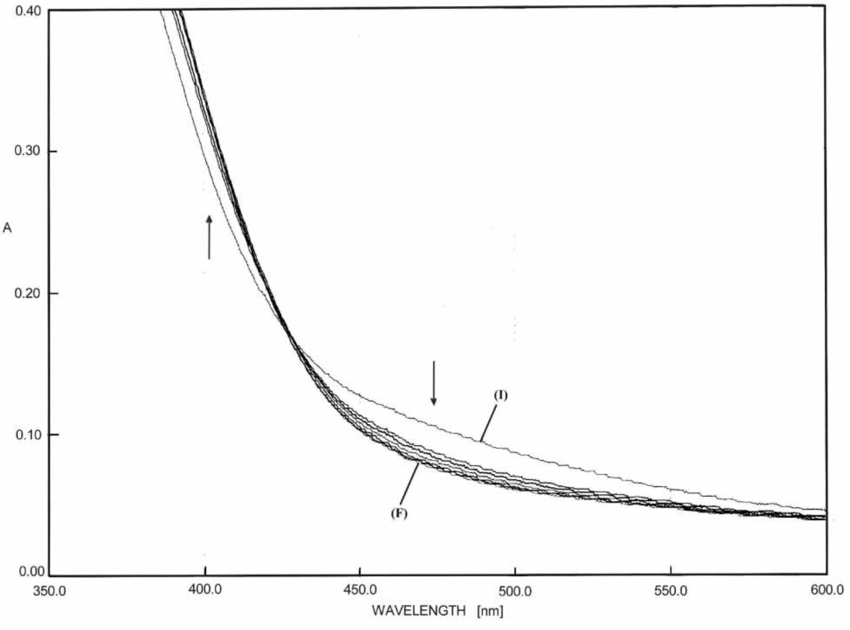

FIGURE 1 Visible spectra of $[(bpy)(CO)_3Re^I(4\text{-}CNpy)Ru^{II}(NH_3)_5]^{3+}$ and $S_2O_8^{2-}$ in water at $[Ru(II)] = 1.1 \times 10^{-4}$ M, $I = 0.1$ M and $T = 25$°C. Reactions time were: 0, 90, 150, 300, 600, 900 and 1500 s from the initial (**I**) to the final (**F**) spectra.

The MMCT (or intervalence) band of **(II)** (detected at a similar wavelength in CH_3CN solution [4]) is shifted to higher energy in **(III)**, as expected from the difference in redox potentials [8], but is masked by the long tail of the metal-to-ligand charge transfer (MLCT) band corresponding to a $d_\pi(Re) \rightarrow \pi^*(bpy)$ transition.

By fixing the measuring wavelength at 470 nm, k_h values have been determined under *pseudo*-first-order conditions: $[complex] = 1.3 \times 10^{-4}\,M$ and $[S_2O_8^{2-}] = 1.3 \times 10^{-3}\,M$. A value of $k_h = (8.6 \pm 0.5) \times 10^{-3}\,s^{-1}$ was obtained at 25°C, pH = 3.0 (CF_3COOH) and $I = 0.1\,M$ (KCl), which can be compared with other metal-catalysed hydrolysis rate constants, as shown in Table I. A similar value was obtained at pH = 5, so we conclude that the nitrile hydrolysis rate constants are pH-independent.

The value obtained for the complex studied in this work is *ca.* three times *higher* than the corresponding one for the mononuclear complex $[(4\text{-CNpy})Ru^{III}(NH_3)_5]^{3+}$ [8], indicating that the catalytic effect of a $Ru^{III}(NH_3)_5$ moiety is enhanced by coordination of the pyridine N of 4-CNpy to a $Re^I(CO)_3(bpy)$ moiety, probably due to an inductive effect. Moreover, the value of k_h is 1.5 times *higher* than that of the complex $[(trpy)(bpy)Ru^{II}(4\text{-CNpy})Ru^{III}(NH_3)_5]^{5+}$ (trpy = 2,2′:6′,2″-terpyridine) [5], in spite of lower charge, evidence that π-backbonding of the $Re^I(CO)_3(bpy)$ group to 4-CNpy is less than that of the $Ru^{II}(trpy)(bpy)$ group to 4-CNpy, a fact which can be explained on the basis that carbonyls are much stronger π-acceptors than polypyridines. However, the measured value of k_h of $[(bpy)(CO)_3Re^I(4\text{-CNpy})Ru^{III}(NH_3)_5]^{4+}$ is still *lower* (*ca.* 30 times) than that of $[(NH_3)_5Ru^{III}(4\text{-NCpy})Ru^{III}(NH_3)_5]^{6+}$ [6], as expected from differences in charge and π-backbonding effects.

Table II shows the value of k_h at different temperatures. From Eyring's rate equation [9], values of $\Delta H^{\#} = 39 \pm 3\,kJ\,mol^{-1}$ and $\Delta S^{\#} = -95 \pm 14\,J\,mol^{-1}\,K^{-1}$ have been determined, which are consistent with activation parameters obtained for similar nitrile hydrolysis reactions and indicate an associative mechanism.

We conclude that the $Re^I(CO)_3(bpy)$ group enhances the catalytic effect of $Ru(NH_3)_5^{3+}$ on the hydrolysis of coordinated 4-CNpy by a factor of three. The measured rate constant at acidic conditions is even higher than that of the $Ru^{II}(trpy)(bpy)$ group, due to the fact that carbonyls are much better π-acceptors than polypyridines.

TABLE I Hydrolysis rate constants for coordinated nitriles in some ruthenium complexes

Complex	k_h, s^{-1}	*Ref.*
$[(NH_3)_5Ru(4\text{-NCpy})]^{3+}$	2.9×10^{-3}	8
$[(trpy)(bpy)Ru^{II}(4\text{-NCpy})Ru^{III}(NH_3)_5]^{5+}$	5.8×10^{-3}	5
$[(bpy)(CO)_3Re^I(4\text{-CNpy})Ru^{III}(NH_3)_5]^{4+}$	8.6×10^{-3}	This work
$[(NH_3)_5Ru^{III}(4\text{-NCpy})Ru^{III}(NH_3)_5]^{6+}$	25.0×10^{-2}	6

TABLE II Hydrolysis rate constants for $[(bpy)(CO)_3Re^I(4\text{-CNpy})Ru^{III}(NH_3)_5]^{4+}$ at different temperatures

T, K	k_h, s^{-1}
288.2	$(4.6 \pm 0.2) \times 10^{-3}$
293.2	$(6.2 \pm 0.5) \times 10^{-3}$
298.2	$(8.6 \pm 0.5) \times 10^{-3}$
303.2	$(1.1 \pm 0.3) \times 10^{-2}$

Acknowledgments

We thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina), Consejo de Investigaciones de la Universidad Nacional de Tucumán (CIUNT, Argentina), Agencia Nacional de Promoción Científica y Técnica (ANPCyT, Argentina) and Fundación Antorchas for financial help. M.G.M. thanks CONICET for a graduate fellowship. F.F. and N.E.K are Members of the Research Career (CONICET).

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