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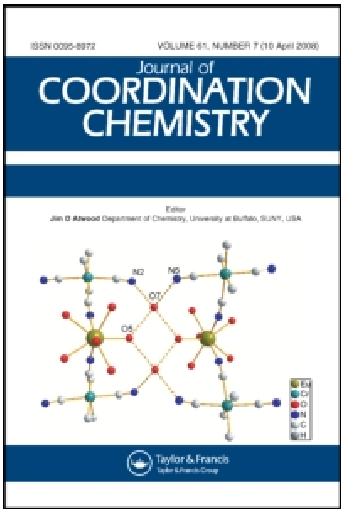

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BENZONITRILE HYDROLYSIS CATALYZED BY A RUTHENIUM(II) COMPLEX

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The rate constant for the basic hydrolysis of benzonitrile (PhCN) to benzamide ($PhCONH_2$) in the [Ru^{II}(tpy)(bpy)] moiety (tpy = 2,2′ : 6′,2″-terpyridine, bpy = 2,2′-bipyridine) ($k_{OH} = 3.7 \times 10^{-2}$ $M^{-1}s^{-1}$) is 5×10^3 times higher than that of the free ligand and two times higher than that corresponding to the analogous acetonitrile complex. This effect is unusual for a transition metal in the (II) oxidation state, and can be attributed to the π-electron acceptor properties of *both* the polypyridyl ligands and the phenyl group. Since amides, being poor π-acceptor ligands, are rapidly released from the coordination sphere of ruthenium(II), the final product of this process is the $[Ru(tpy)(bpy)(OH)]^+$ complex. The activation parameters for this nitrile hydrolysis have been determined and compare reasonably well with other values for similar reactions.

Keywords: Base hydrolysis; Benzonitrile complexes; Catalysis; Ruthenium(II)

INTRODUCTION

The conversion of nitriles to amides catalyzed by transition metals is a subject of biological and industrial interest [1,2]. While searching for new catalytic systems for this reaction, we have found [3] that the Ru^{II}(tpy)(bpy) moiety (with tpy = 2,2′ : 6′,2″-terpyridine and bpy = 2,2′-bipyridine, see Scheme I) can accelerate the hydrolysis of acetonitrile to acetamide in basic solutions by a factor of *ca* 3×10^3. This effect can be ascribed to π backbonding from the metal to the polypyridyl ligands, which makes the Ru center in Ru^{II}(tpy)(bpy) more electropositive than the Ru center in

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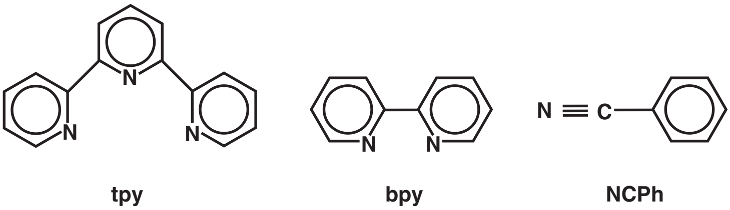


SCHEME I

the $Ru^{II}(NH_3)_5$ moiety. In this work, we have studied the hydrolysis of benzonitrile (PhCN, Scheme I) to benzamide ($PhCONH_2$) in the [Ru(tpy)(bpy)(PhCN)]$^{2+}$ complex, in order to extend our knowledge of the catalytic effect of ruthenium(II)-polypyridyls, a remarkable effect for a transition metal in the (II) oxidation state.

EXPERIMENTAL

Syntheses

The complex [Ru(tpy)(bpy)(NCPh)]$(PF_6)_2$ was prepared as described previously [4–5]. The Br^- salt of the ion [Ru(tpy)(bpy)(NCPh)]$^{2+}$ was obtained by dissolving 50 mg of the PF_6^- salt in 2 cm^3 of acetone and adding 1 g of Bu_4^nNBr previously dissolved in 2 cm^3 of acetone. The precipitate was collected by filtration, washed with cold acetone and dried *in vacuo* over P_4O_{10}. Yield: 30 mg (67%).

Materials, Instrumentation and Techniques

All chemicals were of reagent grade and used as received. Triply distilled water was used for all kinetic determinations; pH measurements were carried out with a precision of ± 0.05 pH units, using a Luftman-Reliance II pH meter. Electronic spectra were run on a Shimadzu UV-160A spectrophotometer equipped with a thermostatted cell compartment.

Stock solutions of NaOH were prepared at the desired total concentrations. A fresh solution of [Ru(tpy)(bpy)(NCPh)](Br_2) in water was used for each set of experiments. The ionic strength was fixed at $I = 0.1$ M (controlled with CF_3SO_3Na). Absorbance vs. time data were recorded at $\lambda = 449$ nm (maximum of the spectrum of [Ru(tpy)(bpy)(NCPh)]$^{2+}$) [5]. Duplicate or triplicate runs were made at each value of pH and temperature.

The *pseudo*-first-order rate constants were determined by least-squares fits of ln $(A_t - A_\infty)$ vs. time, which were linear for more than three half-lives. The estimated error in the base hydrolysis rate constants k_{OH} is $\pm 5\%$.

RESULTS AND DISCUSSION

Figure 1 shows the consecutive spectra obtained at pH = 13.0, $I = 0.1$ M and $T = 25°C$ of an aqueous solution of $[Ru(tpy)(bpy)(NCPh)]^{2+}$ ($C = 1.1 \times 10^{-4}$ M). The lowest-energy metal-to-ligand charge transfer (MLCT) absorption band of this complex at $\lambda = 449$ nm is shifted to higher wavelengths, reaching a value of $\lambda = 495$ nm after 30 min. Isobestic points are observed at 465 and 380 nm. This change is indicative of a hydrolysis process followed by a ligand substitution reaction.

In effect, the maximum of the final product is coincident with that of the ion $[Ru(tpy)(bpy)(OH)]^{+}$. As shown in Fig. 2, when one drop of concen-

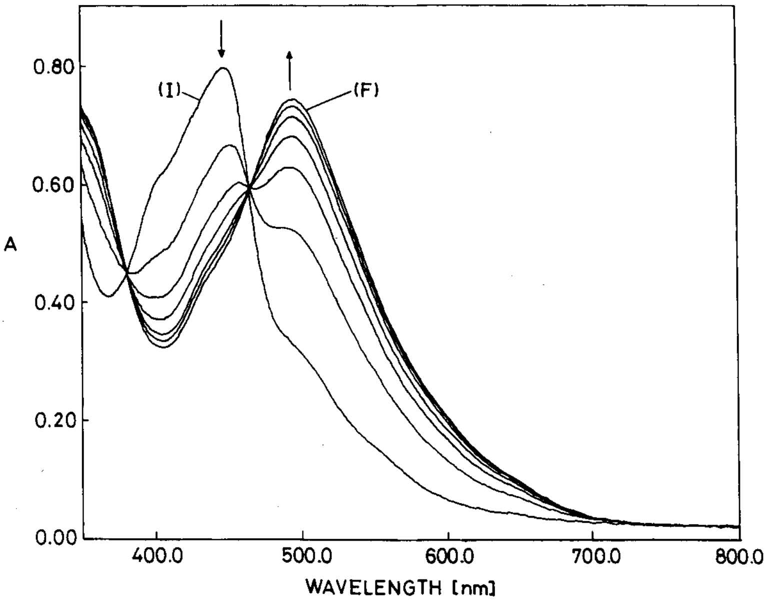
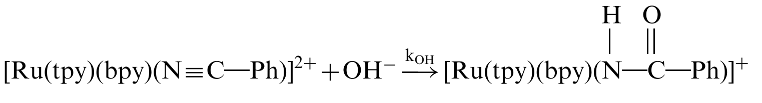


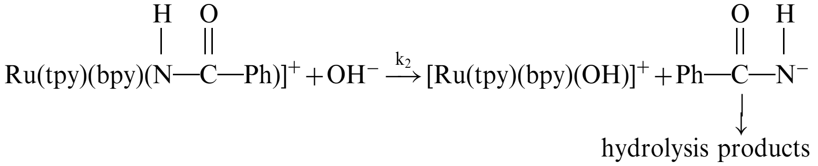
FIGURE 1 Electronic spectra obtained in water at [NaOH] = 0.1 M, [Ru(II)] = 1×10^{-4} M, $I = 0.1$ M and $T = 25°C$. Reaction times were: 0, 2, 4, 5, 7, 10 and 18 min from the initial (**I**) to the final (**F**) spectra.

trated HCl was added to this complex, a band at $\lambda_{max} = 476$ nm developed, a value identical to that expected for the complex $[\mathrm{Ru(tpy)(bpy)(OH_2)}]^{2+}$ [6].

According to the observed changes, the following mechanism can be proposed:



$$[\mathrm{Ru(tpy)(bpy)(N{\equiv}C{-}Ph)}]^{2+} + \mathrm{OH}^- \xrightarrow{k_{OH}} [\mathrm{Ru(tpy)(bpy)(\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}Ph)}]^{+} \quad (1)$$



$$\mathrm{Ru(tpy)(bpy)(\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}Ph)}]^{+} + \mathrm{OH}^- \xrightarrow{k_2} [\mathrm{Ru(tpy)(bpy)(OH)}]^{+} + \mathrm{Ph{-}\underset{\underset{\text{hydrolysis products}}{\downarrow}}{\overset{\overset{O}{\|}}{C}}{-}\overset{\overset{H}{|}}{N}^-} \quad [2]$$

The rate constants for substitution of π-acceptor ligands (such as nitriles) are lower (in various orders of magnitude) than those corresponding to the basic hydrolysis processes, k_{OH} [3]. On the other hand, poor π-acceptors such as deprotonated amides are rapidly released from the coordination

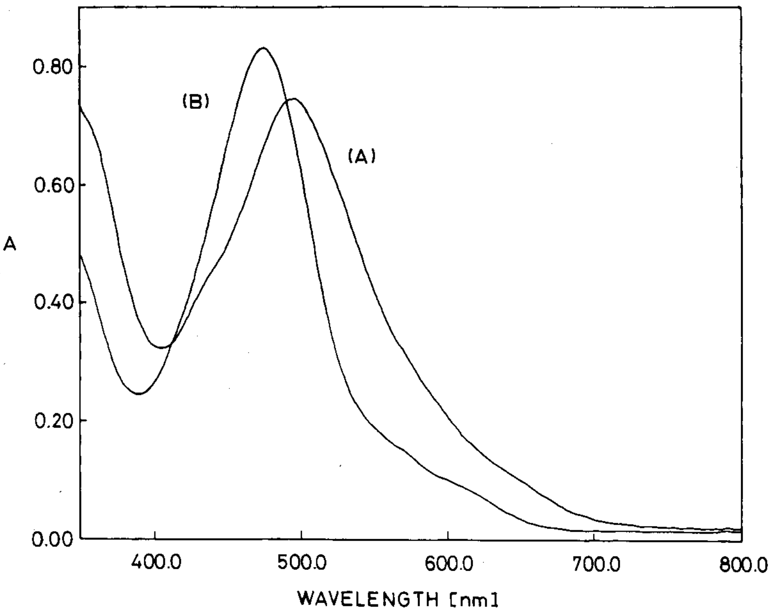


FIGURE 2 Electronic spectra of the hydrolyzed products of the complex [Ru(tpy)(bpy)(NCPh)]$^{2+}$ at pH = 13 (**A**) and at pH = 0 (**B**). [Ru(II)] = 1×10^{-4} M.

sphere of ruthenium(II), i.e., $k_2 \gg k_{OH}$. The rate determining step is thus (1), the nucleophilic attack of an hydroxide ion at a nitrile group.

As shown in Fig. 3 the observed *pseudo*-first-order rate constants k_{obs} for the hydrolysis process vary linearly with $[OH^-]$. From the rate law $k_{obs} = k_{OH}[OH^-]$, a value of $k_{OH} = (3.7 \pm 0.4) \times 10^{-2}\,M^{-1}s^{-1}$ was calculated, which is 5×10^3 times higher than that of the free ligand, as shown in Table I.

This catalytic effect is almost two times higher than that corresponding to the hydrolysis of acetonitrile (coordinated to the Ru^{II}(tpy)(bpy) moiety)

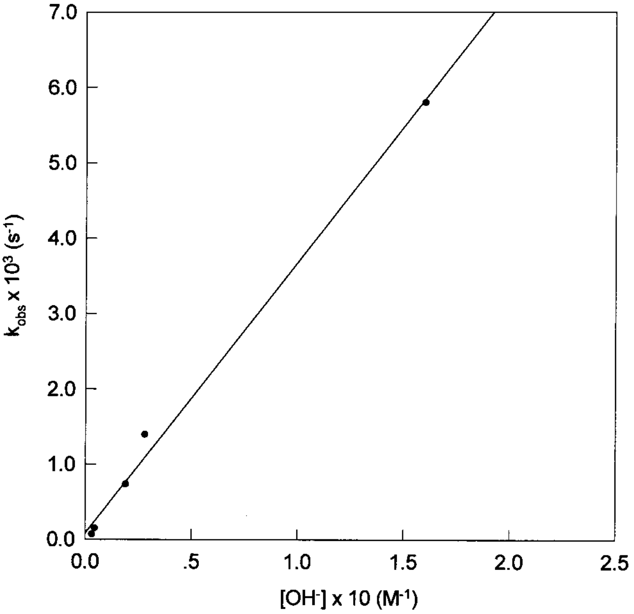


FIGURE 3 Observed rate constants k_{obs} vs. $[OH^-]$ for the hydrolysis of PhCN coordinated to Ru^{II}(tpy)(bpy) at 25°C, $I = 0.1$ M, $[Ru(II)] = 1 \times 10^{-4}$ M.

TABLE I Rate constants for the basic hydrolyses of free and coordinated nitriles

Nitrile	k_{OH}, $M^{-1}s^{-1}$	*Reference*
MeCN	1.60×10^{-6}	7
$[(NH_3)_5Ru(NCMe)]^{2+}$	$< 6 \times 10^{-5}$	7
$[(tpy)(bpy)Ru(NCMe)]^{2+}$	4.6×10^{-3}	3
$[(NH_3)_5Ru(NCMe)]^{3+}$	2.2×10^{2}	7
PhCN	7.2×10^{-6}	7
$[(NH_3)_5Ru(NCPh)]^{2+}$	$< 10^{-5}$	7
$[(tpy)(bpy)Ru(NCPh)]^{2+}$	3.7×10^{-2}	This work
$[(NH_3)_5Ru(NCPh)]^{3+}$	2.0×10^{3}	7

to acetamide, the rate constant being almost an order of magnitude higher. These enhancements can be accounted for by considering the π-electron acceptor properties of *both* the polypyridyl ligands and the benzyl group. The π-backbonding effect from Ru(II) to bpy and tpy causes an increase of the susceptibility of the nitrile C to nucleophilic attack by an hydroxide ion, when compared to the free ligand. On the other hand, the higher π-accepting properties of benzonitrile as compared to acetonitrile also causes an increase in the catalytic effect on the hydrolysis of the nitrile group. Furthermore, the relation between the rate constant of the free ligands [k_{OH}(PhCN)/k_{OH}(MeCN) = 4.5] is half the value for the corresponding complexes [k_{OH}(Ru(tpy)(bpy)(PhCN))$^{2+}$/k_{OH}(Ru(tpy)(bpy)(MeCN))]$^{2+}$ = 8.0], pointing to the conclusion that reinforcement of the electron-accepting properties of the phenyl group enhances the catalytic effect in coordinated benzonitrile.

The variation of ln(k_{OH}/T) with (1/T) is displayed in Fig. 4. From Eyring's rate equation [8], values of $\Delta H^{\#} = (65 \pm 3)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\#} = (-49 \pm 14)\,\mathrm{J\,mol^{-1}\,K^{-1}}$ are determined, which compare reasonably well with the activation parameters for other nitrile hydrolysis reactions. For example, values of $\Delta H^{\#} = 74\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\#} = -42\,\mathrm{J\,mol^{-1}K^{-1}}$ have

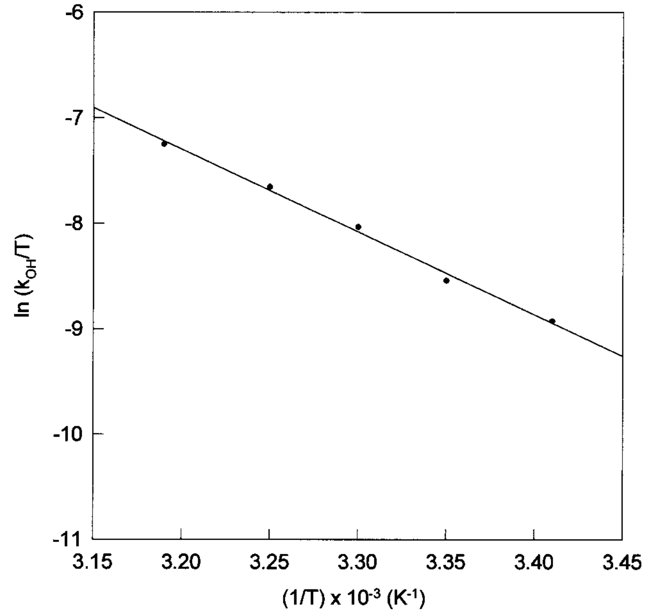


FIGURE 4 Eyring plot for the basic hydrolysis of PhCN coordinated to Ru^{II}(tpy)(bpy).

been obtained for the hydrolysis of acetonitrile in $[Ru(tpy)(bpy)(MeCN)]^{2+}$ [3]. These values are indicative of an associative process.

The $Ru^{II}(tpy)(bpy)$ group exhibits a catalytic action lower than that of the $Ru(NH_3)_5^{3+}$ group but higher than that of the $Ru(NH_3)_5^{2+}$ moiety. This effect is unusual for a transition metal in the (II) oxidation state. If compared to the analogous complex of MeCN, the catalytic effect is two times higher, which can be attributed to the π-electron withdrawing-properties of both the polypyridyl and the benzyl group. Work in progress will address the extent of the catalytic action of the $Ru(tpy)(bpy)^{2+}$ and similar moieties on the hydrolysis rate of other nitrile derivatives.

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