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Base Hydrolysis of Coordinated Organonitriles. Reactions of Ruthenium(III) and Rhodium(III) Complexes

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Specific rates of base hydrolysis of the pentaammineruthenium(III) complexes of acetonitrile (2.2×10^2 M^{-1} sec^{-1}) and of benzonitrile (2.0×10^3 M^{-1} sec^{-1}), $Ru(NH_3)_5(NCR)^{3+}$ (R = CH_3 or C_6H_5), are shown to be approximately 10^8 times faster than the free ligand under the same conditions and about 10^2 times faster than the analogous cobalt(III) complexes. Reaction products are the corresponding amido complexes which reversibly protonate in acidic solution to give the amide complexes. Base hydrolysis of the pentaamminerhodium(III) complex of acetonitrile (1.0 M^{-1} sec^{-1}) occurs at a rate comparable to that of the cobalt(III) complex, while the ruthenium(II) complex is at least 10^6 times less reactive than the corresponding ruthenium(III) complex. In bicarbonate–carbonate buffer solutions the reactions of the Ru(III) complexes display general base catalysis, a result which suggests that in aqueous solution the coordinated nitriles are subject to attack by nucleophiles other than hydroxide ion.

Past efforts in these laboratories have been concerned with interpretation of ligand–metal interactions between organic ligands and metal–ammine complexes of the second transition row.[2-7] Particular emphasis has been directed toward comparisons of ligand properties and reactions between different organonitrile complexes of the type $M(NH_3)_5(RCN)^{n+}$, where M = Ru(II), Ru(III), or Rh(III) and RCN is an organonitrile such as acetonitrile or benzonitrile. In the course of these studies, it was observed[2] that ruthenium(III) complexes of benzonitrile and other substituted aromatic nitriles underwent reactions to unidentified Ru(III) products in hot water unless the solution was acidic, and speculation centered on the possible hydrolysis (hydration) of the coordinated nitrile function. In the context of some recent interest[8-10] in the hydrolysis reactions of coordinated nitriles, we decided to examine this reaction in greater detail for the acetonitrile and benzonitrile complexees of ruthenium(III), $Ru(NH_3)_5(CH_3CN)^{3+}$ and $Ru(NH_3)_5(C_6H_5CN)^{3+}$, and the analogous ruthenium(II) and rhodium(III) complexes of acetonitrile, $Ru(NH_3)_5(CH_3CN)^{2+}$ and $Rh(NH_3)_5(CH_3CN)^{3+}$. Comparisons of the reactions of these structurally analogous complexes allow evaluation of the differences in ligand reactivity resulting from changes in the nature of the central metal ion. For the present cases, rhodium(III) and ruthenium(II) complexes are isoelectronic (both low-spin $4d^6$) yet differ by one electrostatic charge. The rhodium(III) and ruthenium(III) complexes have the same charge, but differ by one d electron (Ru(III) is low-spin $4d^5$). Consequently, relative to rhodium(III), ruthenium(II) has been shown to be an electron donor to π-acceptor unsaturated organic ligands such as organonitriles,[7] while ruthenium(III) is a π acid.[11] The differences in metal–ligand interactions should show up in the reactivity patterns for base hydrolysis of organonitriles coordinated to these substitution-inert metal ions. Comparisons to recent cobalt(III) results can also be made.

Experimental Section

Equipment. Visible and ultraviolet spectra and rate studies were run on a Cary Model 14 spectrophotometer equipped with a thermostated cell compartment. Some measurements were done on a Cary Model 118. Infrared spectra were run on a Perkin-Elmer Model 225 recording spectrophotometer, using 75–100-mg KBr disks containing 1–3 mg of compound. PH measurements were made on a Sargent–Welch Model NX pH meter with a combination minielectrode.

Materials. Reagent grade ligands and chemicals were used throughout. Doubly distilled water was used for solutions. Argon used for deaerating solutions was deoxygenated by passage through Cr(II) solution in gas-scrubbing bottles. DMA (*N,N*-dimethylacetamide) was distilled and stored over molecular sieves. "Tris" refers to tris(hydroxymethyl)aminomethane. The acetonitrile and benzonitrile complexes, $[Ru(NH_3)_5(CH_3CN)](ClO_4)_3$ and $[Ru(NH_3)_5(C_6H_5CN)](ClO_4)_3$, were prepared according to the procedure of Clarke.[2] The ruthenium(III) products were recrystallized from warm (45–50°) dilute perchloric acid (pH 1–2) to minimize any production of amide complex. Purity was judged by comparison of measured extinction coefficients to those previously reported.[2] $[Rh(NH_3)_5(CH_3CN)](ClO_4)_3$ was prepared as described previously.[6]

$[Ru(NH_3)_5(CH_3CONH)](BF_4)_2$. $[Ru(NH_3)_5Cl]Cl_2$ (200 mg, 0.68 mmol) was added to a solution of silver trifluoroacetate (150 mg of Ag_2O, 0.65 mmol, in 3–4 ml of water with a minimum of concentrated HTFA) whereupon AgCl precipitated. The precipitate was digested (3–5 min) and then filtered, after cooling for several minutes. The yellow filtrate was deaerated with argon and reduced with a piece of amalgamated zinc, using a vial with a rubber serum cap as the reaction vessel, and argon was continuously passed through with syringe needles. The reduced solution was added to an open 10-ml beaker containing acetamide (0.8 g, 13.5 mmol) and a piece of Zn(Hg). The pH was adjusted to about 8 with solid tris and the solution became deep amber. After 2–3 min of stirring the Zn(Hg) was removed and the solution was stirred 5 min longer with the color becoming lighter. Solid $NaBF_4$ (300 mg) was added and the solution was stirred in an ice bath to give a yellow precipitate. The product was filtered, washed with ethanol and ether, and air-dried, yielding a bright yellow powder (165 mg, 0.40 mmol, 58% yield). *Anal.* Calcd for $RuC_2H_{19}ON_6B_2F_8$: C, 5.75; H, 4.58; N, 20.1. Found: C, 5.54; H, 4.41; N, 19.4. Calcd for one water of crystallization: C, 5.52; H, 4.86; N, 19.3.

$[Ru(NH_3)_5(C_6H_5CONH)](ClO_4)_2$. A solution of $Ru(NH_3)_5Cl^{2+}$ was produced from $[Ru(NH_3)_5Cl]Cl_2$ (100 mg, 0.34 mmol) as described above. Then the solution was added directly to an open beaker containing benzamide (0.2 g, 1.65 mmol), methanol (1 ml), and Zn(Hg). A precipitate formed on adding saturated $NaClO_4$ solution. This was collected by filtration and washed with an ethanol–ether mixture because the product appeared to be soluble in ethanol alone. A bright yellow powder was obtained (75 mg, 0.15 mmol, 44% yield). This product was recrystallized by dissolution in a minimum of 40° water and then cooled to 0° with addition of saturated $NaClO_4$ solution to yield the yellow salt (40 mg). *Anal.* Calcd for one water of crystallization: Ru, 19.4; H, 4.43; N, 16.1. Found: Ru, 19.3; H, 4.47; N, 16.13. A reasonable carbon analysis was not obtained from two separate preparations. However, the extinction coefficient at 393 nm was 98% of the value obtained from hydrolysis of the benzonitrile complex.

$[Rh(NH_3)_5(CH_3CONH)](ClO_4)_2$. $[Rh(NH_3)_5H_2O](ClO_4)_3$ (100 mg, 0.20 mmol) was dissolved in DMA (5 g) along with acetamide (1.0 g, 17 mmol). Molecular sieves (0.5–1 g) were also added. The reaction mixture was heated (in a round-bottom flask equipped with an air-cooled condenser) for 7–8 hr at 105–110° with continuous stirring. The solution was then filtered warm and the product precipitated by adding 75 ml isobutyl alcohol. The very fine white precipitate was allowed to settle overnight in the refrigerator. The product was then filtered and washed with ethanol and ether and air-dried to give a white powder (62 mg, 0.14 mmol, 70% yield). Recrystallization from warm (35°) water with addition of saturated $NaClO_4$ gave a 40–45% recovery. *Anal.* Calcd for $RhC_2H_{19}N_6O_9Cl_2$: C, 5.40; H, 4.30; N, 18.9. Found: C, 5.02; H, 4.21; N, 18.66.

pK_a Measurements. Ru(III) Complexes. A stock solution of the deprotonated amide (amido)[12] complex was made by dissolving the salt in water or 2.0 *M* $NaClO_4$ at pH 5. The Ru(III) concentration was chosen to give strong uv absorbance. Stock solutions varying in acid concentration from 2.0×10^{-4} to 2.0 *M* and at total perchlorate concentration of 2.0 *M* were also prepared. Mixture of equal volumes of Ru(III) and acid yielded the desired series (11–13 solutions) of pH values. The spectrum (450–250 nm) of each solution was recorded at 25°. The pK_a values were determined using the method described by Clarke and Ford,[3] where $\log (A_{\lambda_1}/A_{\lambda_2})$ is plotted against pH and λ_1 and λ_2 represent absorption maxima for the unprotonated (B) and protonated (BH^+) forms, respectively. The pK_a corresponds to the pH where $\log (A_{\lambda_1}/A_{\lambda_2})$ equals $\log [(\epsilon(B)_{\lambda_1} + \epsilon(BH^+)_{\lambda_1})/(\epsilon(B)_{\lambda_2} + \epsilon(BH^+)_{\lambda_2})]$.

Rhodium(III) Acetamide. These measurements were done in a manner analogous to those of the Ru(III) complexes. Due to low extinction coefficients and small amounts of material, the 0.1 slide wire of the Cary 118 was used for spectral scans (400–230 nm) with Rh(III) at 4.5×10^{-4} *M*. Since the spectra of the protonated and deprotonated forms are very similar, the pK_a was determined at 270 nm where the greatest absorbance difference in the spectra occurs. A_{270} was plotted against pH and the pK_a taken to be the pH where the absorbance equaled $[(\epsilon_{270}(B) + \epsilon_{270}(BH^+))/2][Rh(III)]$. (Note: The pK_a plots used with the Ru(III) complexes is superior when the acid and base forms display characteristic absorption bands at significantly different wavelengths, as this method is independent of errors in complex concentration.)

Rate Studies. Ruthenium(III)–Nitrile Complexes. Stock buffer solutions, $NaHCO_3$–Na_2CO_3, were prepared at the desired total buffer concentrations in 2.0 *M* $NaClO_4$. A fresh Ru(III) stock solution in water was prepared for each set of experiments. Equal volumes of reactants at 25.0° were measured by syringes or pipettes into a 1.0-cm cell which was immediately placed in the spectrophotometer (25.0°) and the absorbance *vs.* time plot was recorded. The pH of reaction was determined by mixing equal volumes of buffer and water and measuring the pH. These values agreed with spot checks on actual reaction solutions.

Rhodium(III) Acetonitrile. Reactions at high pH were done with sodium hydroxide and Rh(III) stock solutions (9.2×10^{-4} *M*) prepared in CO_2-free water at 1.0 *M* $NaClO_4$. Equal volumes of reactants at 25.0° were mixed in 2.0-cm cells and absorbance *vs.* time was recorded on the 0.1 slide wire (Cary 14). Reactions with carbonate were carried out in a similar manner using 1.0-cm cells and the Cary 118.

Table I. Visible–Uv Spectra of Amide and Amido Complexes in Aqueous Solution[a]

	λ_{max} (ϵ)[b]
$Ru(NH_3)_5(CH_3CONH)^{2+}$ [c]	383 (3.46×10^3)
	249 (2.31×10^3)
$Ru(NH_3)_5(CH_3CONH_2)^{3+}$ [d]	322 (1.55×10^3)
$Ru(NH_3)_5(C_6H_5CONH)^{2+}$ [e]	393 (4.08×10^3)
	314 (3.68×10^3)
	270 sh (2.68×10^3)
	219 (9.45×10^3)
$Ru(NH_3)_5(C_6H_5CONH_2)^{3+}$ [f]	385 (1.47×10^3)
	320 (3.45×10^3)
	270 sh (3.78×10^3)
	228 (9.40×10^3)
$Rh(NH_3)_5(CH_3CONH)^{2+}$ [g]	313 (164)
	259 (153)
$Rh(NH_3)_5(CH_3CONH_2)^{3+}$ [h]	308 (157)
	256 (143)

[a] 25°; ±3% experimental uncertainty for extinction coefficients. [b] In nm and M^{-1} cm^{-1}. [c] 1 *M* $NaClO_4$, pH 5. [d] 1 *M* $HClO_4$. [e] H_2O, pH ~8 ($NaHCO_3$). [f] 2 *M* $HClO_4$. [g] 1 *M* $NaClO_4$, pH ~11 (NH_3). [h] 0.1 *M* $HClO_4$.

Ruthenium(II) Acetonitrile. Anaerobic reactions at high pH were done by dissolving the Ru(II) complex in a known concentration of NaOH, which had been deaerated in a 1-cm cell stoppered by a Teflon plug containing a rubber septum.[13] The Ru(II) complex was added quickly and the solution was again purged with argon before spectral data were taken. The spectrum was scanned repeatedly over a period of several days with the cells being stored in the dark at room temperature.

Product Analyses. For each nitrile hydrolysis system reported here uv–visible spectra were recorded for product solutions from ligand hydrolysis reactions and compared to spectra of the authentic amido complexes. For the Ru(III) complexes hydrolysis was achieved by adding a few milligrams of $NaHCO_3$ to a solution of the nitrile in a spectrophotometric cell. In the case of the rhodium(III)–acetonitrile complex, NaOH was used. In addition, for the acetamido complexes, solid products were isolated and characterized by ir spectra.

Hydrolysis of $Ru(NH_3)_5(CH_3CN)^{3+}$. The ClO_4^- salt of the acetonitrile complex (35 mg, 0.067 mmol) was dissolved in 20 ml of H_2O and $NaHCO_3$ was added to give pH 7 (this was accompanied by a color change to deeper yellow). After 10 min the reaction solution was subjected to rotary evaporation which reduced the volume to 3 ml of brownish solution. Addition of saturated aqueous $NaClO_4$ and cooling in ice yielded a yellow precipitate (18 mg, 0.041 mmol, 61% yield) whose uv and ir spectra agreed with those of an authentic acetamido complex, $[Ru(NH_3)_5(CH_3CONH)](ClO_4)_2$.

Hydrolysis of $Rh(NH_3)_5(CH_3CN)^{3+}$. Treatment of a solution of $[Rh(NH_3)_5(CH_3CN)](ClO_4)_3$ (15 mg in 0.5 ml) with 0.1 *N* NaOH (~0.1 ml) for 3 min and then addition of saturated aqueous $NaClO_4$ (~0.1 ml) with cooling at 0° yielded a white powder (~7 mg). The uv and ir spectra of this product corresponded to that of the acetamido complex, $[Rh(NH_3)_5(CH_3CONH)](ClO_4)_2$.

Results

Amido Complexes. The acetamido and benzamido complexes of pentaammineruthenium(III) were prepared directly from the free amide and from the corresponding nitrile complexes. The visible–uv spectra of the product solutions of the bicarbonate-catalyzed hydrolyses of the coordinated nitrile were identical with spectra of authentic amido complexes when the hydrolyses were carried out at low Ru(III) concentrations (*vide infra*). The reversible pH dependences of the spectra were also identical with that of authentic material. The hydrolysis product from the acetonitrile complex was isolated, and its infrared spectrum was the same as that of the acetamido complex. The base hydrolysis product of the pentaamminerhodium(III) complex of acetonitrile displays a pH-dependent uv spectrum and an infrared spectrum identical

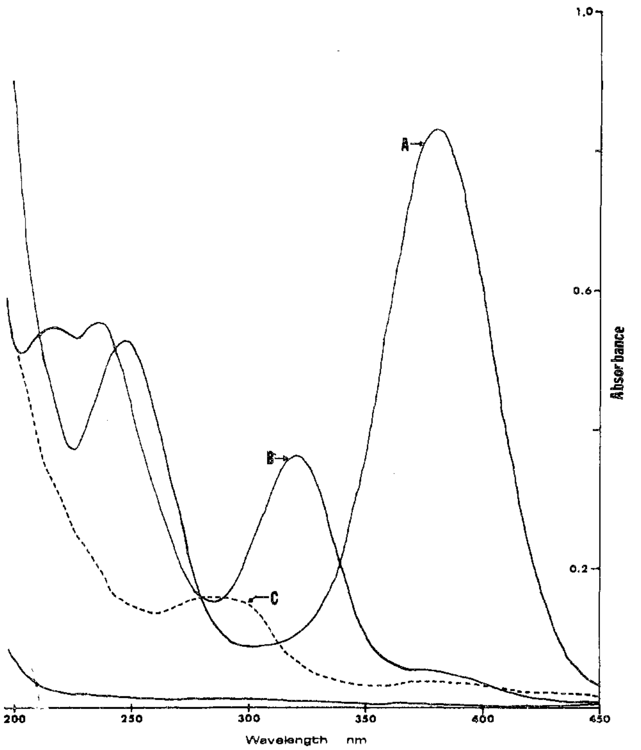


Figure 1. Spectra of $Ru(NH_3)_5(CH_3CONH)^{2+}$ (A), $Ru(NH_3)_5(CH_3CONH_2)^{3+}$ (B), and $Ru(NH_3)_5(CH_3CN)^{3+}$ (C); all in aqueous solution at 2.42×10^{-4} *M*. Spectrum A was measured in pH 5 solution and spectrum B in pH 0.3 solution.

with those of the authentic complex prepared from aquopentaamminerhodium(III) and acetamide. The hydrolysis of the coordinated nitriles can be therefore represented by

$$(NH_3)_5M(N{\equiv}CR)^{3+} + OH^- \rightarrow (NH_3)_5M(NHCOR)^{2+} \qquad (1)$$

where in basic solution the hydrolyzed ligand is in the amido form.

Uv–Visible Spectra. Data from the electronic spectra of the complexes are listed in Table I. The spectrum of the ruthenium(III)–acetamido complex shows strong bands at 381 and 248 nm, probably ligand to metal charge transfer in character given their intensity and the fact that the free ligand shows no band above 200 nm in aqueous solution. The extinction coefficients are too large for d–d transitions. When the coordinated ligand is protonated, a new spectrum arises with a single band at 322 nm, presumably due to a new charge-transfer band. Figure 1 shows the uv–vis spectra of the ruthenium(III)–acetamido complex in acidic and basic solution and of the analogous acetonitrile complex.

The benzamido complex has a more complicated spectrum due to π–π^* transitions of the aromatic ring. The ligand-localized band at 219 nm is acid dependent, shifting to 228 nm, but its intensity remains unchanged. The 393-nm band corresponds to the one at 381 nm in the acetamido complex but does not disappear entirely upon protonation and is shifted slightly to the blue. The band at 314 nm shifts to 320 nm in acid with relatively little change in intensity. A weak broad shoulder at 260–280 nm, corresponding to a weak maximum in the free ligand, shows a marked increase in intensity upon protonation.

The spectrum of the acetamido complex of Rh(III) in aqueous solution shows two relatively low-intensity bands at 313 and 258 nm, which are typical of pentaamminerhodium(III) complexes and can be attributed to d–d transitions. In acid solution the spectrum changes to yield maxima at 308 and 255 nm with little change in intensity.

The differences in the spectra of the amido complexes resulting from changes in solution pH allow measurement of pK_a values for each of these species. These values are listed in Table II along with pK_a values for related complexes.

Table II. pK_a Values for Coordinated Amides and Other Ligands (25°) in Complexes of the Type $M(NH_3)_5L^{3+}$

	M		
Ligand	Ru	Co	Rh
CH_3CONH_2	2.00[a,b] 2.17[a,c]	3.02[b,d]	3.3[a,b]
$C_6H_5CONH_2$	0.90[a,c]	1.65[b,e]	
$SO_3NH_2^-$	2.6[f]	5.70[g]	
OH_2[h]	4.2	6.6 (6.2)[i]	5.9 (6.8)[j]

[a] This work; error limits ±0.05 for Ru and ±0.1 for Rh. [b] 1.0 *M* ClO_4^-. [c] 2.0 *M* ClO_4^-. [d] 1 *M* $NaClO_4$.[9] [e] 1 *M* $LiClO_4$.[8] [f] 0.10 *M* Cl^{-1}: J. N. Armor and H. Taube, *Inorg. Chem.*, 10, 1570 (1971). [g] 1 *M* $NaClO_4$: L. L. Po and R. B. Jordan, *ibid.*, 7, 526 (1968). [h] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 32. [i] R. G. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, 7, 897 (1968). [j] D. A. Palmer and G. M. Harris, *Inorg. Chem.*, 13, 965 (1974).

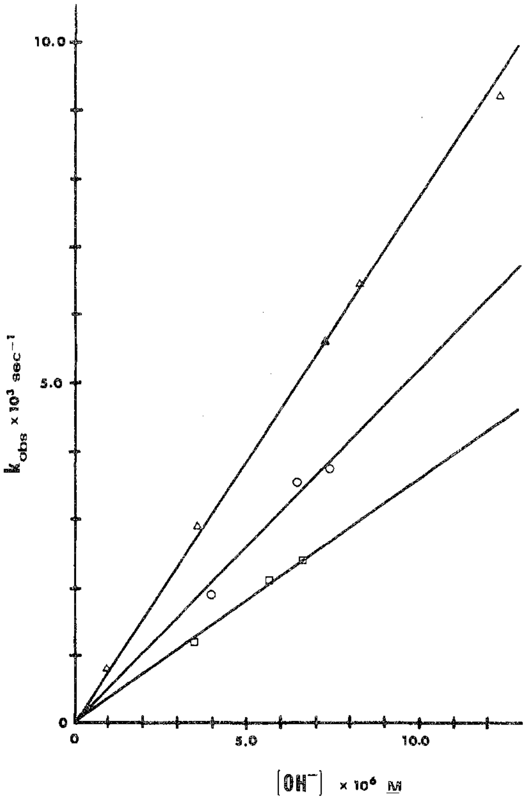


Figure 2. Plots of k_{obsd} *vs.* $[OH^-]$ for the hydrolysis of $Ru(NH_3)_5(CH_3CN)^{3+}$ in different concentrations of HCO_3^-–CO_3^{2-} buffer: triangles, $[CO_3^{2-}] + [HCO_3^-] = 0.01$ *M*; circles, 0.0050 *M*; squares, 0.0025 *M*. All rate constants measured at 25.0°, $\mu = 1.0$ *M* $NaClO_4$; $[Ru(III)]_i = 1.6 \times 10^{-4}$ *M*.

Rate Studies. Hydrolysis of $Ru(NH_3)_5(CH_3CN)^{3+}$. The rates of the coordinated acetonitrile hydrolyses to give the acetamido complex were studied in slightly basic solution at 25° over a range of pH values obtained by using HCO_3^-–CO_3^{2-} buffer mixtures. Formation of acetamido complex was monitored at 380 nm and plots of ln [Abs(∞) – Abs(t)] were essentially linear for low concentrations (1.6×10^{-4} *M*) of Ru(III) implying a first-order rate law

$$\frac{d[\text{ruthenium(III)–amido}]}{dt} = k_{obsd}[\text{ruthenium(III)–nitrile}] \qquad (2)$$

Values of k_{obsd} were taken from the initial slopes, and conversion to the acetamido complex was at least 80%. There was

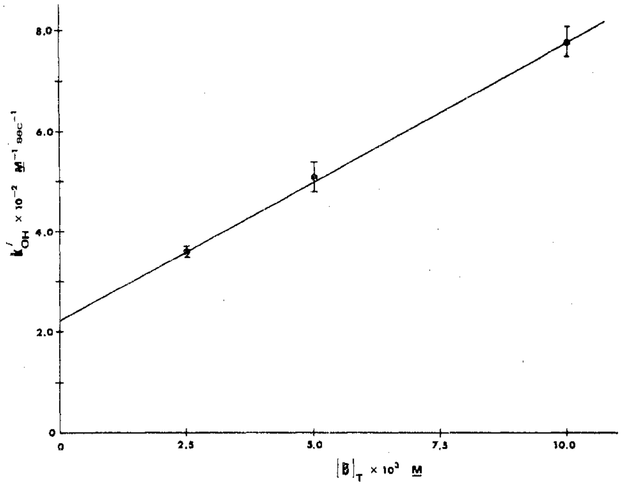


Figure 3. Effect of buffer concentration ($[B] = [CO_3^{2-}] + [HCO_3^-]$) on k_{OH}'; intercept = $(2.2 \pm 0.1) \times 10^2$ M^{-1} sec^{-1}, slope = $(5.5 \pm 0.5) \times 10^4$ M^{-2} sec^{-1}.

some evidence for competitive side reactions especially at the higher pH values and at higher concentrations of the ruthenium(III)–nitrile complex. At least part of this side reaction can be attributed to formation of the ruthenium(II)–acetonitrile complex according to changes in the electronic spectra. Use of other buffers (*e.g.*, Tris, borate, NH_3–NH_4^+) led to substantially more side reaction.

Plots of k_{obsd} *vs.* $[OH^-]$ were linear for each concentration of the carbonate–bicarbonate buffer (Figure 2). Therefore k_{obsd} may be rewritten as

$$k_{obsd} = k_{OH}'[OH^-] \qquad (3)$$

where k_{OH}' is some function of the buffer concentration $[CO_3^{2-} + HCO_3^-]$. A plot of k'_{OH} *vs.* buffer concentration (Figure 3) is linear with a nonzero intercept; thus, eq 3 can be rewritten as

$$k_{obsd} = k_{OH}[OH^-] + k_B[B][OH^-] \qquad (4)$$

where the intercept $[(2.2 \pm 0.1) \times 10^2$ M^{-1} sec$^{-1}]$ is k_{OH}, the rate constant for reaction with hydroxide in the absence of added buffer,[14] and the slope $[(5.6 \pm 0.5) \times 10^4$ M^{-2} sec$^{-1}]$ is k_B (25°, $\mu = 1.0$ M).

Hydrolysis of $Ru(NH_3)_5(C_6H_5CN)^{3+}$. The rates of formation of the ruthenium(III)–benzamido complex from the ruthenium(III)–benzonitrile complex were also measured in HCO_3^-–CO_3^{2-} buffered aqueous solutions at 390 nm. Reaction with base led to some production of the ruthenium(II)–nitrile species; however, this was minimized (≤5%) by using very low concentrations of the benzonitrile complex (~5 × 10^{-5} M). The data were treated as described above, and the values $k_{OH} = (2.0 \pm 0.3) \times 10^3$ M^{-1} sec^{-1} and $k_B = (4.9 \pm 0.8) \times 10^5$ M^{-2} sec^{-1} (25°, $\mu = 1.0$ M) were obtained.

Hydrolysis of $Rh(NH_3)_5(CH_3CN)^{3+}$. Base hydrolysis of the Rh(III)-coordinated acetonitrile proved to be sufficiently slow that the reaction could be studied directly without buffers. Rates were measured by optical density changes at 300 nm, and linear first-order rates were obtained. Observed rate constants proved to be a linear function of $[OH^-]$, giving a second-order rate constant $k_{OH} = 1.0 \pm 0.1$ M^{-1} sec^{-1} (25°, $\mu = 1.0$ M).

The effect of carbonate ion on this reaction was examined cursorily in aqueous solutions of sodium carbonate (0.10, 0.075, and 0.050 M). The hydrolysis of rhodium(III) acetonitrile showed an apparent first-order dependence on carbonate ion concentration, but this could be readily explained in terms of the hydroxide-dependent path. Experiments at lower pH values where bicarbonate is the dominant species were also done. At a total buffer concentration of 0.10 M and pH 8.5, the hydrolysis reaction proceeded quite slowly with $k_{obsd} = 6.3 \times 10^{-5}$ sec^{-1}. When the rate due to hydroxide ion is subtracted, the buffer-dependent contribution to the observed rate constant is 6.0×10^{-5} sec^{-1} (25°, $\mu = 1.0$).

Reaction of $Ru(NH_3)_5(CH_3CN)^{2+}$ in Base. The behavior of the ruthenium(II)–benzonitrile and –acetonitrile complexes in deoxygenated NaOH solution was studied at room temperature. There was no spectral change which could be attributed to the formation of ruthenium(II)–amido complexes; however, very slow spectral changes occurred over a period of days. For the acetonitrile complex the 227-nm maximum of the starting material gradually decreased accompanied by an increase at 380 nm. The product spectrum was principally (>80%) that of the ruthenium(III)–acetamido complex along with some unidentified species. Rates measured for the disappearance of the ruthenium(II) acetonitrile show the reaction to be essentially independent of $[OH^-]$, only doubling between 5×10^{-6} and 0.1 M hydroxide. The rate at the higher concentration was 6×10^{-6} sec^{-1} which gives an upper limit of 6×10^{-5} M^{-1} sec^{-1} for the k_{OH} term for base hydrolysis of Ru(II)-coordinated acetonitrile.

When the reaction at 0.001 M OH^- was done in the presence of oxygen, the rate increased to ~1.2×10^{-5} sec^{-1} and gave the same product spectrum as before. When an anaerobic reaction solution was treated with pure O_2, there were no immediate spectral changes, thus indicating that a spectrally undetectable ruthenium(II)–acetamido complex was not present in the solution since this species should rapidly oxidize to Ru(III).

Discussion

Constitution of Hydrolysis Products. The ir and vis–uv spectra of the hydrolysis products are identical with those of amido complexes prepared independently. No ir band attributable to the nitrile group is seen in the hydrolysis product spectra. Moreover, the reversible pH dependence of the spectra agrees with that observed for authentic amido complexes, thus suggesting the equilibrium

$$(NH_3)_5M(NHCOR)^{2+} + H^+ \rightleftharpoons (NH_3)_5M(NH_2COR)^{3+} \qquad (5)$$

The position of proton attachment cannot be distinguished between the amide N or O from the data in this study. Buckingham, *et al.*,[9] have argued from pmr data obtained in DMSO-d_6 that the proton binds to the carbonyl oxygen in the cobalt(III)–acetamide complex. They also noted that free acetamide has been claimed to protonate almost exclusively at the carbonyl oxygen in strongly acidic solutions.[15] The coordination site for the amide ligand has in this discussion been assumed to be the nitrogen atom. The basis for this assumption is that the nitrogen atom is the initial point of attachment in the nitrile complexes and that Ru(III) and Rh(III) complexes of the type described are not substitution labile under the hydrolysis conditions. However, the failure to observe substitution lability may be a poor criterion for establishing the viability of an intramolecular linkage isomerization. A second consideration comes from examining the electronic spectra of the amido complex of Ru(III). The ligand-to-metal charge-transfer band occurs at a wavelength (393 nm) similar to that of the pentaammineruthenium(III) complex of another N-coordinated anion, $NHSO_3^{2-}$ (398 nm),[16] but at lower energy than that of oxygen coordinated anions such as OH^-, $CH_3CO_2^-$, and $C_6H_5CO_2^-$ (all ~295 nm).[17] Previous studies[8,9] of hydrolysis products of analogous cobalt(III)–nitrile complexes have also concluded that these amido ligands are N coordinated not O coordinated.

pK_a Values for Coordinated Amides. The pentaammineruthenium(III) complexes of acetamide and benzamide were found to have lower pK_a values than the corresponding Co(III)

Table III. Hydroxide Ion Catalyzed Hydrolysis of Nitrile Complexes

Nitrile	k_{OH},[a] M^{-1} sec^{-1}	Rel rates[b]	Ref
CH_3CN	1.60×10^{-6}	1.0	*c*
$(NH_3)_5Ru(CH_3CN)^{3+}$	2.2×10^{2}	1.4×10^{8}	This work
$(NH_3)_5Rh(CH_3CN)^{3+}$	1.0	6.2×10^{5}	This work
$(NH_3)_5Co(CH_3CN)^{3+}$	3.40	2.12×10^{6}	9
$(NH_3)_5Ru(CH_3CN)^{2+}$	$<6 \times 10^{-5}$	<38	This work
C_6H_5CN	7.2×10^{-6}	1.0	*d*
$(NH_3)_5Ru(C_6H_5CN)^{3+}$	2.0×10^{3}	2.8×10^{8}	This work
$(NH_3)_5Co(C_6H_5CN)^{3+}$	18.2[e]	2.53×10^{6}	8

[a] 25.0°, $\mu = 1.0\,M$ except for Ru(II). [b] Relative rate = k_{OH}(complex)/k_{OH}(free ligand). [c] N. Peskoff and J. Meyer, *Z. Phys. Chem., Stoechiom. Verwandschaftslehre*, **82**, 129 (1913), as quoted by ref 9. [d] Extrapolated from higher temperature rate data reported for 50% aqueous acetone by K. B. Wiberg, *J. Amer. Chem. Soc.*, 77, 2519 (1955). [e] 25.6°.

complexes (Table II). This is consistent with the relative acidities of other complexes of these two metal ions and reflects the difference in their electronic configurations. The Ru(III) center, having a low-spin d^5 configuration, acts as a π acceptor in comparison to the d^6 ion. Thus, it stabilizes the anionic amido ligand relative to the uncharged amide making proton dissociation more favorable. The greater acidity of the coordinated benzamide can be attributed to the ability of the aromatic ring to delocalize the negative charge of the amido ligand. The ratio of the acidity of the benzamide complex to that of the acetamide complex is ~20 for both Ru(III) and Co(III). This observation suggests that the individual electronic perturbations due to the metal ion and to the phenyl group are additive and effectively separable.

The rhodium(III)–acetamide complex is quite similar to the Co(III) analog in acidity, as would be expected, since both metal ions have the d^6 configuration. One might also rationalize that the larger rhodium ion would be less electron withdrawing and, thus, slightly less acidic as observed.

Kinetics of Nitrile Hydrolysis. If we consider first the hydroxide-only path (k_{OH}), it is clear that, as has been observed before for Co(III) complexes, coordination to either $Ru(NH_3)_5^{3+}$ or $Rh(NH_3)_5^{3+}$ greatly enhances the hydrolysis rate relative to the free ligands, acetonitrile or benzonitrile. Ruthenium(III) is particularly effective, displaying k_{OH} values larger by more than 8 orders of magnitude than the free ligand values for both ligands. These enhancements are the largest yet reported for the base hydrolyses of coordinated organonitriles and are approximately 2 orders of magnitude greater than the k_{OH} values observed for the analogous Rh(III) and Co(III) complexes (Table III). These differences in rates can be explained qualitatively by considering the electronic characteristics of the central metal ions. The relative effect of the d^5 configuration, cited above in the discussion of pK_a values, can also account for the observed kinetic effect by making the nitrile carbon more electropositive (than in the d^6 Co(III) and Rh(III) complexes) and, therefore, more susceptible to nucleophilic attack by hydroxide ion. The higher rates for the benzonitrile complexes can be attributed to additional electron-withdrawing effect of the phenyl group.

A significant result is the observation that coordination to $Ru(NH_3)_5^{2+}$ leads to very little or no acceleration of the base hydrolysis of the nitrile. The reported rate for the acetonitrile complex (Table III) can only be considered an upper limit as virtually no dependence on $[OH^-]$ was seen and the reaction product observed was the ruthenium(III)–acetamido complex (probably due to slow leakage of air into the reaction cell over the period of days the reaction was observed). Ruthenium(II) has a demonstrated[2,3,7] ability to back-bond to π-unsaturated ligands such as the organonitriles. Thus, this π-back-bonding interaction may serve to increase electron density at the nitrile carbon atom compensating at least partially for the σ-electron-withdrawing (thus activating) effect[7] expected for coordination of the RCN moiety to a dipositive metal center. It is unlikely that a charge difference of only 1 (2+ *vs.* 3+) would be sufficient to explain the difference of more than 4 orders of magnitude in the hydrolysis reactivities of $Ru(NH_3)_5(CH_3CN)^{2+}$ and its isoelectronic rhodium(III) analog. This appears especially true in the context that other 2+ metal ions such as Cu^{2+} and Ni^{2+} have been shown[10c,18,19] to catalyze effectively the hydrolysis of organonitrile.

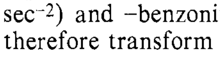
The manner by which buffers affected the reactions of the ruthenium(III)–nitrile complexes in basic solution was not limited to the reaction rates. Several of the buffers tried caused significant side reactions, a principal product being the corresponding ruthenium(II) nitrile, presumably formed by disproportionation of Ru(III) to Ru(II) and Ru(IV) species.[20] These side reactions were virtually eliminated by examining the hydrolysis rates in very dilute Ru(III) solutions (thus suppressing the second-order disproportionation) and by using dilute sodium bicarbonate–sodium carbonate as the buffer system. Nonetheless, even in these solutions the buffer was significantly involved in the formation of the amido complex as evidenced by the rate behavior described in eq 4. The linear dependence on buffer concentration observed is suggestive of general base–general acid catalysis by the buffer; however, it is not immediately obvious why this behavior should hold at all hydroxide concentrations. This question is resolved by examining the pH range (~pH 8–9) used to obtain these data. Under these conditions HCO_3^- is the predominant species and $[CO_3^{2-}]$ is essentially a linear function of $[OH^-]$. Therefore, eq 4 can be rewritten in the approximate form

$$k_{obsd} = k_{OH}[OH^-] + k_B[HCO_3^-][OH^-] \qquad (6)$$

or

$$k_{obsd} = k_{OH}[OH^-] + k_c[CO_3^{2-}] \qquad (7)$$

The second term of eq 6 conceivably could reflect acid catalysis (by HCO_3^-) of hydroxide attack on the carbon atom of the nitrile group. Since this pathway presumably involves protonation of the coordinated nitrogen atom, it appears very unlikely. The second term of eq 7 appears to represent more likely pathways involving carbonate ion. Two such pathways would be general base catalysis of water attack on the nitrile group or rate-determining direct attack of carbonate on the nitrile group to give an adduct such as



$$(NH_3)_5Ru^{III}{-}N{=}\underset{\displaystyle OCO_2^-}{\underset{|}{C}}{-}R$$

which decomposes by more rapid steps to the amido complex product. This latter pathway receives some support from the observation that the ruthenium(III)–benzonitrile complex forms similar adducts with nucleophiles such as hydroxylamine.[21] The rate constant k_c is equal to k_BK_w/K_2, where K_2 is the second dissociation constant for carbonic acid in 1 M $NaClO_4$ (2.69×10^{-10} M).[22] The k_B values obtained (*vide supra*) for the ruthenium(III)–acetonitrile (5.6×10^4 M^{-1} sec^{-2}) and –benzonitrile complexes (4.9×10^5 M^{-2} sec^{-1}) therefore transform to the k_c values 2.1 and 18 M^{-1} sec^{-1}, respectively. The ratio of these two values k_c(benzonitrile)/k_c(acetonitrile) ≈ 9 is virtually identical with the analogous ratio for the k_{OH} values. Furthermore, if these k_c values do represent the direct attact of carbonate on the nitrile, their magnitude indicates that hydroxide ion is a factor of ~100 more reactive than CO_3^{2-} in this respect.

The apparent contribution of buffer to the rate of hydrolysis in the pH 8.5, 0.1 M HCO_3^-–CO_3^{2-} solution of $Rh(NH_3)_5(CH_3CN)^{3+}$ was approximately 6×10^{-5} sec^{-1}. If one assumes this is the consequence of a carbonate ion dependent pathway, a $k_{CO_3^{2-}}$ value of 0.008 M^{-1} sec^{-1} can be calculated. The $k_{OH^-}/k_{CO_3^{2-}}$ ratio for this system would be about 120, comparable to that observed with the ruthenium(III) analogs.

In summary, the data presented in this article demonstrate that for analogous organonitrile complexes of the type $M(NH_3)_5(N{\equiv}CR)^{3+}$ the d^5 Ru(III) species is significantly more reactive toward base hydrolysis to the amido complex than are the d^6 Rh(III) and Co(III) analogs. This effect is presumably due to the relative ability of the Ru(III) center to act as a π acceptor and stabilize the developing negative charge on the ligand which results from rate-determining hydroxide attack on the nitrile carbon atom. The Ru(II) analog in contrast is remarkably unreactive presumably because of this metal center's relative ability to π back-bond into the nitrile ligand.

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Registry No. $[Ru(NH_3)_5(CH_3CONH)](BF_4)_2$, 52843-04-6; $[Ru(NH_3)_5(C_6H_5CONH)](ClO_4)_2$, 52843-06-8; $[Rh(NH_3)_5(CH_3CONH)](ClO_4)_2$, 52843-08-0; $Ru(NH_3)_5(CH_3CONH_2)^{3+}$, 52843-09-1; $Ru(NH_3)_5(C_6H_5CONH_2)^{3+}$, 52843-10-4; $Rh(NH_3)_5(CH_3CONH_2)^{3+}$, 52843-11-5; $(NH_3)_5Ru(CH_3CN)^{3+}$, 44819-54-7; $(NH_3)_5Rh(CH_3CN)^{3+}$, 44819-05-3; $(NH_3)_5Ru(CH_3CN)^{2+}$, 26540-31-8; $(NH_3)_5Ru(C_6H_5CN)^{3+}$, 46343-59-3.

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Dissymmetric Solvent Interactions. Thermodynamic Parameters for the Enantiomerization of Tris(*o*-phenanthroline)nickel(II) Ions in (−)-2,3-Butanediol

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The enantiomerization of solutions of (±)-$Ni(phen)_3^{2+}$ dissolved in (−)-2,3-butanediol has been studied between 4 and 100°. From the temperature dependence of the enantiomerization equilibrium constant the enthalpy of the dissymmetric interaction is evaluated as −119 cal mol^{-1} and the corresponding entropy as −0.28 cal K^{-1} mol^{-1}. A study of the rates of loss of optical activity of solutions of (+)- and (−)-$Ni(phen)_3^{2+}$ in (−)-2,3-butanediol confirms this small chiral discrimination. The origin of the discrimination energy is discussed.

The diastereotopic[1] interactions between chiral molecules have been a matter of continuing interest[2,3] since the early observations of Kuhn[4] and Pfeiffer,[5] who noted that the equilibrium constant between enantiomers could be displaced from unity by the presence of other chiral molecules. Pfeiffer observed that the addition of both chiral cations and anions caused aqueous solutions of labile *o*-phenanthroline– and bipyridyl–metal complexes to develop optical activity which could be ascribed to the preponderance of one enantiomer of the complex over the other. Subsequently, Dwyer[6] suggested that the displacement of the enantiomer equilibrium arose from a differential change in the activity coefficients of the optical antipodes. That enantiomerization,[3,7,8] that is the displacement of the enantiomer equilibrium, does indeed occur was demonstrated by Kirschner,[9] who actually isolated the optically active nickel complexes formed by the induction of *l*-malic acid. These results, although interesting in themselves, suffer from the fact that few quantitative thermodynamic and kinetic data have been obtained which precisely define, in energy terms, the extent of the diastereotopic interactions.

Table I

Temp, °C	K^a	Temp, °C	K^a	Temp, °C	K^a
4.0	1.071^b	49.5	1.047	78.0	1.030
25.0	1.062	64.5	1.037	100	1.020
35.0	1.055				

^{a} The (−) enantiomer predominates at equilibrium. ^{b} This value was not used in the evaluation of $\Delta H°$ and $\Delta S°$ (*vide infra*).

We recently showed[7] that the chiral solvent (−)-2,3-butanediol was a remarkably efficient enantiomerizing medium