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Substitution and Isomerization Reactions of (Polypyridyl)ruthenium(III) Complexes and the Catalysis of Ruthenium(II) Reactions

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The kinetics of substitution of acetonitrile for the aquo ligand of *trans*-$Ru(NN)_2(H_2O)(OH)^{2+}$ (NN = 2,2′-bipyridyl (bpy)) and isomerization of *trans*-$Ru(NN)_2(H_2O)(OH)^{2+}$ (NN = bpy or 1,10-phenanthroline (phen)) were studied. The substitution reaction is a reversible reaction that is first order in acetonitrile and in ruthenium complex, with a forward rate constant of 6.3×10^{-3} M^{-1} s^{-1} and an equilibrium constant of 0.4 M^{-1} at 25 °C and pH 3. The rate is a strong function of pH with no observable contribution from the diaquo species below pK_{a1} (1.5) or from the dihydroxo species above pK_{a2} (5.2). (K_{a1} and K_{a2} are the acid dissociation constants for the diaquo and the aquo hydroxo complexes.) The ruthenium(III) complex catalyzes the substitution reactions of *trans*-$Ru(NN)_2(H_2O)_2^{2+}$, and a catalytic mechanism is defined. The isomerization of *trans*-$Ru(NN)_2(H_2O)(OH)^{2+}$ is first order with observed rate constants of 9.0×10^{-5} s^{-1} (NN = bpy) and 16×10^{-5} s^{-1} (NN = phen) at 50 °C and pH 5.7. The pH dependence of the isomerization is complex. The ruthenium(III) complex catalyzes the isomerization of *trans*-$Ru(NN)_2(H_2O)_2^{2+}$ by a mechanism analogous to the substitution mechanism. Activation enthalpies and entropies are 49 ± 3 kJ/mol and −114 ± 6 J/(mol K) for the substitution reaction of the bpy complex and 62 ± 3 kJ/mol and −111 ± 10 J/(mol K) and 55 ± 2 kJ/mol and −130 ± 5 J/(mol K) for isomerization of the bpy and phen complexes, respectively.

Introduction

In spite of the extensive use of (polypyridyl)ruthenium complexes as photosensitizers and as redox reagents, very few kinetic studies of ligand-exchange reactions of these species have been reported.[1-4] An important property of these reagents is the inert nature of the coordination sphere around the ruthenium(II) and ruthenium(III) centers. One previous study[1] has shown that aquo ligands of cis and trans isomers of ruthenium(II) can substitute fairly rapidly (eq 1 and 2).

$$Ru(NN)_2(H_2O)_2^{2+} + L \rightarrow Ru(NN)_2(H_2O)(L)^{2+} + H_2O \quad (1)$$

$$Ru(NN)_2(H_2O)(L)^{2+} + L \rightarrow Ru(NN)_2(L)_2^{2+} + H_2O \quad (2)$$

NN = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen); L = acetonitrile, pyridine

In that study, catalysis of substitution in the *trans*-$Ru^{II}(NN)_2(H_2O)_2^{2+}$ species (eq 1) was noted. This report identifies the catalytic species as *trans*-$Ru^{III}(NN)_2(H_2O)(OH)^{2+}$ and defines the catalytic mechanism. A study of the isomerization of *trans*-$Ru(NN)_2(H_2O)_2^{n+}$ (n = 2, 3) is also reported. For the isomerization in which n = 2, a catalytic mechanism is identified that shows some characteristics which are different from those of the substitution mechanism.

Experimental Section

Materials. *trans*-$[Ru(bpy)_2(H_2O)_2](PF_6)_2$,[5] *cis*-$[Ru(bpy)_2(H_2O)_2](PF_6)_2$,[6] *trans*-$[Ru(bpy)_2(H_2O)(OH)](ClO_4)_2$,[6] *trans*-$[Ru(phen)_2(H_2O)_2](PF_6)_2$,[5] *trans*-$[Ru(phen)_2(H_2O)(OH)](ClO_4)_2$,[6] and *cis*-$Ru(bpy)_2(Cl)_2 \cdot 2H_2O$[7] were prepared by literature methods, although in some cases procedures for phen and bpy complexes were interchanged. Departmental deionized water was passed through a Barnstead D0809 Demineralizer and then distilled from alkaline potassium permanganate. Acetonitrile was distilled from calcium hydride and phosphorus pentoxide. Other chemicals were reagent grade and were used without further purification. Trifluoroacetic acid, acetate, borate, and phosphate buffers were used to control pH.

Preparation of *cis*-$Ru(bpy)_2(H_2O)_2^{3+}$. Attempts to isolate solid samples containing *cis*-$Ru(bpy)_2(H_2O)_2^{3+}$ were unsuccessful. Therefore, solutions were generated from *cis*-$Ru(bpy)_2(Cl)_2^{+}$ by the following method.[8] *cis*-$[Ru(bpy)_2(Cl)_2]Cl$ was prepared by treating aqueous solutions of *cis*-$Ru(bpy)_2(Cl)_2 \cdot 2H_2O$ with concentrated HCl and HNO_3 and collecting the solid product. *cis*-$[Ru(bpy)_2(Cl)_2]Cl$ (110 mg) was added to a 100-mL flask, and the flask was flushed with nitrogen. Two milliliters of trifluoromethanesulfonic acid was added. The contents of the flask were stirred and heated gently until the nitrogen flow through the flask showed no evidence for further HCl evolution. During this time the flask contents changed from dark to deep green to deep blue. Water was added slowly to the cooled flask. The contents were transferred to a 25-mL volumetric flask, diluted to volume, and stored in a freezer. Solutions stored in this manner seemed to be stable for several weeks. The concentration of *cis*-$Ru(bpy)_2(H_2O)_2^{3+}$ in the final solution was about 8×10^{-3} M by spectral analysis, and the acid concentration was about 0.34 M by titration with sodium hydroxide.

Table I. pK_a Values for Aquoruthenium Complexes (22 ± 2 °C)

complex	pK_{a1}	pK_{a2}	ref
Ruthenium(II)			
cis-$Ru(bpy)_2(H_2O)_2^{2+}$	8.9		*a*
trans-$Ru(bpy)_2(H_2O)_2^{2+}$	9.3		*a*
trans-$Ru(phen)_2(H_2O)_2^{2+}$	10.1		*a*
Ruthenium(III)			
cis-$Ru(bpy)_2(H_2O)_2^{3+}$	1.8	4.9	*b*
trans-$Ru(bpy)_2(H_2O)_2^{3+}$	1.5	5.2	*b*
cis-$Ru(phen)_2(H_2O)_2^{3+}$	1.8	5.0	*b*
trans-$Ru(phen)_2(H_2O)_2^{3+}$	1.5	5.2	*b*

[a] Reference 1. [b] This work.

Equipment. UV–visible spectral information was obtained on a Varian DMS-100, Hitachi 100-80, or Beckman DB-GT spectrophotometer. The temperature was controlled with a Neslab RTE-8 bath/circulator.

Determination of pK_a's. The pK_a's of the aquoruthenium reactants were determined by spectrophotometric methods. Spectra were analyzed at the wavelength where the maximum absorbance change occurred in the reversible process attributed to deprotonation–protonation of the aquo ligands. The inflection points in plots of absorbance vs pH were used to identify the pK_a's (Table I).[9]

Kinetic Methods. Observed rate constants were calculated by linear least-squares fitting of the absorbance vs time data to zero-order (A vs t) and first-order rate expressions ($\ln (A - A_\infty)$ vs t) for catalyzed and uncatalyzed reactions, respectively.

Catalyzed Ruthenium(II) Substitution or Isomerization Reactions. Stock solutions of ruthenium(II), acetonitrile (if needed), and ruthenium(III) or Ce^{IV} were brought to the correct temperature, mixed in the desired proportion, and placed in the thermostated cell holder of the spectrophotometer. Initial studies involved monitoring the visible spectra of the solution at regular intervals during the reaction to characterize the nature of the reaction. Subsequently, absorbance vs time data were obtained by measurements from the spectra or by monitoring of absorbance vs time at an appropriate wavelength. For the trans complex,

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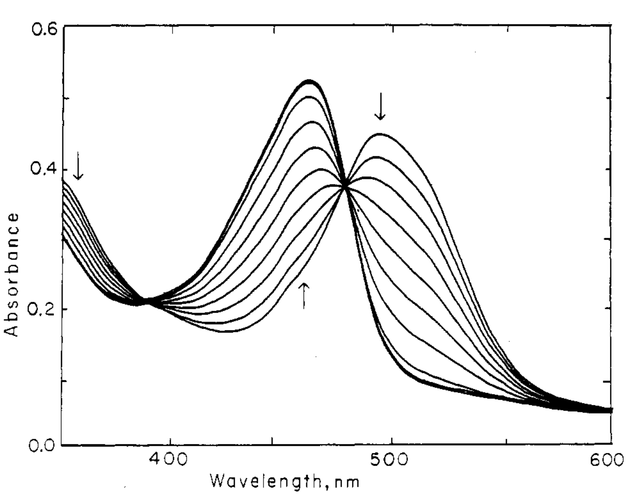

Figure 1. Spectral changes for the reaction of *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ (4×10^{-5} M) with CH_3CN (1 M) in the presence of added *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$ (1×10^{-5} M) at 25 °C and pH 3. Spectra were recorded at 3-min intervals.

near-zero-order behavior was observed and the rate of the reaction, $\Delta C/\Delta t$, was calculated from the slope of the absorbance vs time data near the beginning of the reaction and the molar absorptivity difference ($\Delta\epsilon$) of the reactant and product at the analysis wavelength. The rate law given in eq 3 or 4, where a term is included for both the ruthenium(II)

$$\text{rate} = k^{II}{}_{s}[Ru^{II}][CH_3CN] + k^{III}{}_{obsd}[Ru^{III}][CH_3CN] \qquad (3)$$

$$\text{rate} = k^{II}{}_{i}[Ru^{II}] + k^{III}{}_{i}[Ru^{III}{}_{i}] \qquad (4)$$

and the ruthenium(III) contributions to the rate, was used as the basis for interpretation. The ruthenium(II) reaction rate ($k^{II}{}_{s}[Ru^{II}][CH_3CN]$ or $k^{II}{}_{i}[Ru^{II}]$, where $k^{II}{}_{s} = 1.9 \times 10^{-5}$ M^{-1} s^{-1}[1] or $k^{II}{}_{i} = 6 \times 10^{-6}$ s^{-1} (vide infra)) was subtracted from the total rate and $k^{III}{}_{obsd}$ or $k^{III}{}_{i}$ was calculated by dividing the net rate by the product of the ruthenium(III) and acetonitrile concentrations or ruthenium(III) concentration, respectively. The total ruthenium(III) concentration (added, generated by Ce^{IV}, or inherent in the ruthenium(II) sample) was determined by spectral analysis of the product solution before and after reduction with hydroquinone.

Ruthenium(III) Substitution and Isomerization Reactions. The natures of the chemical reactions were characterized by monitoring the spectra of the reaction solutions at appropriate time intervals. For the isomerization reactions, the spectra of the reactant and product were well characterized at all pHs used and the absorbance changes were as expected for isomerization. Under some conditions, subsequent reactions occurred, such as reduction to ruthenium(II) or oxo-bridged ruthenium dimer formation, and kinetic data were carefully taken to avoid interference from these reactions. For both isomerization and substitution reactions, the nature of the reaction was confirmed by reductive quenching of the reaction solution with hydroquinone at various times during the reaction and then spectral analysis of the resulting ruthenium(II) species, which are well characterized.[1] All evidence suggests that the reduction was fast and no ligand exchange or isomerization occurred during reduction or previous to analysis as ruthenium(II). As such the ruthenium(II) analysis presented an accurate picture of the ruthenium(III) system. For ruthenium(III) substitution studies, small absorbance changes at low acetonitrile concentrations and rapid rates at high concentrations led to relatively high standard deviations in k_{obsd} (typically 10–20%). Therefore, unacceptable uncertainty in the slope and intercept of plots of k_{obsd} vs $[CH_3CN]$ was obtained. The sum of $k_f + k_r$ was determined from the calculated k_{obsd} value at an acetonitrile concentration equal to 1 M. With use of the value of 0.4 M^{-1} for K_{eq} (k_f/k_r), as obtained from spectral studies (vide infra), the individual values of k_f and k_r were calculated.

Results

Substitution Reactions. Catalysis of Ruthenium(II) Substitution by Ruthenium(III). Initial studies of the substitution reaction in eq 1 (L = CH_3CN; NN = phen; trans isomer) indicated a zero-order dependence on ruthenium(II). However, the zero-order rate constants in successive kinetic runs showed a dependence on initial ruthenium concentration, suggesting that some contaminant in the ruthenium sample was catalyzing the reaction. Because of the oxygen sensitivity of the ruthenium(II) complex,[6] an oxidized ruthenium species was the suspected catalyst. Indeed, addition of hydroquinone or ascorbic acid to the kinetic samples as reducing agents eliminated the catalytic effect and well-behaved first-order kinetics were observed for eq 1 and 2.

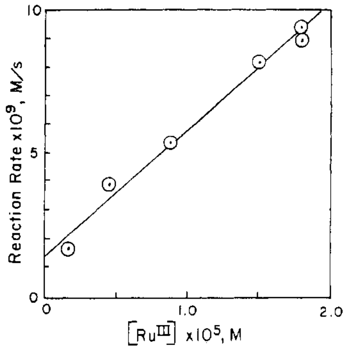

Figure 2. Influence of ruthenium(III) on the rate of substitution of acetonitrile into *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ (25 °C, pH 4.9).

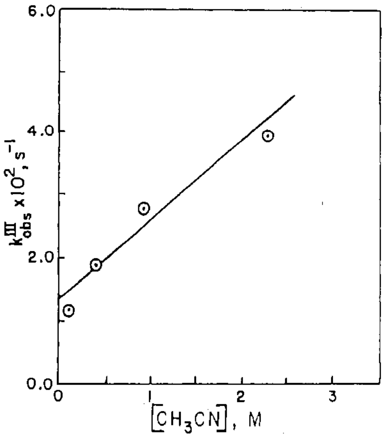

Figure 3. Acetonitrile concentration dependence of the observed rate constant for substitution of acetonitrile into *trans*-$Ru(bpy)_2(H_2O)OH^{2+}$ (25 °C, pH 3.1).

To investigate the catalytic behavior of the reaction in eq 1, solutions of *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ and acetonitrile were partially oxidized to ruthenium(III) by addition of cerium(IV), or ruthenium(III) was added directly as *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$. Cerium(IV) is known to oxidize ruthenium(II) to ruthenium(III),[6] so the same ruthenium content is obtained under each condition. Strictly zero-order dependence on ruthenium(II) was observed (Figure 1). The zero-order reaction rate was enhanced in proportion to the concentration of ruthenium(III) (Figure 2). The intercept in Figure 2 corresponds to the intrinsic ruthenium(II) reaction rate ($k^{II}{}_{s}[CH_3CN][Ru^{II}]$) under the conditions used.

Ruthenium(III) Substitution. Substitution of acetonitrile for an aquo ligand in *trans*-$Ru(bpy)_2(H_2O)OH^{2+}$ (eq 5) was studied under pseudo-first-order conditions similar to those used for the catalytic reactions (pH 3, 25 °C). Pseudo-first-order rate constants that were linearly dependent on acetonitrile concentration were observed. However, the extent of the reaction, as indicated by the absorbance change toward the spectrum of the final product, depended on acetonitrile concentration and was independent of ruthenium concentration. Very high acetonitrile concentrations (2–4 M) were required to achieve significant product formation. The plot of $k^{III}{}_{obsd}$ vs $[CH_3CN]$ exhibited a nonzero intercept (Figure 3). Both observations suggest that an equilibrium exists between the ruthenium(III) species and acetonitrile and, as such, $k^{III}{}_{obsd} = k^{III}{}_{s,f}[CH_3CN] + k^{III}{}_{s,r}$, where $k^{III}{}_{s,f}$ and $k^{III}{}_{s,r}$ are the individual forward and reverse rate constants for eq 5. The plot of $k^{III}{}_{obsd}$ vs $[CH_3CN]$ (Figure 3, 25 °C) has a slope ($k^{III}{}_{s,f}$) of 6.3×10^{-3} M^{-1} s^{-1} and an intercept ($k^{III}{}_{s,r}$) of

$$trans\text{-}Ru(bpy)_2(H_2O)(OH)^{2+} + CH_3CN \xrightarrow{k^{III}{}_{obsd}} trans\text{-}Ru(bpy)_2(CH_3CN)(OH)^{2+} + H_2O \qquad (5)$$

$14 \times 10^{-3}\ s^{-1}$. From this an equilibrium constant of 0.4 M^{-1} is obtained. Attempts to generate *trans*-$Ru(bpy)_2(CH_3CN)(OH)^{2+}$ by chemical or electrochemical oxidation of *trans*-$Ru(bpy)_2(CH_3CN)(H_2O)^{2+}$ in water resulted in formation of *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$, confirming that rapid solvolysis of the acetonitrile ligand occurs when the ruthenium is in the +3 oxidation state.

The nature of the substitution reaction was confirmed by a quenching study, where an aliquot of the reaction mixture was rapidly reduced to ruthenium(II) with hydroquinone or ferrous sulfate at various times during the reaction. The spectrum of the resulting solution was recorded before any significant change in the ruthenium(II) species could occur. There was no indication that the reduction process produced any change in the ruthenium coordination sphere except possibly protonation of a hydroxo ligand when present. The quenching study showed that a smooth reaction from aquo reactant toward acetonitrile-substituted product (eq 5) occurred at a rate similar to that determined from the spectral changes observed in the ruthenium(III) solution. On the basis of the known spectra[5,6,10] of *trans*-$Ru(NN)_2(H_2O)_2^{2+}$ and *trans*-$Ru(NN)_2(CH_3CN)(H_2O)^{2+}$, the spectral changes observed in the quenching studies also confirmed the value of 0.4 M^{-1} found for the equilibrium constant in the rate studies.

Substitution Catalysis Mechanism. The rate constant calculated from the ruthenium(III) study ($k^{III}_{s,f} = 6.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 25 °C, pH 3) is considerably larger than the ruthenium(II) rate constant under the same conditions ($k^{II}_s = 1.9 \times 10^{-5}\ M^{-1}\ s^{-1}$) and could easily provide the catalytic substitution route. A mechanism that can account for the catalysis of the ruthenium(II) substitution is shown in Scheme I (coordinating $(NN)_2(X)$ groups ($X = H_2O, OH^-$) are omitted):

Scheme I

$$Ru^{II}(H_2O) + CH_3CN \xrightarrow{k^{II}_s} Ru^{II}(CH_3CN) + H_2O$$

$$Ru^{III}(H_2O) + CH_3CN \xrightarrow{k^{III}_{s,f}} Ru^{III}(CH_3CN) + H_2O$$

$$Ru^{III}(CH_3CN) + Ru^{II}(H_2O) \xrightarrow{k_{et}} Ru^{II}(CH_3CN) + Ru^{III}(H_2O)$$

According to the scheme, the rate of appearance of $Ru^{II}(CH_3CN)$ would be

$$d[Ru^{II}(CH_3CN)]/dt = k^{II}_s[Ru^{II}(H_2O)][CH_3CN] + k_{et}[Ru^{II}(H_2O)][Ru^{III}(CH_3CN)]$$

The electron-transfer step is known to be thermodynamically favorable.[10] (Reduction potentials are 1.15 V for *trans*-$Ru(bpy)_2(CH_3CN)(H_2O)^{3+/2+}$ in CH_2Cl_2 and 0.46 V for *trans*-$Ru(bpy)_2(H_2O)_2^{3+/2+}$, in 1 N CF_3CO_2H, each vs SCE. Although the potentials were measured in different media, they indicate that *trans*-$Ru(bpy)_2(CH_3CN)(H_2O)^{3+}$ is undoubtedly capable of oxidizing the diaquoruthenium(II) complex in aqueous solution.) If we assume that k_{et} is large (as usually observed for (polypyridyl)ruthenium complexes[6,11,12]) and apply the steady-state approximation to $[Ru^{III}(CH_3CN)]$, the rate reduces to

$$d[Ru^{II}(CH_3CN)]/dt = k^{II}_s[Ru^{II}(H_2O)][CH_3CN] + k^{III}_{s,f}[Ru^{III}(H_2O)][CH_3CN]$$

If $k^{III}_{s,f}[Ru^{III}(H_2O)] \gg k^{II}_s[Ru^{II}(H_2O)]$, the rate law dependence would reduce to

$$\text{rate} = k^{III}_{s,f}[Ru^{III}(H_2O)][CH_3CN]$$

Thus, the catalyzed reaction rate is independent of $[Ru^{II}(H_2O)]$ and exhibits the ruthenium(III) and acetonitrile dependence observed. The rate constant $k^{III}_{s,f}$, calculated from catalyzed substitution ($2 \times 10^{-3}\ M^{-1}\ s^{-1}$), is comparable to that observed during the ruthenium(III) substitution study, which suggests that *trans*-$Ru(NN)_2(H_2O)(OH)^{2+}$ is the species responsible for the ruthenium(II) catalysis.

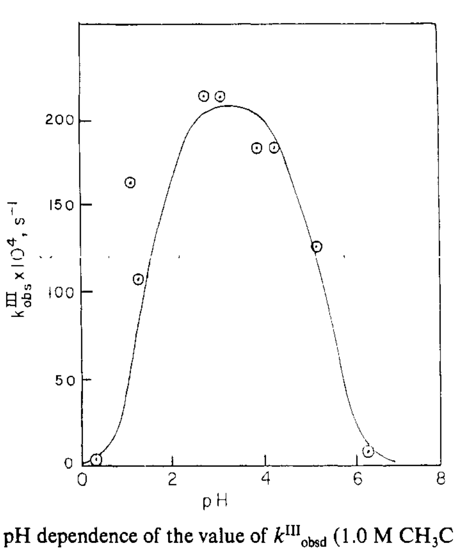

Figure 4. pH dependence of the value of k^{III}_{obsd} (1.0 M CH_3CN, 25 °C).

pH Dependence of k^{III}_{obsd}. Aquometal complexes become more acidic as their oxidation state increases. Therefore, the pK_a's for a number of aquo complexes relevant to this study were determined and are listed in Table I. These pK_a's, obtained from spectral studies, agree well with those obtained from electrochemical measurements.[13] The diaquoruthenium(III) species are considerably more acidic (p$K_{a1} \approx 1.5$) than the ruthenium(II) species (p$K_{a1} \approx 10$) and indeed show a second deprotonation at low pH (p$K_{a2} \approx 5.2$). In the pH range studied (0–8) ruthenium(II) exists as the diaquo complex. Ruthenium(III) exists as the diaquo, aquo hydroxo, and dihydroxo complexes at pH <1.5, 1.5 < pH < 5, and pH >5, respectively. The possible ruthenium(III) substitution reactions are then

$$Ru(H_2O)_2^{3+} + CH_3CN \xrightarrow{k^{III}_{obsd}{}'} Ru(H_2O)(CH_3CN)^{3+} + H_2O \quad (6)$$

$$Ru(H_2O)(OH)^{2+} + CH_3CN \xrightarrow{k^{III}_{obsd}} Ru(CH_3CN)(OH)^{2+} + H_2O \quad (7)$$

$$Ru(OH)_2^{+} + CH_3CN \xrightarrow{k^{III}_{obsd}{}''} Ru(CH_3CN)(OH)^{2+} + OH^- \quad (8)$$

(The pK_a values for the acetonitrile complexes are unknown but are assumed to be similar to those for the diaquo complexes on the basis of a comparison within the ruthenium(II) species.[1]) Therefore, the total ruthenium(III) substitution rate over the pH range studied may be expressed as

$$\text{rate} = k^{III}_{obsd}{}'[CH_3CN][Ru(NN)_2(H_2O)_2^{3+}] + k^{III}_{obsd}[CH_3CN][Ru(NN)_2(H_2O)(OH)^{2+}] + k^{III}_{obsd}{}''[CH_3CN][Ru(NN)_2(OH)_2^{+}]$$

The pH dependence of the calculated substitution rate constant, k^{III}_{obsd}, at 1 M acetonitrile concentration is shown in Table II and Figure 4. The rate shows a significant decrease at pH < pK_{a1} and pH > pK_{a2}. The rates at high or low pH are highly uncertain and may represent an upper limit because competitive reactions occur under those conditions (vide infra). The data suggest that *trans*-$Ru(NN)_2(H_2O)OH^{2+}$ is the only ruthenium(III) species that exhibits significant substitution rates in the pH range from 0 to 8, i.e. $k^{III}_{obsd}{}'$ and $k^{III}_{obsd}{}''$ are small compared to k^{III}_{obsd} and may be neglected. It is possible that the forward or reverse reactions in eq 6 and 8 do make a contribution to the rate law

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Table II. pH Dependence of the Substitution Rate Constant for the Reaction of Acetonitrile with *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$ at 25.0 ± 0.2 °C

pH	$[CH_3CN]$, M	$10^4k^{III}_{obsd}$, s^{-1}	$10^4k^{III}_{obsd}$ at 1 M $[CH_3CN]$, s^{-1}	$10^4k^{III}_{s,f}$, $M^{-1}\ s^{-1}$
0.3	1.43	3	2	0.6
	2.31	4		
	3.10	5		
1.1	0.164	90	168	48
	0.476	130		
	0.909	170		
	1.43	200		
	3.10	340		
1.2	1.02	120	110	31
	2.04	130		
	4.08	200		
2.8	1.02	210	220	63
	2.04	280		
	4.08	320		
3.1	0.164	110	220	63
	0.909	190		
	1.43	280		
	2.31	370		
3.9	1.02	180	190	54
	2.04	280		
	4.08	390		
4.3	1.02	190	190	54
	2.04	240		
	4.08	320		
5.2	1.02	120	130	37
	2.04	150		
	4.08	120		
6.3	0.95	2	2	1
	3.82	6		
3.1[a]	0.476	75	81	30
	1.43	90		
	2.30	95		
	3.10	140		
3.1[b]	0.909	100	108	59
	1.43	130		
	2.31	160		
	3.10	190		
3.1[c]	0.625	240	306	220
	0.909	250		
	2.00	560		

[a] 3.4 °C. [b] 11.1 °C. [c] 34.5 °C.

under some conditions, but the data obtained and the presence of competitive reactions preclude consideration of these reactions. Thus, the rate law considered is

$$\text{rate} = k^{III}_{obsd}[Ru(H_2O)(OH)^{2+}] = (k^{III}_{s,f}[CH_3CN] + k^{III}_{s,r})[Ru(H_2O)(OH)^{2+}]$$

With use of the measured pK_a values, $[Ru(H_2O)(OH)^{2+}]$ can be related to the total ruthenium(III) concentration $[Ru^t]$ by the expression

$$[Ru(H_2O)(OH)^{2+}] = K_{a1}[Ru^t][H^+]/A$$

$$A = [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}$$

and the final rate law is

$$\text{rate} = (k^{III}_{s,f}[CH_3CN] + k^{III}_{s,r})K_{a1}[Ru^t][H^+]/A \quad (9)$$

The curve shown in Figure 4 was obtained by using eq 9 with $k^{III}_{s,f} = 6.3 \times 10^{-3}$, $k^{III}_{s,r} = 14 \times 10^{-3}$, and $[CH_3CN] = 1$ M. The agreement between experimental and calculated results is reasonably good, considering the quality of the data.

The catalyzed ruthenium(II) reaction shows the same pH dependence as for the ruthenium(III) reaction, which provides further support for the identification of *trans*-$Ru(bpy)_2(OH_2)(OH)^{2+}$ as the catalytic species.

The activation enthalpy and entropy for $k^{III}_{s,f}$ as calculated from the temperature dependence shown in Table II are 49 ± 3 kJ/mol and −120 ± 6 J/(mol K), respectively.

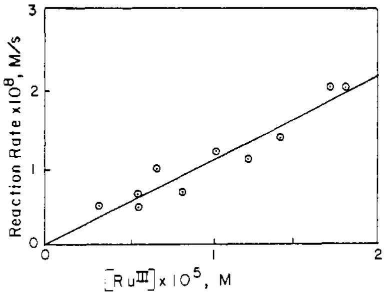

Figure 5. Influence of ruthenium(III) on the rate of trans to cis isomerization of *trans*-$Ru(phen)_2(H_2O)_2^{2+}$ at 50 °C and pH 5.

***cis*-$Ru(bpy)_2(H_2O)_2^{3+}$.** The cis ruthenium(II) complex is not subject to catalytic rate enhancement by ruthenium(III). Both kinetic and thermodynamic factors contribute to this situation. First, the ruthenium(II) substitution rate constant is considerably larger for the cis isomer ($80 \times 10^{-5}\ M^{-1}\ s^{-1}$) than for the trans species ($1.9 \times 10^{-5}\ M^{-1}\ s^{-1}$),[1] so the ruthenium(II) rate may be more competitive with the ruthenium(III) rate for the cis isomer. Second, the formation of the ruthenium(III)–acetonitrile complex appears to be thermodynamically less favorable for the cis isomer than for the trans species. Addition of acetonitrile to solutions of *cis*-$Ru(bpy)_2(H_2O)(OH)^{2+}$ gave no indication of complex formation by spectral analysis. However, solutions of *cis*-$Ru(bpy)_2(H_2O)(OH)^{2+}$ containing acetonitrile did indicate slow formation of an acetonitrile-substituted ruthenium(II) species, which may result from spontaneous reduction of trace quantities of an acetonitrile-substituted ruthenium(III) species. The equilibrium concentration of this species must be too small to produce significant spectral changes or to contribute to a catalytic mechanism. The larger equilibrium constant for the acetonitrile adduct of the trans complex is reasonable if metal–ligand π-interaction involving trans ligands is important. Hydroxide, as a good π-donor in a trans position, may provide π-electron density to enhance the trans acetonitrile–ruthenium(III) bond strength through π-acceptor interaction.

Isomerization. Because the isomerization reactions were fairly slow, particularly for ruthenium(II), rate constants were measured at 50 °C. The spectra of the ruthenium(II) and ruthenium(III) reactants and products are well-characterized, and spectral changes during isomerization are as expected for complete conversion to cis products. In some cases, an increase in absorbance at about 650 nm occurred during the later stages of the reaction, indicating formation of oxo-bridged species.[14]

Catalyzed Ruthenium(II) Isomerization. The trans to cis isomerization reactions of *trans*-$Ru(NN)_2(H_2O)_2^{2+}$ are also subject to catalysis by ruthenium(III). In the presence of *trans*-$Ru(phen)_2(H_2O)(OH)^{2+}$ the isomerization of *trans*-$Ru(phen)_2(H_2O)_2^{2+}$ occurs by a zero-order process. The isomerization rate is proportional to the concentration of the ruthenium(III) (Figure 5), as observed for the substitution reaction. In this case the intercept is equal to zero, within experimental error, indicating that the ruthenium(II) isomerization rate is insignificant compared to that of ruthenium(III).

A mechanism analogous to the substitution mechanism is presented in Scheme II to account for the isomerization catalysis:

Scheme II

$$trans\text{-}Ru(NN)_2(H_2O)_2^{2+} \xrightarrow{k^{II}_i} cis\text{-}Ru(NN)_2(H_2O)_2^{2+} \quad (10)$$

$$trans\text{-}Ru(NN)_2(H_2O)(OH)^{2+} \xrightarrow{k^{III}_i} cis\text{-}Ru(NN)_2(H_2O)(OH)^{2+} \quad (11)$$

$$cis\text{-}Ru(NN)_2(H_2O)(OH)^{2+} + trans\text{-}Ru(NN)_2(H_2O)_2^{2+} \xrightarrow{k_{et}'} cis\text{-}Ru(NN)_2(H_2O)_2^{2+} + trans\text{-}Ru(NN)_2(H_2O)(OH)^{2+} \quad (12)$$

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(14) Geselwitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015 and references therein.

Table III. pH Dependence of the Isomerization Rate Constants for *trans*-$Ru(NN)(H_2O)(OH)^{2+}$ ($[Ru^{III}] \approx 5 \times 10^{-5}$ M, 50.6 ± 0.4 °C, 0.01 M Ionic Strength)

trans-$Ru(NN)_2(H_2O)(OH)^{2+} \rightarrow$ *cis*-$Ru(NN)_2(H_2O)(OH)^{2+}$

pH	$10^4k^{III}_i$, s^{-1}	pH	$10^4k^{III}_i$, s^{-1}
	NN = 1,10-Phenanthroline		
0.0	6.4	5.8	16
0.4	5.9	6.0	20
0.5	5.6	6.1	18
1.1	3.5	6.4	16
1.5	2.2	7.2	6.6
1.7	2.2	8.5	3.5
1.8	1.7	9.7	0.1
2.2	2.7	4.9	0.69 (9.8 °C)
3.5	4.5	4.9	1.9 (19.4 °C)
4.0	8.0	4.9	4.3 (31.1 °C)
5.0	13	4.9	9.8 (41.7 °C)
5.1	17		
	NN = 2,2′-Bipyridyl		
0.5	4.0	7.3	2.9
1.3	2.2	8.5	1.6
2.8	1.2	8.8	3.0
2.9	1.3	9.7	0.3
4.0	4.7	4.9	0.29 (10.3 °C)
4.9	11	4.9	1.00 (19.8 °C)
5.7	9	4.9	2.4 (30.1 °C)
6.3	8	4.9	4.6 (40.0 °C)
6.6	5.4		

Again the electron-transfer step is thermodynamically favorable[6] with reduction potentials for *cis*- and *trans*-$Ru(bpy)_2(H_2O)_2^{3+/2+}$ of 0.63 and 0.46 V (vs SSCE in aqueous trifluoroacetic acid), respectively. The predicted rate law based on Scheme II reduces to

$$d[trans\text{-}Ru^{II}]/dt = k^{II}_i[trans\text{-}Ru^{II}(H_2O)] + k^{III}_i[trans\text{-}Ru^{III}(H_2O)] \quad (13)$$

The reaction was analyzed under conditions where the first term is small and the value of k^{III}_i (NN = phen) was found to be 13 $\times 10^{-4}$ s^{-1} at pH 5 and 50 °C.

Ruthenium(III) Isomerization. Rate constants for the trans to cis isomerization of trans Ru^{III} complexes (eq 11) are fairly low, even at 50 °C (Table III). The phen complex isomerizes about twice as rapidly as the bpy complex at this temperature. For the phen complex, the rate constant measured directly for the ruthenium(III) ($k^{III}_i = 13 \times 10^{-4}$ s^{-1}) agrees well with the value obtained under conditions where the net isomerization is carried by electron transfer catalysis in Scheme II ($k^{III}_i = 13 \times 10^{-4}$ s^{-1} at pH 5 and 50 °C).

The observed pH dependence of the isomerization rate constant for *trans*-$Ru(NN)_2(H_2O)(OH)^{2+}$ (Figure 6: part a, NN = phen; part b, NN = bpy) is significantly different from the results obtained for substitution. The slight increase at pH <2 could conceivably be a medium effect since 0.01 M ionic strength was typically used at higher pH. However, variation of ionic strength of the buffer system from 0.001 to 0.1 M at pH 5 had no significant effect on the reaction rate, suggesting that an acid-catalyzed path may contribute to the overall rate at low pH.

The maximum rate constant near pH = pK_{a2}, where *trans*-$Ru(NN)_2(H_2O)(OH)^{2+}$ and *trans*-$Ru(NN)_2(OH)_2^+$ are in equal concentration, may suggest that a bimolecular reaction between these species is responsible for the isomerization. However, the rate data definitely fit first-order and not second-order kinetics with respect to the ruthenium. In addition, the calculated rate constants are independent of initial ruthenium(III) concentration. A mechanistic interpretation of the observed pH dependence is not known.

The activation enthalpy and activation entropy for the isomerization reactions, obtained from the temperature dependence of the rate constants k^{III}_i of the bpy and phen ruthenium(III) complexes at pH 5, were found to be 62 ± 3 and 55 ± 2 kJ/mol and −111 ± 10 and −130 ± 5 J/(mol K), respectively.

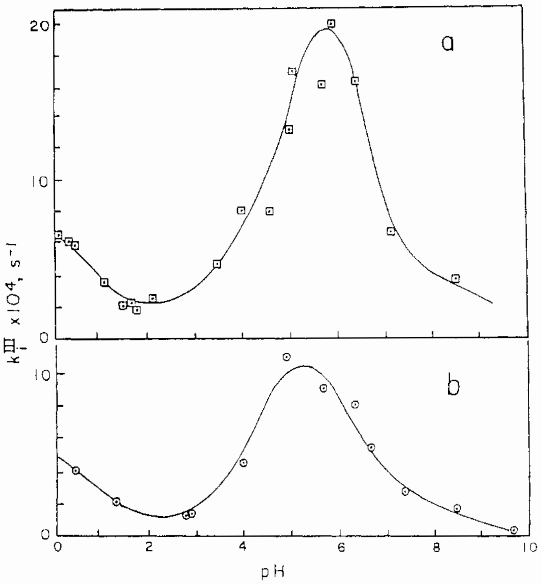

Figure 6. pH dependence of the rate constant for isomerization of (a) *trans*-$Ru(phen)_2(H_2O)(OH)^{2+}$ and (b) *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$ at 50 °C. (Curves are presented merely to indicate trends in data.)

Ruthenium(II) Isomerization. The intrinsic rate constant for isomerization of the ruthenium(II) complexes *trans*-$Ru(phen)_2(H_2O)_2^{2+}$ and *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ was so slow, even at 50 °C, that only an upper limit of 6 × 10^{-6} s^{-1} could be established for k^{II}_i. The slow rate of isomerization was complicated by competitive reactions. Trace quantities of ruthenium(III) may not have been the sole contributing factor since complications persisted when reductants such as ascorbic acid and hydroquinone were used to eliminate oxidized contaminants.[1] Evacuation of reaction solutions or deaeration by flushing with nitrogen had no significant effect on the results. From the data obtained, the ruthenium(II) isomerization reactions appear to have a pH dependence similar to the ruthenium(III) dependence.

Discussion

Substitution. Ruthenium(III) substitution reactions are often slower than those for ruthenium(II) complexes,[15,16] so, on the surface, the catalysis of ruthenium(II) reactions by ruthenium(III) appears unusual. However, the catalysis is partially an artifact of the pK_a's of the aquo complexes. The acetonitrile substitution rate constant for *trans*-$Ru(bpy)_2(H_2O)(OH)^+$ (1.9×10^{-3}) is similar to that of *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$ (6.3×10^{-3}), and that of *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ is presumably greater than that of *trans*-$Ru(bpy)_2(H_2O)_2^{3+}$ since no definitive evidence for substitution in the latter was obtained.

The enhancement of the rate constant for substitution at the ruthenium(II) or ruthenium(III) center when a nonsubstituting aquo ligand is converted to a hydroxo ligand is not unusual.[4,17] In this case the rate for the hydroxoruthenium(III) complex exceeds the aquoruthenium(II) rate and the redox potentials are appropriate for the existence of a catalytic process in the pH regions where diaquoruthenium(II) and aquohydroxoruthenium(III) are the dominant species in solution.

"Inverted" redox catalysis; where a ruthenium(III) complex promotes a ruthenium(II) complex substitution has been reported for the $Ru^{II/III}$(EDTA) system.[18] The catalysis was attributed to the influence of a pendant carboxylate group of the EDTA ligand. Obviously, such a mechanism is not occurring in this case. A pH study for the EDTA case showed a pH dependence qualitatively similar to that observed for *trans*-$Ru(bpy)_2(H_2O)(OH)^{2+}$

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(17) Tobe, M. L. *Inorganic Reaction Mechanisms*; Thomas Nelson: London, 1972; p 89.

(18) (a) Matsubara, T.; Creutz, C. *Inorg. Chem.* **1979**, *18*, 1956. (b) Matsubara, T.; Creutz, C. *J. Am. Chem. Soc.* **1978**, *100*, 6255.

substitution. At high pH deprotonation of the exchanging aquo ligand in *trans*-Ru(bpy)$_2$(H$_2$O)(OH)$^{2+}$ or in Ru(EDTA)(H$_2$O)$^-$, to produce a hydroxo ligand, greatly retards that ligand-exchange rate. At the lower pH end, the aquo ligand-exchange rate is greatly reduced by protonation of other ligands for both the EDTA and the bpy species, although the mechanism of action is greatly different. Protonation of the free carboxylate group for the EDTA system presumably retards the rate through a mechanism external to the metal center. For the bpy system, the retardation of the rate occurs by protonation of a trans hydroxo ligand and the action must be through the metal center.

Although the substitution reactions of *trans*-Ru(NN)$_2$(H$_2$O)$_2$$^{2+}$ occur by a dissociative route and those of *trans*-Ru(NN)$_2$(H$_2$O)(OH)$^{2+}$ appear to occur by an associative route, neither activation route opens the way to rearrangement to cis products. One substitution reaction, involving reaction of *trans*-Ru(bpy)$_2$(CH$_3$CN)(H$_2$O)$^{2+}$ with acetonitrile, is accompanied by isomerization[1] but the corresponding phen complex and other closely related reactions exhibit no isomerization during substitution. In general, substitution reactions of ruthenium(II) and ruthenium(III) are stereoretentive.

Hydrolysis of the substitution product Ru(NN)$_2$(CH$_3$CN)(OH)$^{2+}$ is possible because Ru(NH$_3$)$_5$(CH$_3$CN)$^{3+}$ undergoes extremely rapid acetonitrile hydrolysis to produce an acetamide-coordinated product.[19] If the rate constant for hydrolysis of the NN complex is comparable to that for the pentaammine (k = 220 M^{-1} s^{-1}), the hydrolysis rate would still be small compared to the rate of substitution in the pH range studied. No evidence for acetamide complexes was observed in the spectral analysis of product solutions. Therefore, interference from this reaction probably does not occur in the system studied.

The large negative entropy of activation and fairly small enthalpy of activation suggest that the substitution reaction proceeds by an associative route. The decrease in entropy is consistent with an increase in bonding on forming the transition state. The entropy of activation is considerably more negative than values typically observed for six-coordinate complexes, such as chromium(III) and manganese(II),[20,21] which are thought to undergo substitution by an associative route. In fact, the values obtained here are very close to those usually observed for substitution reactions of four-coordinate square-planar and tetrahedral complexes,[17,22] which are generally considered to undergo substitution by an associative mechanism.

Isomerization. The stability of *trans*-Ru(NN)$_2$(H$_2$O)$_2$$^{2+,3+}$ toward isomerization is obviously a kinetic effect since the cis isomer is thermodynamically favored. The steric hindrance due to the trans NN ligands is not great enough to induce excessive instability in these species, and their fairly recent introduction[5,6] is surprising in reflection. Theoretical calculations[23] have suggested that trans to cis rearrangement for d^6 complexes by either an intramolecular twist mechanism or a dissociative mechanism is energetically unfavorable and the observed slow ruthenium(II) isomerization is expected.

The more rigid 1,10-phenanthroline system induces a ruthenium(III) isomerization rate only twice that of the bipyridyl system. The somewhat smaller $\Delta H^\ddagger$ value for the phen complex probably reflects the greater steric strain in this species relative to that for the bpy complex. Since the strain is probably removed on moving to the transition state, the lower activation barrier is attributed to the higher energy ground state. The ruthenium(III) isomerization activation parameters are very close to those observed for substitution. However, the vastly different pH dependences suggest that the activation mechanisms may be quite different. The large negative entropy of activation is consistent with the Ray and Dutt intramolecular twist process for the isomerization reaction.[24]

Because the pH dependence and therefore the overall mechanism cannot be explained, the reason for the enhanced ruthenium(III) isomerization rate over that of ruthenium(II) is unclear. The hydroxo ligand is present in the ruthenium(III) complex, whereas ruthenium(II) exists as the aquo complex under the conditions studied. The hydroxo ligand tends to behave as a rate enhancer in the reaction of these species. A major effect may be net charge reduction on the complex and therefore weakening of metal–ligand bonding, making distortion of the complex a lower energy process.

Acknowledgment. The financial assistance of the UNCG Research Council and helpful discussions with Professor T. J. Meyer are gratefully acknowledged.

Registry No. *trans*-Ru(bpy)$_2$(H$_2$O)(OH)$^{2+}$, 72155-92-1; *trans*-Ru(phen)$_2$(H$_2$O)(OH)$^{2+}$, 108340-25-6; *trans*-Ru(bpy)$_2$(H$_2$O)$_2$$^{2+}$, 72174-10-8; *trans*-Ru(phen)$_2$(H$_2$O)$_2$$^{2+}$, 85439-53-8; acetonitrile, 75-05-8.

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