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Substitution Reactions of Ruthenium(II) Complexes Containing 2,2′-Bipyridine and 1,10-Phenanthroline

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The rates of substitution of a series of complexes of the general form $Ru(NN)_2(H_2O)X^{q+}$, where NN is bipyridine or phenanthroline and X is a monodentate ligand, have been examined in aqueous solution. For both the cis and trans isomers, the second-order rate constants for the substitution of water by acetonitrile depend on the X ligand in the following manner: $SO_2 > OH^- \simeq PPh_3 > H_2O > CH_3CN \simeq$ pyridine $>$ CO. Although no specific trans effect was noted, the rate constants for substitution in the cis isomers were larger than those for substitution in the corresponding trans isomers by a factor of about 10.

Introduction

In recent years, the chemistry of ruthenium(II) complexes containing 2,2′-bipyridine (bpy) and related chelates has become a major topic of discussion. Studies of electron-transfer reactions have relied heavily on these complexes[1] because of their apparent reluctance to undergo thermal substitution reactions. Fundamental studies of the photochemistry of metal complexes[2,3] have also featured polypyridyl complexes of ruthenium(II). Complexes containing three chelating ligands such as $Ru(bpy)_3^{2+}$ have played a major role in the study of the conversion of light energy into a more useful form.[4]

Despite this intense interest, only a few papers have appeared that deal with the thermal substitution reactions of ruthenium(II) coordinated to heteronuclear aromatic chelates.[5] This is in sharp contrast[7] to the chemistry of the simple ammine complexes[6–9] such as $Ru(NH_3)_5L^{n+}$. One of the few published studies[5] is that of Davies and Mullins, which deals with the substitution reactions of $Ru(bpy)_2(H_2O)_2^{2+}$ and some closely related complexes. Davies and Mullins pointed out, at that time, the advantages these complexes shared with the much studied Co(III) and Pt(II) complexes in the investigations of substitutional processes. The initial work was, unfortunately, not continued.

We wish to report an extension of this investigation. The reactivities of both cis and trans isomers of complexes of the general type $Ru(NN)_2XY^{n+}$, where NN is 2,2′-bipyridine or 1,10-phenanthroline, have been examined. Attention has been focused on possible trans effects and potential problems caused by the sterically constrained chelate rings. The data clearly show a wide range of reactivities and are similar in some respects to results obtained with the simple ammine complexes.[7] The results also suggest that an alternative interpretation of the kinetic data reported by Davies and Mullins[5] is necessary.

Experimental Section

Materials. The complexes *trans*-$[Ru(bpy)_2(H_2O)_2](ClO_4)_2$,[10] *trans*-$[Ru(phen)_2(H_2O)_2](PF_6)_2$,[11] *trans*-$[Ru(bpy)_2(CH_3CN)(H_2O)](ClO_4)_2$,[12] *trans*-$[Ru(phen)_2(CH_3CN)(H_2O)](PF_6)_2$,[11] *trans*-$[Ru(bpy)_2(SO_2)(H_2O)](PF_6)_2$,[13] *cis*-$[Ru(phen)_2(H_2O)_2](PF_6)_2$,[11] and *cis*-$[Ru(bpy)_2(NO_2)H_2O](PF_6)$[14] were prepared according to published procedures. The preparative procedures for the phenanthroline complexes were adapted from the procedures developed for the analogous bipyridine complexes. Water was either house distilled water redistilled over alkaline potassium permanganate or passed through a Bantam Demineralizer with a SYBRON/Barnstead Ultrapure cartridge (D0809). Acetonitrile was distilled from calcium hydride and phosphorus pentoxide. All other chemicals were reagent grade or better and were used as received.

***cis*-$[Ru(phen)_2(CH_3CN)(H_2O)](PF_6)_2\cdot H_2O$.** Fifteen milliliters of acetonitrile was cooled in an ice bath, 0.244 g of *cis*-$[Ru(phen)_2(H_2O)_2](PF_6)_2$ was added, and the reaction was monitored spectrally every few minutes. When the spectrum indicated that all of the diaquo complex had reacted, the reaction mixture was poured into 300 mL of ethyl ether. The product was collected by filtration and recrystallized by dissolving in acetone, adding water, and rotary evaporating. A small quantity of the disubstituted product was removed by filtering the mixture midway through the evaporation. The desired product, which precipitated following complete removal of acetone, was recovered by the filtration. Anal. Calcd for $[Ru(C_{12}H_8N_2)_2(CH_3CN)(H_2O)](PF_6)_2\cdot H_2O$: C, 37.69; H, 2.79; N, 8.45. Found: C, 37.78; H, 2.84; N, 8.57.

Kinetic Measurements. Rate measurements were carried out under pseudo-first-order conditions. The incoming ligand concentrations were usually 0.1 M or higher with the metal complex concentration between 10^{-4} and 10^{-5} M. Nitrite ion concentrations were in the range of 0.001–0.1 M. Ionic strength was similar for all reactions and was maintained by using 0.1 M buffers or 0.1 M CF_3SO_3H. Acetate buffer was used at pHs up to 5.5, and phosphate, borate, and MOPS (morpholinopropanesulfonic acid) buffers were used at higher pHs. Duplicate measurements were made at the higher pHs with the two different buffers to ensure that the buffers were not interfering with the reaction. Partially neutralized CF_3SO_3H solutions were used to check the reactions buffered with acetate buffer. In the case of the trans isomers of the diaquo complexes, reducing agents were added to the reaction mixtures to eliminate catalysis by metal complexes in higher oxidation states. Typically, 1.2 mg of hydroquinone or L-ascorbic acid was used in 25 mL of solution. Control experiments indicated that the observed rates were independent of the nature of the reducing agent. Since deaeration had no effect on measured rates, kinetic measurements were made with air-saturated solutions.

Samples were maintained at constant temperature in a Neslab RTE-8 temperature bath or in a temperature-controlled cell holder of the spectrophotometer (Varian DMS-90, Beckman DB-GT or Gilford). Absorbance vs. time data were either collected manually or collected by a Commodore 64 microcomputer through a home-built interface. All reactions were monitored at wavelengths of maximum absorbance or in the case of competing secondary reactions at an isosbestic point of the second reaction. In all cases, the initial and final spectra were consistent with those expected for the reactant and product, respectively.

Data Treatment. The observed rate constants were obtained from plots of ln $(A_t - A_\infty)$ vs. time where $-k_{obsd}$ = slope. In cases where a second reaction followed the initial reaction but did not interfere, A_∞ was calculated from the extinction coefficients of the initial products and only data taken at times at which the second reaction was insignificant were used. These reactions showed clean isosbestic points throughout the period in which data were collected.

Calculation of the slopes of the above plots was done using weighted least squares with the weighting factors given by $w_t = A_t - A_\infty$. The fit

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Table I. Second-Order Rate Constants for the Reactions of $Ru(NN)_2(H_2O)X^{2+}$ with Various Ligands (Y) at 25 °C

		10^5k, M^{-1} s^{-1}	
X	Y	NN = bpy	NN = phen
	Trans Isomers		
CH_3CN	CH_3CN	0.47	3.3
CH_3CN	3-Acpy	0.62	
H_2O	4-Acpy	1.4	
H_2O	CH_3CN	1.9	2.7
H_2O	py		2.8
OH^-	CH_3CN	190	
SO_2	CH_3CN	8400	
	Cis Isomers		
CO	CH_3CN	1.0	
py	CH_3CN	10	
CH_3CN	CH_3CN	14	6.8
NO_2^-	CH_3CN	40	
H_2O	CH_3CN	80	170
NO_2^-	NO_2^-	110	
OH^-	CH_3CN	170	
PPh_3	CH_3CN	180	
H_2O	NO_2^-	1800	

to first-order kinetics was also checked by a visual comparison of the exponential decay to that calculated on the basis of the derived rate constants. Second-order rate constants were obtained from the relation $k_{obsd} = k_{2nd}[\text{ligand}]$. Plots of k_{obsd} vs [ligand] were linear with intercepts of zero within experimental error except for the reaction of *trans*-$Ru(bpy)_2(SO_2)(H_2O)^{2+}$ with acetonitrile, which had a nonzero intercept. Curvature at high concentrations (>1.5 M) was noted in some cases.

The rate constants for the reaction of the hydroxo complexes were obtained from the dependence of reaction rate on pH. The relation

$$k_{obsd} = (k_1 + k_2K_a/[H^+])[\text{ligand}]$$

was used to obtain the second-order rate constants for the reaction of the aquo complex (k_1) and the hydroxo complex (k_2). The acid dissociation constant, K_a, was measured independently as described below.

Acid Dissociation Constants. The acid dissociation constants of the cis and trans isomers of $Ru(bpy)_2(H_2O)_2^{2+}$ were determined by the method described by Rosenblatt.[15] The method required absorbance measurements of solutions with three different pHs that bracket the approximate pK_a of the system under study. The pH was maintained with 0.1 M phosphate buffer or borate buffers and carefully measured with a pH meter. The absorbance of the solutions was measured at several different wavelengths with little variation in the calculated pK_a. The reported values are the average of all measurements.

Results

Substitution of $Ru(NN)_2(H_2O)_2^{2+}$. The ligand replacement reactions of the cis and trans isomers of $Ru(bpy)_2(H_2O)_2^{2+}$ and $Ru(phen)_2(H_2O)_2^{2+}$ have been extensively studied and found to exhibit well-behaved second-order kinetics with a variety of incoming ligands. In general, the species undergo substitution of water by acetonitrile, 4-acetylpyridine, or nitrite ion in two steps, represented by eq 1 and 2, which are separable by an appropriate

$$Ru(bpy)_2(H_2O)_2^{2+} + X \rightarrow Ru(bpy)_2(H_2O)X^{2+} \quad (1)$$

$$Ru(bpy)_2(H_2O)X^{2+} + X \rightarrow Ru(bpy)_2X_2^{2+} \quad (2)$$

choice of observation wavelengths. These observations indicate that the second-order rate constants for the second step are comparable to or smaller than those of the first step. The rate data summarized in Table I confirm these general observations. The only case where the two steps were inseparable was the substitution of *trans*-$Ru(phen)_2(H_2O)_2^{2+}$ by pyridine. The rate constants listed in Table I were determined under pseudo-first-order conditions with ligand concentrations in the range of 0.1–4 M and complex concentrations on the order of 1 × 10^{-4} M. Plots of $[CH_3CN]$ vs. k_{obsd} were linear up to 1.5 M, but in some cases curvature was observed at very high acetonitrile concentrations. Intercepts were zero within experimental error. Figure 1 illustrates the ligand dependence typically observed.

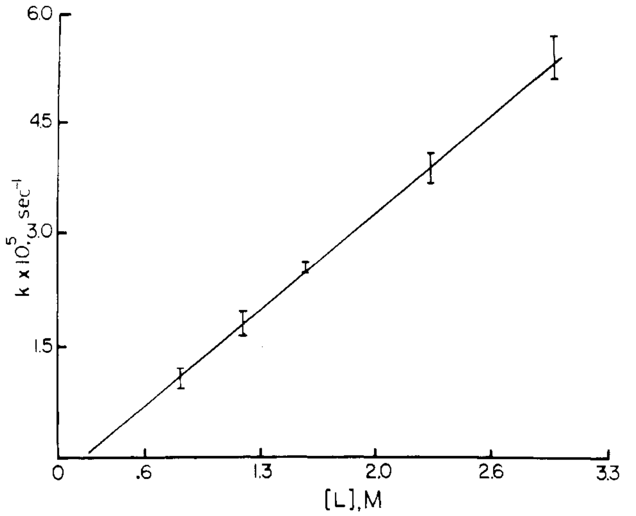

Figure 1. Plot of the pseudo-first-order rate constants as a function of ligand concentration for the reaction of *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ with acetonitrile at 25 °C.

The reactions were also studied as a function of pH and found to be independent of pH below a pH of 7. Acetate buffers were used as well as trifluoromethanesulfonic acid to maintain constant pH during the reactions. The ionic makeup of the solutions had no effect on the rates of reaction with acetonitrile, which was the test case for these investigations.

Kinetic measurements of substitution reactions with charged ligands was limited to the nitrite ion. The pH range over which measurements were made was 7.4–9.0. In this pH range, the predominant form of coordinated nitrite ion is in the N-bound NO_2^- form. In more acidic medium, the conversion to coordinated NO^+ takes place. Although the reactions involving nitrite ion are significantly faster than those involving neutral ligands, well-behaved second-order kinetics were noted over the entire range of ligand and hydrogen ion concentrations employed. Only the cis isomer of the bipyridine complexes was investigated because the products of the reaction between coordinating anions and *trans*-$Ru(NN)_2(H_2O)_2^{2+}$ are extremely insoluble in water.

The substitution reactions of the trans diaquo complexes were complicated by isomerization to the cis isomer, which is catalyzed by complexes in higher oxidation states. Since it was impossible to purify the complexes sufficiently to prevent the catalysis, small amounts of reducing agents were added to the reaction solutions. Hydroquinone or L-ascorbic acid was used for this purpose. The measured rates of substitution were independent of the nature of the reducing agent used. The nature of the catalysis reaction is currently under investigation.

Substitution of $Ru(NN)_2X(H_2O)^{2+}$. Substitution reactions of the general type represented by eq 3 were also studied. These

$$Ru(bpy)_2(H_2O)X^{2+} + Y \rightarrow Ru(bpy)_2XY^{2+} \quad (3)$$

included complexes of bipyridine with X = CH_3CN, SO_2, CO, PPh_3, and OH^- and of 1,10-phenanthroline with X = CH_3CN. In all cases, one-step reactions with characteristics analogous to the diaquo complexes were observed except as noted below. The second-order rate constants are listed in Table I.

A study of the pH dependence of the reactions of $Ru(bpy)_2(H_2O)_2^{2+}$ above a pH of 7 allowed the examination of the reactivity of $Ru(bpy)_2(H_2O)(OH)^+$. A plot of the observed rate constants as a function of pH is shown in Figure 2. The rate constants fit the relation

$$k_{obsd} = k_1 + k_2K_a/[H^+]$$

where k_1 is the second-order rate constant for the reaction of the diaquo complex (eq 1), k_2 the rate constant for the hydroxo–aquo complex (eq 3, X = OH^-), and K_a the acid dissociation constant. The pK_a's of the cis and trans isomers of $Ru(bpy)_2(H_2O)_2^{2+}$ were determined by methods that were independent of the kinetic analysis.

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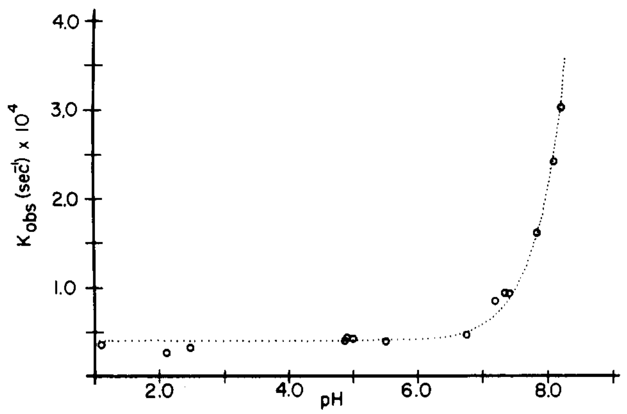

Figure 2. Plot of the dependence of the observed rate constants on pH for the reaction of *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ with acetonitrile at 25 °C.

The sulfur dioxide complex, *trans*-$Ru(bpy)_2(SO_2)H_2O^{2+}$, reacts rapidly with added ligands, and the rate is sensitive to the pH of the reaction medium. Within the range of pH employed the predominant form of the complex contains S-bound SO_2. Above this pH range, the visible absorption spectrum indicates that the sulfur dioxide is converted to bound HSO_3^- and at higher pHs to bound SO_3^{2-}. The reactivity of this species is still under investigation. Second-order kinetics was observed with *trans*-$Ru(bpy)_2(SO_2)(H_2O)^{2+}$ but the plot of k_{obsd} vs. [ligand] exhibits an intercept that is five standard deviations above zero. We have interpreted the nonzero intercept as indication of the presence of a significant back-hydrolysis reaction:

$$Ru(bpy)_2(SO_2)H_2O^{2+} + CH_3CN \rightleftarrows Ru(bpy)_2(SO_2)CH_3CN^{2+} + H_2O \quad (4)$$

In this case, the kinetic equation that applies is

$$k_{obsd} = k_1[\text{ligand}] + k_{-1}$$

The intercept corresponds to the hydrolysis reaction rate k_{-1}. The equilibrium constant is then 5.3 based on k_1/k_{-1}.

All of the above reactions, except the reaction of *trans*-$Ru(bpy)_2(CH_3CN)(H_2O)^{2+}$ with acetonitrile, proceed with retention of stereochemistry as determined by spectral characterization of the final products. In the case of *trans*-$Ru(bpy)_2(CH_3CN)(H_2O)^{2+}$, the reaction proceeds with a clean isosbestic point to the final spectrum of the disubstituted cis isomer. Several substitution reactions were performed in neat acetonitrile. The measured rates were only slightly faster than those observed in aqueous solution with acetonitrile concentrations of 4 M.

Activation Parameters. Temperature dependences of the second-order rate constants were measured for a small number of systems. Plots of ln (k/T) vs. $1/T$ were used to obtain the enthalpies and entropies of activation. The results are shown in Table II. Corrections were made in the case of pyridine for the variation of pK_b as a function of temperature.

Acid Dissociation Constants. Acid dissociation constants of the cis and trans isomers of $Ru(bpy)_2(H_2O)_2^{2+}$ and *trans*-$Ru(phen)CH_3CN(H_2O)^{2+}$ were determined spectrophotometrically. Values of 8.9 (1), 9.3 (1), and 10.1 (1), respectively, were obtained. These values are similar to those determined previously for *cis*-$Ru(bpy)_2(py)(H_2O)^{2+}$ (10.8)[16] and *cis*-$Ru(bpy)_2(NO_2)(H_2O)^+$ (10.9)[17] complexes. These results support the assumption that the hydroxo complexes do not contribute measurably to the reaction rates obtained at pH 1–7.

Discussion

Rate constants determined in this work agree with those of Davies and Mullins.[5] However, our observations and other information presently available on the nature of nitrite complexes of ruthenium(II) suggest that an alternative interpretation of their kinetic data would be more appropriate. Meyer and Murphy[17] have investigated the chemistry of *cis*-$Ru(bpy)_2(H_2O)NO_2^+$ and found the equilibria described by (5) and (6) to have pK_a's of 10.9

$$Ru(bpy)_2(H_2O)NO_2^+ \rightleftarrows Ru(bpy)_2(OH)NO_2 + H^+ \quad (5)$$

$$Ru(bpy)_2(OH)NO^{2+} + H_2O \rightleftarrows Ru(bpy)_2(H_2O)NO_2^+ + H^+ \quad (6)$$

and 6.5, respectively. Therefore, the product of the reaction of *cis*-$Ru(bpy)_2(H_2O)_2^{2+}$ with nitrite ion will be *cis*-$Ru(bpy)_2(H_2O)NO_2^+$ only in the range of pH 7–10. Our studies were performed at pH 7.5 to ensure that the nitrite substitution would produce only nitrite-containing complexes and no nitrosyl or hydroxo complexes. Although pH control was not described in the earlier work, spectral changes suggest significant $Ru(bpy)_2(OH)NO^{2+}$ formation.

Table II. Activation Parameters for the Reactions of $Ru(NN)_2X(H_2O)^{n+}$ with Various Y Ligands

		bpy		phen	
X	Y	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$
		Trans Isomers			
H_2O	CH_3CN	92 (9)	−30 (12)	85 (8)	−45 (24)
CH_3CN	CH_3CN			77 (6)	−71 (18)
H_2O	py			98 (11)	−3 (40)
		Cis Isomers			
H_2O	CH_3CN			50 (1)	−130 (1)
CH_3CN	CH_3CN			90 (17)	−30 (5)
H_2O	NO_2^-	90 (11)	23 (37)		
NO_2^-	NO_2^-	93 (3)	11 (10)		

[a] kJ/mol (std dev). [b] J/(K mol) (std dev).

The spectral changes observed in this work also indicate that nitrite substitution occurs in two distinct steps. The first exhibits a rate and spectral changes consistent with that reported by Davies and Mullins.[5] At the end of the first step, the solution spectra match that reported for *cis*-$Ru(bpy)_2(H_2O)NO_2^+$. A subsequent, slower step was also observed, and the final product exhibited a spectrum characteristic of *cis*-$Ru(bpy)_2(NO_2)_2$. The infrared spectra of the products isolated from the solution after each step gave no indication of O-bound nitrite.

Finally, the dependence of k_{obsd} on $[NO_2^-]$ was linear for both steps over the entire range of concentrations investigated. The nonlinear dependence noted earlier,[5] which leads to the suggestion of an O-bound intermediate, may have been the result of the influence of the second substitution step on the rate constant calculations. The nonlinearity was most noticable at the higher NO_2^- concentrations, where the reactions are faster and the unexpected influence of the second step would be the greatest.

In general, the reactions involving neutral ligands appear well-behaved and predominantly dissociative. The lack of sensitivity to the nature of the incoming ligand and the narrow range of values of $\Delta H^{\ddagger}$ suggest a considerable degree of bond breaking in the transition state. Two features of these reactions are particularly worthy of note: (1) the effect of the fifth or nonexchanging monodentate ligand on the rates of substitution and (2) the difference in reactivity of the cis and trans isomers.

The rate constants given in Table I suggest a general ordering of reaction rate that depends on the fifth ligand in the following way:

$$SO_2 > OH^- \simeq PPh_3 > H_2O > CH_3CN \simeq \text{pyridine} > CO$$

The ordering of the last four members of the series is also the ordering by 3+/2+ redox potentials, which has been taken as a measure of the relative charge of the ruthenium center. The metal center of the carbon monoxide complex would, by this reasoning, be expected to have the higher effective charge. Given the well-established relation between substitutional lability and the metal charge in complex ions, it appears that the relative charge of the ruthenium center may be one of the major controlling

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features of these reactions. Furthermore, these four ligands also appear to be ordered by increasing π-acceptor strength. Since water, the leaving ligand, is generally not considered a π-bonding ligand, it does not appear that specific σ or π interactions of the fifth ligand with the leaving ligand play a major role in rate determination with most ligands. The major effect of the fifth ligand is to donate or remove electron density from the metal center, irrespective of specific σ or π interactions. The hydroxo complex cannot be included in this comparison because of the strong influence of charge type on the redox potential.

The sulfur dioxide complex is out of place and may be a special case in which specific trans bonding influence or other type of interaction does play a major role in rate determination. In this context, it is interesting to note that similar behavior has been reported for the simple ammine complexes with related sulfur-containing ligands,[7] and an adequate explanation remains to be presented. The accelerated rates observed in Co(III)–sulfito complexes were explained in terms of stabilization of the transition state through a distortion of the proposed square-pyramidal intermediate.[19] Such an explanation is inappropriate for the trans isomers described in this study because any significant distortion in the transition state would be likely to lead to cis products.

The triphenylphosphine complex also appears to be out of place. Comparison of the energies of the charge-transfer transitions of triphenylphosphine-containing complexes to the corresponding carbonyl-containing complexes suggest that triphenylphosphine should appear very near CO in this series. The large rate constant, however, can be interpreted as a steric effect in which the coordinated water is labilized by repulsion of the bulky triphenylphosphine.

Rate constants obtained with anionic entering ligands show a significant increase in rate over those observed with neutral ligands. To some extent this behavior is attributable to the differences in charge and the effect of charge type on outer-sphere association constants. A comparison to reactions of $Ni(H_2O)_6^{2+}$ [18] or $Ru(NH_3)_5(H_2O)^{2+}$ [9] suggests that a 10-fold increase is typically observed when neutral ligands are compared to singly charged anions. In the present studies, substitution of water by nitrite ion is about 10 times faster than substitution by acetonitrile into an equivalent complex. The differences in reactivity displayed in the reactions of azide and thiocyanate ions reported by Davies and Mullins[5] is perplexing in view of the apparent dissociative nature of the substitution process. It is not clear from the report, however, whether appropriate corrections were made in these cases for the basicity of the ions or for ionic strength. Less negative values of $\Delta S^‡$ are observed for the reactions involving anionic incoming ligands, as expected for reactions between oppositely charged species. This is a consequence of the anticipated reduction in overall charge and the resulting solvent reorganization in the transition state.

The reactivity of the polypyridyl complexes may be compared to that of the $Ru(NH_3)_4L(H_2O)^{2+}$ complexes described by Taube and coworkers.[6-9] Since both systems react by a predominantly dissociative mechanism, useful comparisons of the two may be made without regard to the nature of the entering ligand. The most obvious difference between the two series of complexes is the fact that the substitution reactions of the ammonia complexes with a given ligand L are 100–1000 times faster than those of the corresponding L-containing polypyridyl complex except in the cases where large degrees of deactivation or activation are evident. Given the dissociative nature of the reaction, this behavior can also be rationalized in terms of effective charge at the metal center. The polypyridyl complexes are certainly less electron rich and, therefore, would be expected to be more substitutionally inert than the ammonia complexes. This is again reflected in the redox potentials of the two sets of complexes. The polypyridyl complexes typically exhibit 3+/2+ redox potentials that are at least 0.5 V greater than those of the corresponding simple ammine complexes.

If the differences in absolute rates are ignored, a similarity in the ordering of reactivity of the polypyridyl complexes to that exhibited by the simple ammine complexes is evident. The range of rate constants obtained with the polypyridyl complexes, however, is very small compared to that for the ammine complexes. This apparent difference may be a manifestation of sensitivity of the simple ammine complexes to deactivation. Rate constants for complexes containing ligands more deactivating than water cover a range of 5 orders of magnitude whereas activating ligands provide a range of slightly more than 1 order of magnitude. The polypyridyl complexes, on the other hand, appear to be more sensitive to the activating ligands. The trans isomers of the bipyridine complexes exhibit a range of rate constants of 3 orders of magnitude with activating ligands. Very little deactivation relative to water is observed. This behavior could be a result of the extensive π bonding in the polypyridyl complexes, which tends to minimize the impact of the fifth ligand on the bonding within the complex. On the other hand, the absence of competitive ligands in the ammine complexes allows the fifth ligand to exhibit a more significant influence on the bonding within the complex and ultimately on the rate of substitution.

Taube and coworkers[8] ascribed the delabilization effect noted in the ammonia complexes to a trans effect, and in a few cases the directionality of the effect was indicated by experiment. This was particularly evident in the case of complexes containing derivatives of sulfur dioxide. In most cases, however, both cis and trans isomers reacted at nearly identical rates. In the present study, the cis isomers react by a factor of 10 faster than the corresponding trans isomers but the orderings of reactivity with respect to the fifth ligand are, with a few exceptions, identical for both isomers. At this time it appears unreasonable to describe the effect of the fifth ligand as anything more than an inductive effect. That is, an effect that acts by altering the bonding to all ligands rather than predominantly those either cis or trans to a particular group.

The enhanced reactivity of the cis isomers relative to the trans isomers is inconsistent with arguments concerning the effects of relative charge of the metal center on reactivity. Specifically, the cis isomers have higher oxidation potentials than the corresponding trans isomers. Differences of 100–150 mV are typically observed. These differences are also manifested in the energy of the lowest energy charge-transfer bands of the complexes. Cis isomers absorb at energies greater than or equal to the energies at which the corresponding trans isomers absorb. The enhanced reactivity is also counter to the arguments based on the expected relief of steric strain in the trans isomers.

Finally, there is little difference in reactivity of phenanthroline complexes vs. bipyridine complexes. To a large extent, the phenanthroline complexes were included in this study because of the known similarities in bonding properties of phenanthroline and bipyridine and the decidedly different flexibility of the two chelates. Several structure determinations[10,11] demonstrate the ability of bipyridine moiety to flex in order to relieve steric strain in complexes such as *trans*-$Ru(bpy)_2L_2^{2+}$. A comparative study of a phenanthroline compelx[20] indicated little departure from planarity. The insignificant differences in reactivity observed between the phenanthroline and bipyridine complexes are in keeping with little change in the geometry of the complex ions as they approach the transition state. This and the observation that the substitution reactions are stereoretentive (with one exception) suggest that the stretching of the Ru–OH_2 bond does not appear to be accompanied by significant changes in the remainder of the complex.

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