Contribution from the Istituto Chimico "G. Ciamician",
dell'Università, 40126 Bologna, Italy

Kinetics of Ligand Substitution of Tris(2,2′-bipyridine)chromium(III) in Aqueous Solutions

M. MAESTRI,* F. BOLLETTA, N. SERPONE,[1] L. MOGGI, and V. BALZANI

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The kinetics of ligand substitution reactions of $Cr(bpy)_3^{3+}$ have been investigated in aqueous solutions at constant ionic strength (1.0 M) in the pH range 0–10.7 and in the temperature range 11.0–60.5 °C. The solvolysis reaction was found to be base but not acid catalyzed. The pH dependence of the rate of substitution was studied at 11.0 °C. In solutions of pH >9, the solvolysis is $Cr(bpy)_3^{3+} + 2OH^- = Cr(bpy)_2(OH)_2^+ + bpy$. The value of the pseudo-first-order rate constant is dependent on hydroxide concentration: $k_{obsd} = [OH^-]/(B + A[OH^-])$. The temperature dependence of the substitution reaction was investigated at pH 9.8; the activation parameters (25 °C) are: $\Delta H^\ddagger = 22.3 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -8.8 \pm 1.9$ eu, $k = 3.3 \times 10^{-6}\ s^{-1}$. At least four mechanisms are consistent with the observed kinetic behavior: (i) dissociative mechanism (D), (ii) associative mechanism (A), (iii) Gillard's general mechanism, and (iv) the ion-pair mechanism (I). On the basis of various evidences, the solvolysis reaction is viewed as occurring by a nucleophilic attack on the complex by water to form a "heptacoordinate" species which subsequently undergoes deprotonation by OH^-, followed by rupture of a Cr–N bond.

Introduction

The substitution reactions of metal chelates of the type $M(AA)_n^{z+}$ (M = transition metal; AA = 2,2′-bipyridine or 1,10-phenanthroline) have been the subject of many discussions (for reviews see ref 2 and 3). While the mechanism of acid catalysis of these reactions is reasonably well understood,[2,4] the reasons why OH^- enhances ligand replacement are not yet clear. Since these complexes contain no ionizable protons, a simple conjugate base mechanism is implausible. For the bipyridine complexes, a mechanism has been proposed that is based on the nucleophilic attack of OH^- on an intermediate in which one bipyridine molecule is only partially bonded to the metal[2] (D mechanism). In the case of $Fe(phen)_3^{2+}$, however, a nucleophilic attack directly on the reactant was thought to be more plausible[5] (A mechanism). Direct attack of hydroxide ion has also been demonstrated to occur in the $Fe(TPTZ)_2^{2+}$ chelate (TPTZ = 2,4,6-tripyridyl-*s*-triazine), for which the dissocation exhibits an extraordinarily complex pH dependence.[6] In two recent studies,[3,7] Gillard had pointed out that the acceleration by OH^- of the substitution reaction is only one of the many long-standing unexplained properties of $M(AA)_n^{z+}$ complexes. He has also suggested that a general explanation for such anomalies can be found in the hydroxyl ion attack on the C-6 position of the ligand. This mechanism is also thought[3] to be responsible for the observed promotion[8] by base of the hydrolysis of the first chloride ion from $M(AA)_2Cl_2^+$ (M = Cr(III) or Co(III)). Nord,[9] however, has recently reported some evidence indicating that Gillard's general mechanism is not valid, at least in the case of the base hydrolysis of $Pt(bpy)_2^{2+}$.

Recent investigations[10] in this laboratory have focused attention on the photochemical behavior of $Cr(bpy)_3^{3+}$ in aqueous solutions. Since the thermal (dark) behavior of this complex, under similar conditions, had not been previously reported, an investigation of ligand substitution reactions of the ground state complex in aqueous solutions at various pH's was also undertaken. This report presents the results of such a study.

Experimental Section

Materials. Tris(2,2′-bipyridine)chromium(III) perchlorate, $[Cr(bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$, was prepared by the method of Baker and Mehta.[11] The absorption spectrum is in agreement with that reported by Konig and Herzog.[12] Diaquobis(2,2′-bipyridine)chromium(III) perchlorate, $[Cr(bpy)_2(H_2O)_2](ClO_4)_3$, was prepared photochemically using the following procedure. A solution of $Cr(bpy)_3^{3+}$ (ca. 10^{-2} M and pH 9.2) was irradiated at room temperature with λ >365 nm light until the absorption maximum of $Cr(bpy)_2(OH)_2^+$ at 520 nm reached a constant value. Free bipyridine was then extracted with *n*-heptane and the aqueous solution, acidified to pH ~1, was concentrated to about 2 ml with a rotary evaporator. The reddish mixture was filtered and the product recrystallized from methanol, washed with ca. 2 ml of a solution 0.1 M in $HClO_4$, and subsequently dried in vacuo. The visible spectra of the acid and basic forms, $Cr(bpy)_2(H_2O)_2^{3+}$ and $Cr(bpy)_2(OH)_2^+$, respectively, were in good agreement with those reported by Inskeep and Bjerrum.[13] All chemicals and solvents were of reagent grade quality.

Procedures and Measurements. All the experiments were carried out in dim, red light owing to a strong light enhancement of the rate of ligand substitution.[10] The solutions were thermostated (±0.1 °C) at the desired temperatures. The $Cr(bpy)_3^{3+}$ concentration was 1.0×10^{-3} M unless noted otherwise. Constant ionic strength was maintained at 1.0 M with NaCl. Unless otherwise noted, Britton–Robinson buffers 8×10^{-3} M were used for the experiments in the pH range 10.7–4.5. The experiments at the lower pH were carried out in hydrochloric acid. Spectrophotometric measurements were performed with a Perkin-Elmer 323 spectrophotometer; luminescence measurements were carried out with a Perkin-Elmer MPF3 spectrofluorimeter. The emission lifetime was determined with an apparatus described previously.[14] pH measurements were done with a pH M64 Radiometer instrument. The concentration of free bipyridine was measured using the following standardized procedure. An aliquot of the solution was brought to pH ~9; subsequently, 2 ml of this solution was vigorously shaken with 5 ml of n-heptane. The concentration of free bipyridine in the upper *n*-heptane phase was then determined spectrophotometrically at 282 nm, and the amount of free bipyridine in the original solution was obtained by means of calibration plots.

Results

The absorption spectrum of a freshly prepared solution of $Cr(bpy)_3^{3+}$ is pH independent in the range 0–10.7 to within an experimental error of 3%. The relative intensity of the maxima at 695 and 727 nm of the emission spectrum did not vary by more than 5% in the same pH range.[10] The lifetime of the excited $Cr(bpy)_3^{3+}$ was 80 μs in aerated solution at 11 °C and independent of pH in the range 7–10.7.[10]

As previously reported by Inskeep and Bjerrum,[13] the absorption spectrum of $Cr(bpy)_2(H_2O)_2^{3+}$ is strongly pH dependent (pK_a ~ 3.5 and 6.1). The spectra of $Cr(bpy)_2(H_2O)_2^{3+}$ [λ_{max} (log ε): 311 (4.30), 492 (1.68)] and $Cr(bpy)_2(OH)_2^+$ [λ_{max} (log ε): 247 (4.23), 305 (4.35), 518 (1.69)] are illustrated in Figure 1.

The pH dependence of the kinetics of the reaction was studied at 11 °C. For solutions of pH ≤4.51, no spectral changes were observed, even after 5 days, irrespective of the concentration (8×10^{-3} and 3×10^{-2} M) and nature (phosphate or acetate) of the buffer.

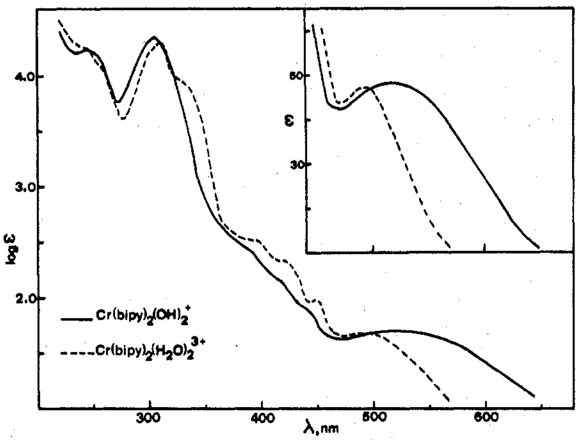


Figure 1. Ultraviolet and visible absorption spectra of $Cr(bpy)_2(H_2O)_2^{3+}$ and $Cr(bpy)_2(OH)_2^+$ in acid (pH ~0) and base (pH 9.8) solutions, respectively, at ambient temperature.

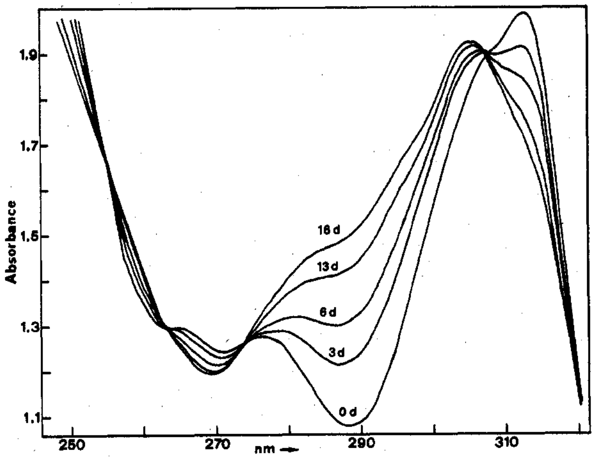


Figure 2. Ultraviolet absorption spectrum of a 7.57×10^{-5} M solution of $Cr(bpy)_3^{3+}$ at pH 9.8 and 11 °C at various times. The four isosbestic points occur at 255, 263, 274, and 307 nm.

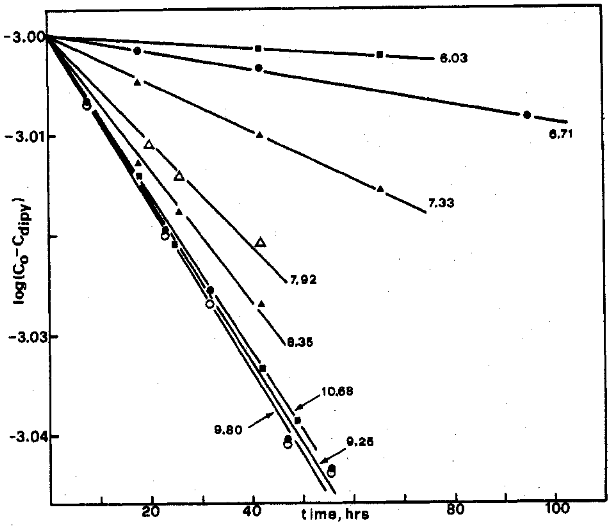


Figure 3. Plots of log $(C_0 - C_{bpy})$ vs. time at various pH's: 11 °C, 1×10^{-3} M solutions in $Cr(bpy)_3^{3+}$, $\mu = 1.0$ M NaCl.

In basic solutions (pH ≥7.33) the spectrum of $Cr(bpy)_3^{3+}$ changed with time as depicted in Figure 2. The spectral variations until the isosbestic points were maintained (more than 50% of reactant disappearance) are just those expected for the overall reaction

$$Cr(bpy)_3^{3+} + 2OH^- \xrightarrow{k_{obsd}} Cr(bpy)_2(OH)_2^+ + bpy \qquad (1)$$

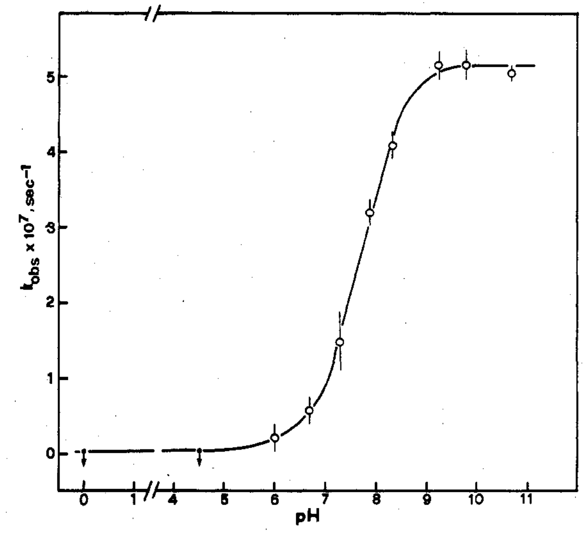


Figure 4. Plot of the pH dependence of the pseudo-first-order rate constant, k_{obsd}, for the hydrolysis of $Cr(bpy)_3^{3+}$, at 11 °C, $\mu = 1.0$ M NaCl.

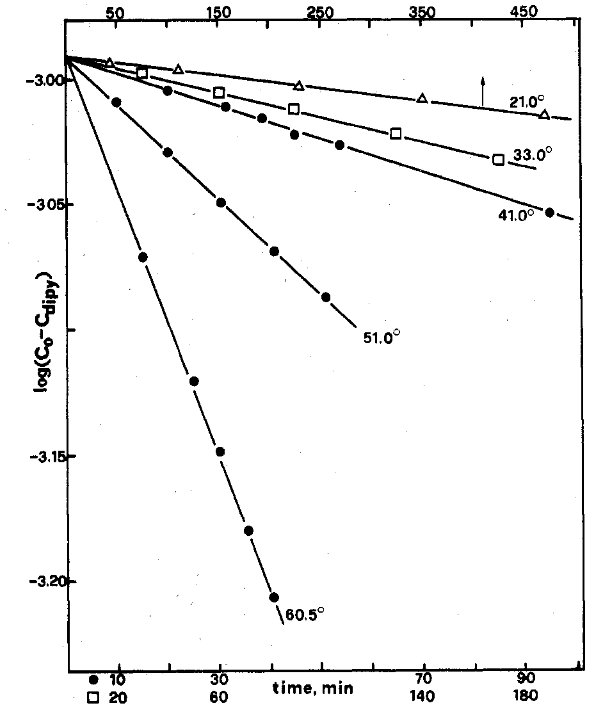


Figure 5. Plots of log $(C_0 - C_{bpy})$ vs. time at various temperatures: pH 9.8, 1×10^{-3} M solutions in $Cr(bpy)_3^{3+}$, $\mu = 1.0$ M NaCl.

The occurrence of reaction 1 was confirmed by the decrease in pH (for solutions containing $<10^{-3}$ M buffer) and by the release of free bipyridine. For weakly acidic solutions (pH 6.03 and 6.71), the spectral changes were different from those shown in Figure 2. However, upon addition of a sufficient amount of base to bring the solution to pH ~9, a spectrum was obtained which indicated the presence of $Cr(bpy)_2(OH)_2^+$ and bpy as the only reaction products. These results can be easily accounted for on the basis of the acid–base equilibrium of $Cr(bpy)_2(H_2O)_2^{3+}$. Pseudo-first-order plots were obtained for the rate of bipyridine release, as illustrated in Figure 3. The pH dependence of the observed pseudo-first-order rate constants is shown in Figure 4.

The temperature dependence (11–60.5 °C) of the reaction rate was investigated at pH 9.8; the results are summarized in Figure 5. At each temperature, isosbestic points as in

Figure 2 were maintained for more than ~50% of reactant disappearance.

A linear regression, least-squares analysis on the Arrhenius plot of ln k_{obsd} vs. $1/T$ yielded a slope and intercept from which the following activation parameters were estimated: $E_a = 22.9 \pm 0.6$ kcal/mol, $\Delta H^{\ddagger}_{298} = 22.3 \pm 0.6$ kcal/mol, ln $A = 26.05 \pm 0.31$, $\Delta S^{\ddagger}_{298} = -8.8 \pm 1.9$ eu, $\Delta G^{\ddagger}_{298} = 24.9 \pm 0.8$ kcal/mol, $k_{298} = 3.3 \times 10^{-6}$ s^{-1}. The entropy of activation was calculated from the relation,[15] $\Delta S^{\ddagger} = R(\ln A - \ln RT/Nh) - R$, where N, R, and h have their usual significance and T is taken as 298 °K. Errors are reported at the 95% confidence level, and reflect the scatter of the data points only; systematic errors are estimated to be not more than 10%.

Discussion

The results obtained show that in buffered solutions at pH ≥6.03, the replacement of a bipyridine ligand in the coordination sphere of $Cr(bpy)_3^{3+}$ follows pseudo-first-order kinetics:

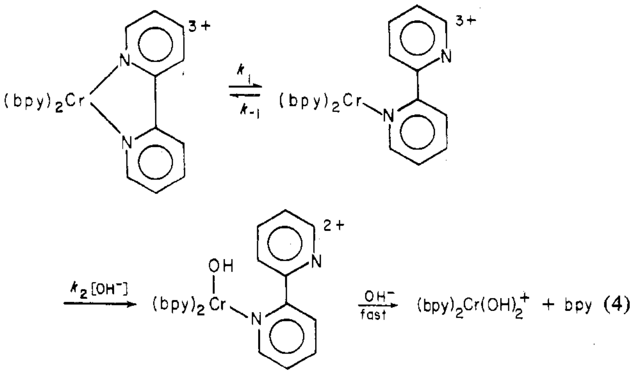
$$Cr(bpy)_3^{3+} \xrightarrow[OH^-, H_2O]{k_{obsd}} Cr(bpy)_2(OH)_2^{+} \text{ or } Cr(bpy)_2(H_2O)(OH)^{2+} + bpy \quad (2)$$

The results also indicate that the pseudo-first-order rate constant, k_{obsd}, is a function of the pH of the solution (Figure 4). A plot of k_{obsd} vs. $[OH^-]$ is not linear, implying that a simple bimolecular reaction between $Cr(bpy)_3^{3+}$ and OH^- is inconsistent with the observed results. In contrast, a plot of $1/k_{obsd}$ vs. $1/[OH^-]$ is linear showing that the $[OH^-]$ dependence of the pseudo-first-order rate constant is given by

$$k_{obsd} = [OH^-]/[B + A[OH^-]) \quad (3)$$

With $A = 2.1 \pm 0.2 \times 10^6$ s and $B = 0.82 \pm 0.02$ M s at 11 °C. At least four reaction pathways[16] suggest themselves to account for eq 3.[18]

Dissociative Mechanism (D).



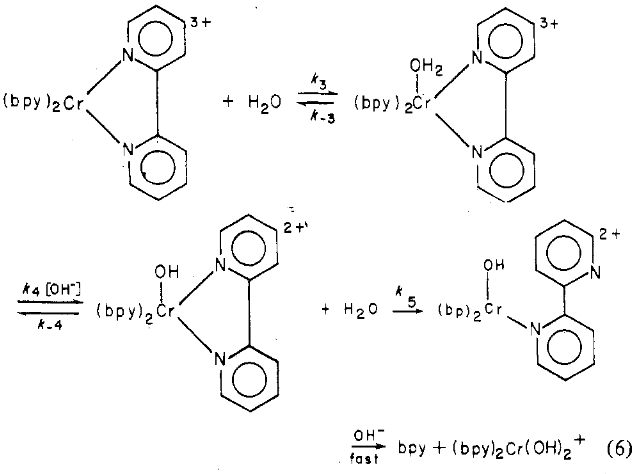
(4)

The steady-state treatment on the concentration of the five-coordinate intermediate leads to expression 5. This

$$k_{obsd} = k_1k_2[OH^-]/(k_{-1} + k_2[OH^-]) \quad (5)$$

equation and the values of A and B quoted above give $k_1 = 4.7 \times 10^{-7}$ s^{-1} and $k_1k_2/k_{-1} = 1.2$ M^{-1} s^{-1}. Also, two limiting cases of expression 5 are of interest: (i) if $k_2[OH^-] \gg k_{-1}$, then $k_{obsd} = k_1$ for large values of $[OH^-]$ such that a limiting rate is reached which is first order and independent of $[OH^-]$; (ii) if $k_2[OH^-] \ll k_{-1}$, $k_{obsd} = k_1k_2[OH^-]/k_{-1}$ at low pH. In accordance with expectation (i), at pH 9–11 and at 11 °C, the mean value of k_{obsd} is $5.1 \pm 0.2 \times 10^{-7}$ s^{-1} in good agreement with the calculated $k_1 = 4.7 \pm 0.4 \times 10^{-7}$ s^{-1}. Under such conditions, the rate-determining step is viewed as a Cr–N bond rupture in $Cr(bpy)_3^{3+}$ as noted in eq 4. The "vacant" coordination site in the five-coordinate species is most probably occupied by a water molecule whence the second step could be regarded as an acid–base reaction or as a substitution of water by hydroxide ion.

Associative Mechanism (A).



(6)

This mechanism assumes that the heptacoordinate complex obtained upon H_2O coordination undergoes an acid–base equilibrium, and that the heptacoordinate base form, which contains the more strongly bonded OH^- ligand, only collapses by rupture of a Cr–N bond. Applying the steady-state approximation to the concentrations of the acid and base form of the heptacoordinate species results in eq 7, in which $k_i' =$

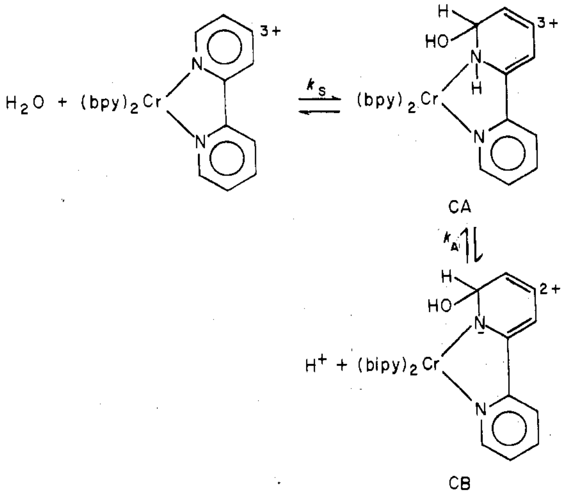
$$k_{obsd} = \frac{k_3'k_5k_4[OH^-]}{k_{-3}(k_5 + k_{-4}') + k_5k_4[OH^-]} \quad (7)$$

$k_i[H_2O]$, $k_3' = 4.7 \times 10^{-7}$ s^{-1}, and $k_3'k_5k_4/k_{-3}(k_5 + k_{-4}') = 1.2$ M^{-1} s^{-1}. It is apparent that a limiting rate is expected at high pH where the term $k_{-3}(k_5 + k_{-4}')$ is negligible compared to $k_5k_4[OH^-]$, with the consequence that the pseudo-first-order rate constant $k_{obsd} = k_3'$. In the other limiting case, where $k_{-3}(k_5 + k_{-4}') \gg k_5k_4[OH^-]$, expression 7 reduces to $k_{obsd} = k_3'k_5k_4[OH^-]/k_{-3}(k_5 + k_{-4}')$ and so the limiting rate of the ligand substitution becomes pH dependent.

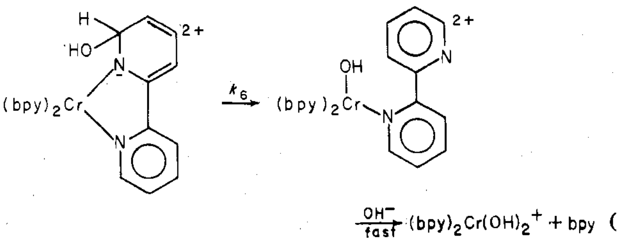
While the relative values of the other rate constants are not available to ascertain the rate-determining step in the above analysis, it is nevertheless instructive to consider the various steps in reaction 6 in an effort to deduce the most plausible slow step. We note, for example, that step 4 represents a deprotonation–protonation of the two "hepta" species, and consequently it is reasonable to suppose that k_4 and k_{-4} be relatively large. In addition, a seven-coordinate stereochemistry must certainly represent an intolerable crowded situation for chromium(III) complexes, and therefore it is not inconceivable that the two "hepta" species relax relatively fast to the more stable octahedral stereochemistry. This would then leave k_3, formation of the aquo heptacoordinate intermediate, as the slowest step in the chain of events depicted in the associative mechanism.

Gillard's Mechanism. In recent articles,[3,7] Gillard proposed a general mechanism for the hydrolysis of complexes containing N-heterocyclic bases. Borrowing examples from organic chemistry (covalent hydrates), he suggested that various manifestations of $M(AA)_n^{z+}$ complexes can be explained in terms of the equilibria in reaction 8. In this scheme, the nucleophile attacks the C-6 (or C-6′) position of the N-heterocycle to give the hydrated species (conjugate acid, CA) which can undergo deprotonation at the quaternary nitrogen. Intramolecular shift of the hydroxyl group to the Cr could then lead to the solvolysis products. The assertion of the equilibria in the above scheme was based on spectroscopic, electrochemical, kinetic, and various other evidences.[3,7]

Assuming that the CB of scheme 8 undergoes an irreversible reaction (reaction 9), a kinetic treatment of reactions 8 and



(8)



(9)

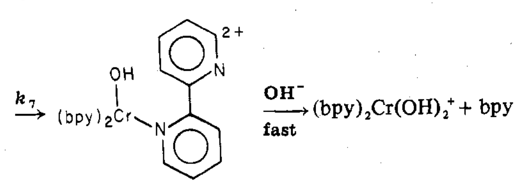
9 produces expression 10. In the case where $K_SK_A[OH^-] \gg$

$$k_{obsd} = \frac{k_6K_SK_A[OH^-]}{(1 + K_S) + K_SK_A[OH^-]} \tag{10}$$

$(1 + K_S)$, $k_{obsd} = k_6 = 4.7 \times 10^{-7}$ s^{-1}. From the ratio of the intercept to the slope of a plot of $1/k_{obsd}$ vs. $1/[OH^-]$ for expression 10 and the values of A and B of eq 3 we get $K_A = 2.6 \times 10^6(1 + K_S)/K_S$ M^{-1}. Since the ratio $(1 + K_S)/K_S > 1$, the lower limit for K_A is 2.6×10^6 ($pK_a \leq -6.4$) for the conjugate acid, $Cr(bpy)_2(bpy{-}H_2O)^{3+}$, of reaction 8.

Ion-Pair Mechanism (Interchange, I). An alternative solvolysis pathway for the ligand replacement of a bipyridine molecule in $Cr(bpy)_3{}^{3+}$ involves the formation of outer-sphere complexes (ion pairs) as depicted in reaction 11. A material

$$Cr(bpy)_3{}^{3+} + OH^- \overset{K_{ip}}{\rightleftharpoons} [Cr(bpy)_3{}^{3+},OH^-]$$



(11)

balance on the ion pair produces a relationship

$$k_{obsd} = \frac{k_7K_{ip}[OH^-]}{1 + K_{ip}[OH^-]} \tag{12}$$

for the pseudo-first-order rate constant that also conforms to the observed results. From this expression and the values of A and B (eq 3), $k_7 = 4.7 \times 10^{-7}$ s^{-1} and $K_{ip} = 2.6 \times 10^6$ M^{-1}. At pH >9, $K_{ip}[OH^-] \gg 1$ so that the limiting $k_{obsd} = k_7$.

Comments on the Reaction Mechanisms. Although the mechanisms discussed above are all consistent with the observed reaction kinetics, they present a different degree of consistency in the light of the following considerations.

For the dissociative mechanism, both base and acid catalysis are expected to occur.[2] Acid catalysis was experimentally found for $Ni(bpy)_3{}^{2+}$ [2] and $Fe(bpy)_3{}^{2+}$.[2,4] Since no acid catalysis was observed for $Cr(bpy)_3{}^{3+}$, even in 1 M HCl, the dissociative mechanism does not seem plausible, though a very low pK_a value for the partially coordinated bipyridine molecule cannot be excluded.

With regard to the associative mechanism (reaction 6), we find no indications from our data that would preclude this pathway. Furthermore, results from a recent study[10] of the photochemical behavior of $Cr(bpy)_3{}^{3+}$ are not incompatible with an associative mechanism.

Gillard's mechanism implies a pH-dependent equilibrium. For some complexes of the $M(AA)_n{}^{z+}$ type, reversible changes in the absorption spectrum with pH were observed and they were taken as an indication of such an equilibrium (reaction 8).[3] Assuming Gillard's general mechanism to be operative in the present case, our presently available data would require that the concentration of the conjugate base $Cr(bpy)_2(bpy{-}OH)^{2+}$ be <1% at pH ≤4, and >99% at pH ≥9 with respect to the initial concentration of $Cr(bpy)_3{}^{3+}$. Since neither absorption nor emission spectral changes were observed, the operation of Gillard's equilibria appears unlikely. Moreover, we note that from our experiments the upper limit of pK_a is −6.4, in contrast to the estimated value[3] of about 0.

Similarly, the ion-pair mechanism does not appear likely because the ion-pairing constant, K_{ip} (2.6×10^6 M^{-1}), is exceedingly high as compared with "normal" ion pairs of coordination compounds.[3,20,21] Such a high value might be reconciled if OH^- ions are viewed as penetrating the "pockets" between the ligands, so as to closely interact with the central metal ion. In such a case, however, 100% formation of ion pairs (at pH >9) would imply spectral changes not observed in the present system.

In conclusion, the most plausible mechanism seems to be the associative pathway, which falls in the general pattern of chromium(III) substitution reactions.[20]

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Registry No. $[Cr(bpy)_2(H_2O)_2](ClO_4)_3$, 59448-72-5; $Cr(bpy)_3{}^{3+}$, 15276-15-0.

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