Hydroxide Ion Assisted Aquation of Tris(2,2'-bipyridine)chromium(III) Ion

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Previous studies on the kinetics of the thermal aquation of $Cr(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine) in aqueous solutions and constant ionic strength (1.0 M, NaCl) have been extended to include the pH range 10.7–14. The aquation reaction is OH^- catalyzed. The pH dependence of the rate of aquation has been studied at 11 °C, and the pH profile (including the previous data) consists of four regimes. The stoichiometry of the aquation at pH >9 is

$$Cr(bpy)_3^{3+} + 2OH^- \xrightarrow{k_{obsd}} Cr(bpy)_2(OH)_2^+ + bpy$$
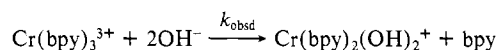
The pseudo-first-order rate constant, k_{obsd}, is dependent on hydroxide concentration: $k_{obsd} = [OH^-]/(B + A[OH^-]) + C[OH^-] + D[OH^-]^2$ in the pH range 6–14. The solvolysis is pH independent below pH 6. Eyring activation parameters at 25 °C are the following: (1) pH 9.8, $\Delta H^\ddagger = 22.3 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -8.8 \pm 0.6$ eu, $k_{obsd} = 3.3 \times 10^{-6}$ s^{-1}; (2) pH 11.8, $\Delta H^\ddagger = 20.7 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -12.6 \pm 0.6$ eu, $k_{obsd} = 6.9 \times 10^{-6}$ s^{-1}; (3) 0.50 M OH^-, $\Delta H^\ddagger = 18.9 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -11 \pm 2$ eu, $k_{obsd} = 2.9 \times 10^{-4}$ s^{-1}. The kinetic results are interpreted in terms of an associative mechanism involving the formation of a seven-coordinate intermediate via direct nucleophilic attack of a water molecule (pH 6–10.7) or OH^- (pH 10.8–12.2) at the metal center. The second-order dependence of k_{obsd} on $[OH^-]$ ($[OH^-] \geq 0.1$ M) is rationalized in terms of the formation of ion pairs followed by attack of the ion pair by another OH^- ion to form, also, some seven-coordinate intermediate which, also, ultimately and irreversibly, releases bpy into solution.

Introduction

We have recently reported[2] that the thermal aquation of $Cr(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine) in the pH range 0–10.7 occurs via pH-dependent first-order kinetics where $k_{obsd} < 10^{-8}$ s^{-1} at pH <6 and $= (4.7 \pm 0.4) \times 10^{-7}$ s^{-1} at pH 9–10.7 (11 °C). The inflection in the values of k_{obsd} in the pH 6–9 region (Figure 4 of ref 2) was attributed to the acid–base properties of the postulated, initially formed intermediate. Arguments were presented against dissociative, ion-pair interchange and Gillard-type covalent hydrate mechanisms. An associative mechanism, involving the formation of a seven-coordinate intermediate via nucleophilic attack of a water molecule at the metal center as the rate-determining step, was proposed. Similarly, the photochemical aquation[3] of $Cr(bpy)_3^{3+}$ exhibits the same pH dependence of the quantum yield as k_{obsd} suggesting that the same seven-coordinate intermediate is formed by the reaction of (^2E) $Cr(bpy)_3^{3+}$ with H_2O. Flash photolysis results[4] indicate that $Cr(bpy)_3(H_2O)^{3+}$ eliminates H_2O via acid-dependent and -independent paths to re-form the substrate, thus accounting for the photochemical and thermal inertness of $Cr(bpy)_3^{3+}$ in acidic solution.

Hydroxide ion is known to quench the ^2E excited states of $Cr(bpy)_3^{3+}$,[4] *trans*-$Cr(en)_2(NCS)_2^+$,[5] $Cr(NH_3)_6^{3+}$,[6] and $Cr(en)_3^{3+}$.[7] The former two systems are believed to involve formation of a seven-coordinate intermediate; for the latter two, involvement of an ammine–hydrogen deprotonation step has been proposed. A recent study[8] shows that OH^- also quenches the phosphorescence and enhances the photoracemization of $Cr(phen)_3^{3+}$ (phen = 1,10-phenanthroline). These reports have prompted us to examine the interaction of OH^- with ground-state $Cr(bpy)_3^{3+}$ in the pH range 10.8–14.

Experimental Section

The sample of $[Cr(bpy)_3](ClO_4)_3 \cdot ^1/_2H_2O$ used in this study was the same as used before.[2] All chemicals were of reagent grade quality, and the water was monodistilled.

In the pH range 10.8–12.2, solutions were prepared with Britton-Robinson buffer[9] (0.008 M); at higher pH, solutions were made up with standard solutions of NaOH of varying concentrations. Constant ionic strength (1.0 M) was established by NaCl. In all cases, experiments were carried out under dim, red light to prevent photochemical enhancement of the aquation process.[3,4] Unless otherwise noted, $[Cr(bpy)_3^{3+}] \sim 1 \times 10^{-3}$ M. Spectrophotometric measurements were performed with an AMINCO-Bowman DW-2 UV/VIS

Table I. Arrhenius and Eyring Activation Parameters for the Aquation of Tris(2,2'-bipyridine)chromium(III)[a]

	pH		$[OH^-]$,[c]
	9.8[b]	11.8	0.50 M
E_a, kcal/mol	22.9 ± 0.2	21.3 ± 0.2	19.5 ± 0.5
$\Delta H^\ddagger_{298}$, kcal/mol	22.3 ± 0.2	20.7 ± 0.2	18.9 ± 0.5
ln A	26.1 ± 0.1	24.1 ± 0.2	24.8 ± 0.9
$\Delta S^\ddagger_{298}$, eu	−8.8 ± 0.6	−12.6 ± 0.6	−11 ± 2
$\Delta G^\ddagger_{298}$, kcal/mol	24.9 ± 0.3	24.5 ± 0.3	22.2 ± 1.1
k_{298}, s^{-1}	3.3 × 10^{-6}	6.9 × 10^{-6}	2.9 × 10^{-4}

[a] Britton–Robinson buffer; $\mu = 1.0$ M (NaCl); standard errors. [b] Reference 2. [c] NaOH solution; $\mu = 1.0$ M (NaCl).

spectrophotometer. The kinetics of the aquation process were followed at constant temperature (±0.1 °C) by determining the concentration of bpy released into solution using a procedure used previously;[2] 2 mL of each solution was vigorously shaken with 5 mL of *n*-heptane for 1 min and, after a 2-min rest period, the spectrum of bpy in the nonaqueous phase was recorded. For the calibration plots, aqueous solutions (pH 6 and 10.5) of various concentrations of bpy were prepared gravimetrically in Britton-Robinson buffer and the bpy was extracted with *n*-heptane as noted above. Identical Beer's law plots of the absorbance at 282 nm vs. [bpy] were obtained at both pH values. Thus, the same calibration plot was used to determine the concentration of free bpy at all the pH investigated.

Results

Consistent with our previous report,[2] the overall thermal reaction at pH 11.8 and in 0.50 M OH^- results in the release of free bpy into solution with concomitant spectral changes (isosbestic points at 255, 263, 271, and 307 nm) representing the formation of $Cr(bpy)_2(OH)_2^+$ as a product. The release of bpy, represented by reaction 1, occurs via first-order kinetics. The values of the rate constant, k_{obsd}, at 11 °C as a function of pH and $[OH^-]$ are depicted in Figure 1 in which the results obtained previously[2] (pH 0–10.7) have been included for completeness.

$$Cr(bpy)_3^{3+} \xrightarrow[H_2O, OH^-]{k_{obsd}} Cr(bpy)_2(OH)_2^+ + bpy \quad (1)$$
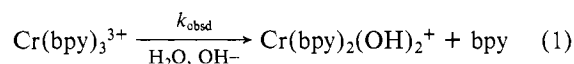
The temperature dependences of k_{obsd} were determined at pH 11.8 (11–30 °C) and at 0.50 M OH^- (5–24 °C). Activation parameters were obtained from the least-squares analysis of linear plots of log k_{obsd} vs. $10^3/T$ or log (k_{obsd}/T)
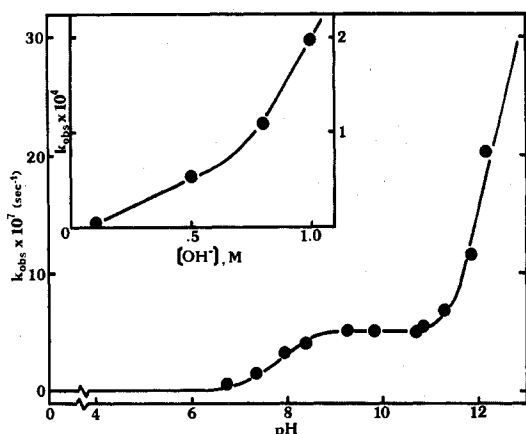
Figure 1. pH reaction profile for the aquation of $Cr(bpy)_3^{3+}$ at 11.1 ± 0.1 °C. $[Cr(bpy)_3^{3+}] \sim 1 \times 10^{-3}$ M; μ = 1.00 M (NaCl); Britton–Robinson buffer (0.008 M) between pH 0 and 12.2; NaOH solutions at pH >12.2.

vs. $10^3/T$ and are shown in Table I in comparison with the values for pH 9.8 reported previously.[2]

Discussion

Possible Mechanisms. We[2] had earlier considered four possible mechanisms for the thermal aquation of $Cr(bpy)_3^{3+}$ (pH 6–10.7) for which bipyridine substitution follows pseudo-first-order kinetics (reaction 1). These were (i) a dissociative mechanism (D) in which the first step was viewed as a Cr–N bond rupture leading to a five-coordinate intermediate, (ii) an ion-pair mechanism (interchange, I) involving the formation of the ion-pair $\{Cr(bpy)_3^{3+},OH^-\}$ as the initial step, (iii) an associative pathway (A) implicating the seven-coordinate intermediate $Cr(bpy)_3(H_2O)_3^+$, and (iv) Gillard's[10] recent proposal that H_2O attacks the C-6 (or C-6') position of the bpy framework to form a covalent hydrate intermediate. The D pathway was not considered likely inasmuch as no acid catalysis was observed for $Cr(bpy)_3^{3+}$, even in 1 M HCl, in contrast to the behavior of $Ni(bpy)_3^{2+}$[11] and $Fe(bpy)_3^{2+}$.[11,12] The interchange mechanism was also thought unlikely since the estimated[2] ion-pairing constant K_{ip} (2.6×10^6 M^{-1}) was unusually high compared to the values of "normal" ion pairs of coordination compounds.[13,14] The previously available data were not unequivocal in delineating between the associative mechanism and Gillard's covalent hydrate formation. These two pathways are again reexamined below.

It is clear from the pH profile of the thermal aquation (Figure 1) that the plot of k_{obsd} for reaction 1 as a function of pH exhibits a number of discrete regimes. At pH <6, k_{obsd} is very small and independent of pH. This can be explained by the relaxation of the initially formed $Cr(bpy)_3(H_2O)^{3+}$ intermediate back to the substrate via acid-dependent (k_a = 4×10^5 M^{-1} s^{-1}) and -independent ($k_{-2} \lesssim 10$ s^{-1}) paths.[4]

$$Cr(bpy)_3^{3+} + H_2O \underset{H^+}{\rightleftharpoons} Cr(bpy)_3(H_2O)^{3+} \quad (2)$$
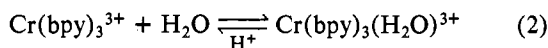
The inflection point at pH 6–9 represents the deprotonation

$$Cr(bpy)_3(H_2O)^{3+} \rightleftharpoons Cr(bpy)_3(OH)^{2+} + H^+ \quad (3)$$
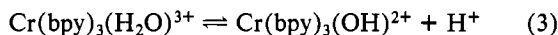
of $Cr(bpy)_3(H_2O)^{3+}$ to form the short-lived ($\tau \sim 10^{-4}$ s)[4] $Cr(bpy)_3(OH)^{2+}$ species which undergoes ring opening[15] and leads, ultimately, irreversibly, and quantitatively, to loss of the monodentate bpy.
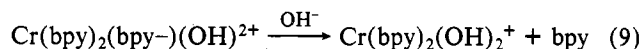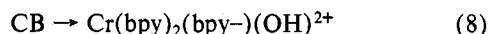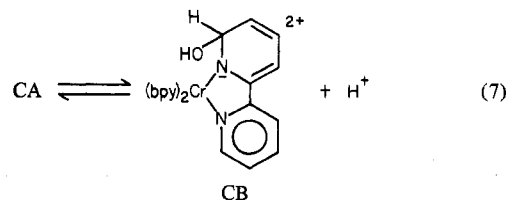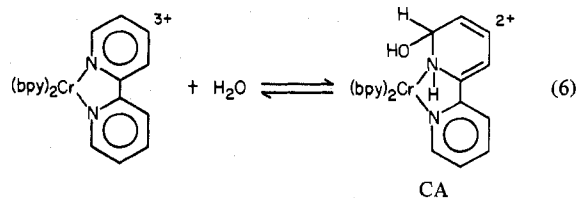
$$Cr(bpy)_3(OH)^{2+} \rightarrow Cr(bpy)_2(bpy-)(OH)^{2+} \quad (4)$$
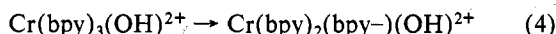
The region pH 9–10.7 reflects the complete titration of $Cr(bpy)_3(H_2O)^{3+}$ so that k_{obsd} represents the rate constant of the rate-determining attack of H_2O on $Cr(bpy)_3^{3+}$;[16] k_2 = 4.7×10^{-7} s^{-1}.

$$Cr(bpy)_2(bpy-)(OH)^{2+} \xrightarrow{OH^-} Cr(bpy)_2(OH)_2^+ + bpy \quad (5)$$
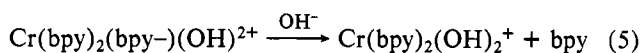
The recent isolation and characterization of Ru(II) and Ir(III) complexes containing a monodentate bpy ligand [e.g., $Ir(bpy)_2(bpy-)(OH)^{2+}$][15] might suggest that reaction 5 may not be as fast[17] as originally thought.[2] A kinetic treatment of reactions 2–5 with the assumptions that k_5 is the rate-determining step and that reactions 2 and 3 are rapidly established equilibria[10] leads to k_{obsd} = $k_4k_5K_2K_3[OH^-]^2/K_w(k_{-4} + k_5[OH^-])$. This functionality of k_{obsd} on $[OH^-]$ is inconsistent with the experimentally determined $[OH^-]$ dependence of k_{obsd} (cf. eq 3 of ref 2). In addition, we wish to point out that while, for example, $Ir(bpy)_2(bpy-)(OH)^{2+}$ has absorption and emission spectral features different from the parent $Ir(bpy)_3^{3+}$ complex,[15] spectral features for the corresponding $Cr(bpy)(bpy-)(OH)^{2+}$ analogue were not observed;[2,4] the absorption spectrum of a freshly prepared solution of $Cr(bpy)_3^{3+}$ is pH independent (0–10.7), and the relative intensity and positions of the emission maxima at 695 and 727 nm did not vary in the same pH range. The above considerations lead us to believe that replacement of the second end of the leaving bpy ligand by a second hydroxide is not rate determining.

Gillard's mechanism involving a covalent hydrate was previously[2] considered in terms of rapidly formed equilibria, as originally proposed.[10] A more general treatment leads to reactions 6–9 and a steady-state consideration on [CA] and

$$CB \rightarrow Cr(bpy)_2(bpy-)(OH)^{2+} \quad (8)$$

$$Cr(bpy)_2(bpy-)(OH)^{2+} \xrightarrow{OH^-} Cr(bpy)_2(OH)_2^+ + bpy \quad (9)$$

[CB] gives eq 10 (where k_6' = $k_6\{H_2O\}$) in agreement with

$$k_{obsd} = \frac{k_6'k_7k_8[OH^-]}{k_{-6}k_{-7}K_w + (k_{-6} + k_7)k_8[OH^-]} \quad (10)$$

eq 3 of ref 2. With the usual assumptions regarding the relative magnitudes of terms in the denominator, k_{obsd} = k_6' if $(k_{-6} + k_7)k_8[OH^-] > k_{-6}k_{-7}K_w$ and $k_7 > k_{-6}$; k_{obsd} = $k_6'k_8K_7[OH^-]/k_{-6}K_w$, if $k_{-6}k_{-7}K_w > (k_{-6} + k_7)k_8[OH^-]$. The rate-determining step is thus viewed as a nucleophilic attack by H_2O at the C-6 (or C-6') site of the bpy ring system; k_6' = 4.7×10^{-7} s^{-1}.[2]

Above pH 10.8, k_{obsd} increases dramatically with increase of pH; k_{obsd} is linearly dependent on $[OH^-]$ (Figure 2a) in the pH region 10.8–12.2. The slope of the line, 1.1×10^{-4} M^{-1} s^{-1}, is identified with the rate constant k_{11} for the direct attack of OH^- on $Cr(bpy)_3^{3+}$; the intercept is 4.7×10^{-7} s^{-1}. Reactions 4 and 5 then lead to the observed products.

$$Cr(bpy)_3^{3+} + OH^- \rightarrow Cr(bpy)_3(OH)^{2+} \quad (11)$$

This first-order dependence of k_{obsd} on $[OH^-]$ may also be interpreted in terms of Gillard's covalent hydrate mechanism[10] in which the initial OH^- attack at the C-6 position of the bpy
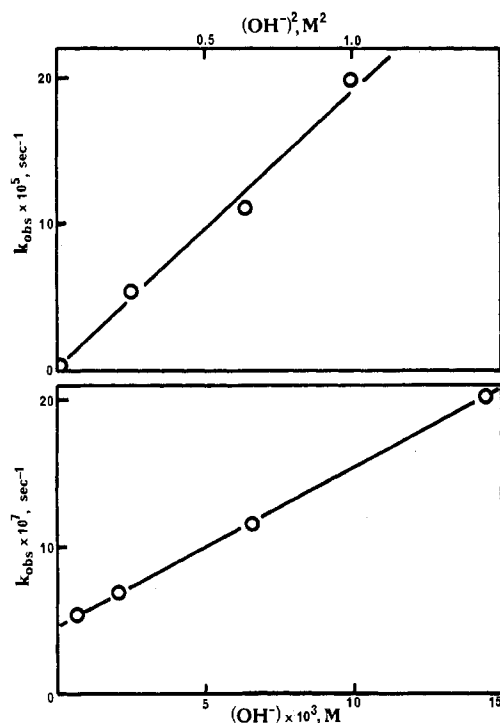
Figure 2. (a) First-order hydroxide ion dependence of k_{obsd} (lower plot) in the aquation of $Cr(bpy)_3^{3+}$ in the pH range 10.8–12.2. (b) Second-order hydroxide ion dependence of k_{obsd} (upper plot) in the aquation of $Cr(bpy)_3^{3+}$ at pH >12.2.

ligand is seen as the rate-determining step. An intramolecular shift of OH to the metal center would then lead to the same seven-coordinate intermediate as in reaction 3. It is noteworthy that an analogous mechanism has been proposed for the hydroxide ion reduction of $Ru(bpy)_3^{3+}$ [18] and of various substituted polypyridyl complexes of Fe(III) and Os(III).[19]

In the region where $[OH^-] = 0.10$–1.00 M, k_{obsd} is linearly dependent on $[OH^-]^2$ (Figure 2b). Here, the slope of the line equals 1.9×10^{-4} M^{-2} s^{-1} and the intercept has a value of $\sim 3 \times 10^{-7}$ s^{-1}. This second-order dependence of k_{obsd} on $[OH^-]$ places severe restrictions on any proposed mechanism. One plausible explanation involves the formation of outer-sphere (ion-pair) complexes at high $[OH^-]$ (reaction 12), followed
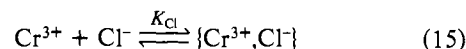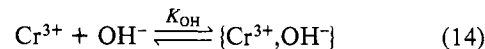
$$Cr(bpy)_3^{3+} + OH^- \xrightarrow{K_{ip}} \{Cr(bpy)_3^{3+},OH^-\} \qquad (12)$$
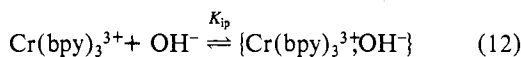
by attack of the ion-pair by another OH^- to form some

$$\{Cr(bpy)_3^{3+},OH^-\} + OH^- \rightarrow$$
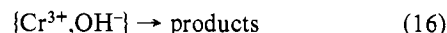$$\{Cr(bpy)_3(OH)^{2+},OH^-\} \text{ or } Cr(bpy)_2(bpy^-)(OH)_2^+ \quad (13)$$

seven-coordinate intermediate which, also, ultimately and irreversibly, leads to the release of bpy via reaction 5 or its equivalent. A kinetic treatment of reactions 12, 13, and 5 leads to the expectation that $k_{obsd} = k_{13}K_{ip}[OH^-]^2$ with $k_{13}K_{ip} = 1.9 \times 10^{-4}$ M^{-2} s^{-1}. Taking k_{13} as $\sim 10^{-4}$–10^{-5} M^{-1} s^{-1} (note that $k_{11} = 1.1 \times 10^{-4}$ M^{-1} s^{-1}), $K_{ip} \sim 2$–20. Such a value for an ion-pairing equilibrium constant is consistent with other values in the literature.[13,14] Interestingly, Creutz and Sutin[18] have also observed a second-order $[OH^-]$-dependent path at pH >13 in the reduction of $Ru(bpy)_3^{3+}$.

Changes in the solution medium, as occurs above pH 13, can also explain the apparent second-order dependence of k_{obsd} on $[OH^-]$. If major fractions of $Cr(bpy)_3^{3+}$ were present as $\{Cr(bpy)_3^{3+},OH^-\}$ ion pairs for $[OH^-]$ in the range 0.10–1.00 M, it is also likely that ion pairing with Cl^- ions may be important, according to Beck's[13] compilation of K_{ip}. Indeed, if the formation constant for the chloride ion pair were sig-

nificantly larger than that for the hydroxide analogue, the apparent increase in the reaction order with respect to $[OH^-]$ above 0.10 M could then be rationalized without invoking attack of OH^- on the $\{Cr(bpy)_3^{3+},OH^-\}$ ion pair (reaction 13). It could be argued, for instance, that hydrolysis occurs exclusively by reaction within the OH^- ion pair (reaction 16) throughout the pH range 11–14. Taking $Cr(bpy)_3^{3+}$ as Cr^{3+}, we obtain

$$Cr^{3+} + OH^- \xrightarrow{K_{OH}} \{Cr^{3+},OH^-\} \qquad (14)$$

$$Cr^{3+} + Cl^- \xrightarrow{K_{Cl}} \{Cr^{3+},Cl^-\} \qquad (15)$$

and

$$\{Cr^{3+},OH^-\} \rightarrow \text{products} \qquad (16)$$

from which rate = $k_{16} [\{Cr^{3+},OH^-\}]$. From reactions 14 and 15 and $[Cr^{3+}]_0 = [Cr^{3+}] + [\{Cr^{3+},OH^-\}] + [\{Cr^{3+},Cl^-\}]$, where $[Cr^{3+}]_0$ is the total concentration of the $Cr(bpy)_3^{3+}$ complex

$$[\{Cr^{3+},OH^-\}] = \frac{K_{OH}[OH^-][Cr^{3+}]_0}{1 + K_{OH}[OH^-] + K_{Cl}[Cl^-]} \qquad (17)$$

from which

$$\text{rate} = \frac{k_{16}K_{OH}[OH^-][Cr^{3+}]_0}{1 + K_{OH}[OH^-] + K_{Cl}[Cl^-]} \qquad (18)$$

and

$$k_{obsd} = \frac{k_{16}K_{OH}[OH^-]}{1 + K_{Cl} + (K_{OH} - K_{Cl})[OH^-]} \qquad (19)$$

with $[OH^-] + [Cl^-] \sim 1.0$ M. Equation 19 indicates that, at low $[OH^-]$ (<0.10 M) and $[Cl^-] = 1.0$–0.9 M, the complex probably exists largely as the chloride ion pairs[16] in near-constant concentration, thus leading to first-order kinetics in $[OH^-]$. At lower $[Cl^-]$ (i.e., $[OH^-]$ > 0.10 M), the concentration of the chloride ion pairs falls markedly as $[OH^-]$ increases thereby leading to an apparent order >1 in $[OH^-]$, inasmuch as k_{obsd} increases faster than $[OH]^-$ (cf. insert in Figure 1) when the latter is comparable to 1 and $K_{Cl} > 1$ and $\gg K_{OH}$ in eq 19. We hasten to note, however, that k_{obsd} is linearly dependent on $[OH^-]^2$ (Figure 2b, correlation coefficient > 0.99) which a priori would not be expected, unless fortuitously, if the second-order dependence on $[OH^-]$ were attributable to solution medium effects. We conclude that in the $[OH^-]$ range 0.10–1.00 M, the thermal aquation of $Cr(bpy)_3^{3+}$ follows second-order kinetics in $[OH^-]$.

This second-order OH^- dependence can also be reconciled with the involvement of covalent hydrates insofar as the functionality of k_{obsd} is concerned. Adapting the mechanism suggested by Nord and Wernberg[19] for the reduction of polypyridyl complexes of Fe(III) and Os(III) to the aquation of $Cr(bpy)_3^{3+}$ yields reactions 20 and 21. The steady-state

$$CB + OH^- \rightarrow \text{products} \qquad (21)$$
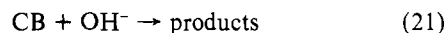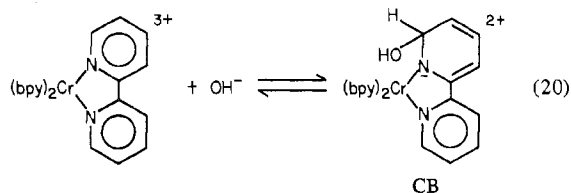
treatment on [CB] yields eq 22, from which $k_{obsd} =$

$$k_{obsd} = \frac{k_{20}k_{21}[OH^-]^2}{k_{-20} + k_{21}[OH^-]} \qquad (22)$$

$k_{21}K_{20}[OH^-]^2$ if $k_{-20} > k_{21}[OH^-]$, and $k_{obsd} = k_{20}[OH^-]$ if $k_{-20} < k_{21}[OH^-]$. It should be noted that the products from the OH^- reaction with $Fe(bpy)_3^{3+}$ and $Os(bpy)_3^{3+}$ are O_2 and the reduced forms of the complexes, in contrast to the aquation products of reaction 1.

Mechanistic Remarks. The presently available data, unfortunately, do not afford an unequivocal delineation between the associative pathway and Gillard's covalent hydrate mechanism. Notwithstanding this, the following considerations lead us to the conclusion that Gillard's mechanism may be inconsequential in the thermal aquation of $Cr(bpy)_3^{3+}$.

1. We note, for example, that the rate constant equivalent to k_{20} has been identified by Nord and Wernberg[19] as the rate-determining step in the OH^- reduction of $Fe(bpy)_3^{3+}$ and $Os(bpy)_3^{3+}$ with $k_{20} = 8$ and 2 M^{-1} s^{-1}, respectively. The rate constant for the first-order dependence of k_{obsd} on $[OH^-]$ in the aquation of $Cr(bpy)_3^{3+}$ ($\sim 1 \times 10^{-3}$ M and pH 10.8–12.2) is $\sim 10^{-3}$ M^{-1} s^{-1}. Inasmuch as $Cr(bpy)_3^{3+}$ is nearly identical with $Fe(bpy)_3^{3+}$ (charge, size), it is difficult to explain why the rate constants would differ by as much as 4 orders of magnitude if the same covalent hydrate is formed in the initial step of the reduction of $Fe(bpy)_3^{3+}$ and of the aquation of $Cr(bpy)_3^{3+}$.

2. No spectral variations in $Cr(bpy)_3^{3+}$ solutions were observed, even in very alkaline solutions ($[OH^-] = 0.50$ M), as would have been expected if the covalent hydrate $Cr(bpy)_2(bpy-OH)^{2+}$ were the intermediate in the aquation reaction (note that formation of this intermediate would appear to be relatively rapid, 8 M^{-1} s^{-1}).[19] Also, as originally proposed by Gillard,[10] covalent hydrates are rapidly formed in aqueous solutions.

3. k_{obsd} for the thermal aquation of the ground-state species, ($^4A_2$) $Cr(bpy)_3^{3+}$, and the quantum yield[4] for bpy formation in the photoaquation of the luminescent state (^2E) $Cr(bpy)_3^{3+}$ have the same pH profile (pH 6–10.7).[4] This has led to the conclusion that both aquation reactions occur via a common mechanism, which has been identified[4] as one implicating the seven-coordinate intermediate, $Cr(bpy)_3(H_2O)^{3+}$.

4. Hydroxide ion quenches the luminescence from (^2E) $Cr(bpy)_3^{3+}$ via a mechanism which probably also involves the seven-coordinate intermediate $Cr(bpy)_3(OH)^{2+}$;[4] the OH^- ion has been described as a noninnocent quencher.[5]

5. Moreover, OH^- ions quench the phosphorescence from (^2E) $Cr(en)_2(NCS)_2^+$ apparently also via the formation of a seven-coordinate intermediate[5] since no Gillard-type covalent hydrate formation is possible for this species.

6. Finally, it is also noteworthy that the nearly identical values of the activation parameters of Table I across the pH range 6–14 preclude a sudden shift in mechanism throughout the three pH regimes (Figure 1) discussed above, and, insofar as the Gillard pathway does not appear plausible for aquation at pH >10.8 (point 1 above), this pathway is also not considered likely at pH <10.8.

Energetic Considerations. To the extent that three major pathways have been identified (see Scheme I) for the thermal aquation of $Cr(bpy)_3^{3+}$ at pH >6, it is useful to compare the energetics of these three pathways. The appropriate Arrhenius and Eyring activation parameters are collected in Table I. We note, for example, that the energy of activation decreases with increasing $[OH^-]$. This is not an unexpected result[20] inasmuch as the OH^- is a better nucleophile than H_2O, and the Cr–OH bond is stronger than the $Cr-OH_2$ bond in the seven-coordinate intermediate. Spees, Perumareddi, and Adamson[21] have calculated energies of activation for substitution reactions of some 17 Cr(III) complexes using a crystal field model. Assuming a spin-paired (doublet) transition state, they have noted that activation energies ought to be $\sim 46.6 \pm 1.4$ kcal/mol (C_{4v})[22] and $\sim 56.1 \pm 2.3$ kcal/mol (D_{3h}) for a

Scheme I
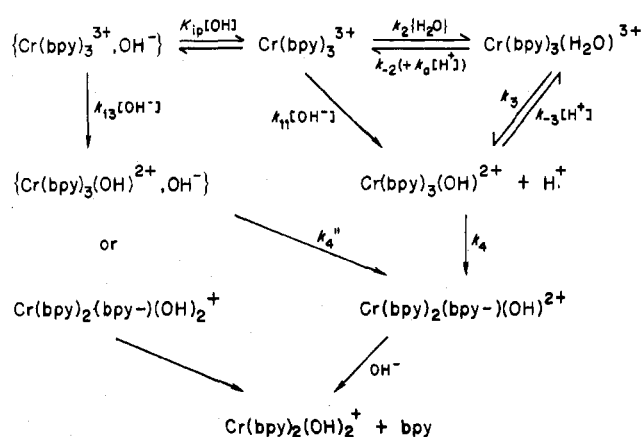
dissociative mechanism and $\sim 28.4 \pm 1.6$ kcal/mol (D_{5h}) and $\sim 33.8 \pm 1.3$ kcal/mol (C_{2v}) for an associative pathway. As crude as the model employed might be, it does suggest that dissociative mechanisms may implicate higher energies of activation (however,[23] see ref 14). The values of E_a obtained in our investigations (Table I) are in line with those ($E_a \sim 24.3 \pm 2.8$ kcal/mol) obtained for the 17 complexes analyzed.[21] This analysis, together with Swaddle's inferences[14] that Cr(III) substitution reactions proceed via associative pathways, Langford's[24] recent findings that photoanation reactions of $Cr(Me_2SO)_6^{3+}$ with N_3^- and NCS^- ions occur via an associative mechanism, and Henry and Hoffman's report[25] that the photosolvolysis reaction of $Cr(bpy)_3^{3+}$ is quenched by H^+ in 0.2 mole fraction DMF in H_2O suggesting that, also, the photoreaction occurs by an associative mechanism, lends further credence for the proposed mechanisms (see scheme below) and for the formation of seven-coordinate intermediates in the aquation of $Cr(bpy)_3^{3+}$. Additional support for the associative mechanism is also afforded by the near similarity in the values of the activation entropies and by the negative values of $\Delta S^{\ddagger}$, respectively.[26] In the absence of strong solvent effects, dissociative mechanisms are expected to show positive $\Delta S^{\ddagger}$ values.[27] The slightly more positive value of $\Delta S^{\ddagger}$ at pH 9.8 probably reflects differences between $Cr(bpy)_3(OH)^{2+}$ and $Cr(bpy)_3(H_2O)^{3+}$.

Conclusions

The thermal aquation $Cr(bpy)_3^{3+}$ across the entire pH range can be summarized by Scheme I. The following expression for k_{obsd} can be derived and the values of the component rate constants assigned:

$$k_{obsd} = \frac{k_2'k_3k_4[OH^-]}{k_{-2}(k_3' + k_4) + k_3k_4[OH^-]} + k_{11}[OH^-] + k_{13}K_{ip}[OH^-]^2$$

where $k_i' = k_i\{H_2O\}$; $k_{-2} \lesssim 10$ s^{-1} and $k_a = 4 \times 10^5$ M^{-1} s^{-1} (pH <6),[4] $k_2' = (4.7 \pm 0.4) \times 10^{-7}$ s^{-1} (pH 6–10.7), $k_{11} = 1.1 \times 10^{-4}$ M^{-1} s^{-1} (pH 10.8–12.2), and $k_{13}K_{ip} = (1.9 \pm 0.1) \times 10^{-4}$ M^{-2} s^{-1} ($[OH^-] = 0.10$–1.00 M) from which $K_{ip} \sim 2$–20 if $k_{13} \sim 10^{-4}$–10^{-5} s^{-1} (see above).

References and Notes

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(16) Since the aquation reaction was carried out at an ionic strength of 1.0 M (NaCl), it is not unreasonable to assume that $Cr(bpy)_3^{3+}$ ions (~ 1

$\times 10^{-3}$ M) are not only solvated by water molecules but also by an electrolytic sheath of Cl^- ions. It is therefore plausible that $Cr(bpy)_3^{3+}$ exists largely as the $\{Cr(bpy)_3^{3+},Cl^-\}$ ion pairs and that aquation may involve these ion pairs rather than $Cr(bpy)_3^{3+}$. For simplicity, the latter is considered in our discussion.
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Kinetics of the Chelate Effect. Ring Closing and Ring Opening in *cis*-Dichloro(dimethyl sulfoxide)((3-aminopropyl)ammonium)- and -((4-aminobutyl)ammonium)platinum(II) Chloride. Effect of Ring Size

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The kinetics of the reaction *cis*-$[Pt(dmso)(N\text{-}NH)Cl_2]^+ \rightleftharpoons [Pt(dmso)(N\text{-}N)Cl]^+ + H^+ + Cl^-$ (dmso = S-bonded dimethyl sulfoxide; N-N = chelated 1,3-diaminopropane or 1,4-diaminobutane; N-NH = the protonated monodentate form of the diamine) have been studied in both directions in aqueous solution at 30.0 °C, using phosphate buffers where necessary. The mechanism is identical with that established for the 1,2-diaminoethane complex which, for ring closing, involves a rapid reversible solvolysis of the chloride trans to the dimethyl sulfoxide, equilibrium constant K_{Cl}, and rapid acid–base equilibria between the protonated and unprotonated forms of the amine (equilibrium constants K_a' and K_a'' for the chloro and aquo complexes, respectively), followed by a rapid first-order ring closing of the unprotonated species, rate constants k^f_{Cl} and $k^f_{H_2O}$. In the case of the 1,4-diaminobutane complex, k^f_{Cl} could be measured directly in alkaline solution. For the 1,3-diaminopropane complex ($\mu = 2.0$, $NaClO_4$), $K_{Cl} = (4.4 \pm 0.8) \times 10^{-4}$ M, $K_a'k^f_{Cl} = (1.01 \pm 0.07) \times 10^{-6}$ M s^{-1}, and $K_a''k^f_{H_2O} = (3.0 \pm 0.7) \times 10^{-5}$ M s^{-1}, while for the 1,4-diaminobutane complex ($\mu = 1.2$, $NaClO_4$) $K_a'k^f_{Cl} = (2.13 \pm 0.02) \times 10^{-9}$ M s^{-1} and $k^f_{Cl} = 22.3$ s^{-1} (all at 30 °C). Temperature variation studies of k^f_{Cl} give $\Delta H^\ddagger = 9.80 \pm 0.18$ kcal mol^{-1} and $\Delta S^\ddagger = -20.4 \pm 0.6$ cal K^{-1} mol^{-1} for the closing of the seven-membered ring. The second-order rate constants for ring opening, k^r_{Cl}, are 3.1×10^{-5} M^{-1} s^{-1} for the six-membered ring and $(1.04 \pm 0.03) \times 10^{-4}$ M^{-1} s^{-1} for the seven-membered ring. This behavior is compared to that of the previously reported 1,2-diaminoethane complex[1] and the analogous bis-(monodentate amine) systems and the significance of ring size and amine basicity in determining the reactivity of these systems is examined.

Introduction

In a recent paper[1] we examined the kinetics of the forward and reverse processes of the reaction,

$$cis\text{-}[Pt(dmso)(enH)Cl_2]^+ \rightarrow [Pt(dmso)(en)Cl]^+ + H^+ + Cl^-$$
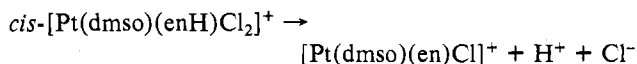
the purpose of the work being to establish the parameters governing the dimethyl sulfoxide system in order to be able to examine the effect of increasing the size of the chelate ring. A number of other studies involving flexible five-membered chelate rings have been reported, notably those of Carter and Beattie[2] and, more recently, of Natile et al.[3] There are few systematic and relevant kinetic studies of the ring-opening and ring-closing processes with flexible six-membered ring systems and none, to our knowledge, involving a seven-membered ring. In this paper we examine the above reaction with the complexes of 1,3-diaminopropane (tn) and 1,4-diaminobutane (bn).

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Experimental Section

cis-**Dichloro(dimethyl sulfoxide)((3-aminopropyl)ammonium)-platinum(II) Chloride.** $[Pt(dmso)(tn)Cl]Cl$ (0.16 g, 0.40 mmol), prepared by the method of Romeo et al.,[4] was dissolved in the minimum amount of methanol and the solution stirred vigorously while concentrated hydrochloric acid (0.20 cm³, 2 mmol) was added. The mixture was left to stand for 24 h at room temperature and the required product separated out as a white powder. This was filtered off, washed carefully with 2 or 3 drops of concentrated hydrochloric acid to remove a small amount of yellow impurity and then washed with ether, and finally air-dried.

Anal. Calcd for $C_5H_{17}N_2OCl_3PtS$: C, 13.2; H, 3.77; N, 6.16; Cl, 23.4; S, 7.05. Found: C, 13.5; H, 3.90; N, 6.17; Cl, 23.6; S, 7.02.

The infrared spectrum is characterized by a barely resolved strong doublet at 1112 and 1105 cm⁻¹, assigned to $\nu_{S\text{-}O}$ of S-bonded dimethyl sulfoxide. In the range 500–300 cm⁻¹ there are peaks at 447 (m), 378 (m), 348 (s), and 319 (s) cm⁻¹, the latter two being assigned to $\nu_{Pt\text{-}Cl}$, the splitting being characteristic of a pair of cis chlorines.

cis-**Dichloro(dimethyl sulfoxide)((4-aminobutyl)ammonium)platinum(II) chloride** was prepared in a similar way from $[Pt(dmso)(bn)Cl]Cl$[4] but using ethanol as solvent.