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Pressure Effects on the Aquation Reactions of Tris(2,2′-bipyridine)chromium(III) Ion and Tris(1,10-phenanthroline)chromium(III) Ion

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The effects of high pressure on the rates of aquation reactions of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ have been measured. The activation volumes of aquation were derived as -0.9 ± 0.5 and $+5.2 \pm 0.4$ cm³ mol⁻¹ for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, respectively. These values are consistent with those expected from an interchange mechanism involving water penetration to the coordination sphere and an extension of one or both of the Cr-polypyridine bonds.

The substitution reaction mechanisms of polypyridyl transition metal complexes: $M(NN)_m^{n+}$ have been extensively studied.[1] Maestri et al.[2] have reported that the aquation reactions of polypyridyl chromium(III) complexes were catalyzed by hydroxide ion. The hydroxide concentration dependence of a pseudo-first-order rate constant is given by

$$k_{obsd} = [OH^-]/(B + A \cdot [OH^-]) \quad (pH < 11), \qquad (1)$$

where A and B are constants. They discussed the mechanisms which were suited to Eq. 1, and proposed that the most favorable mechanism is an associative one involving the formation of a seven-coordinate intermediate via a nucleophilic attack of a water molecule.

These complexes have also drawn much attention to the photochemical and photophysical behaviors.[2c,3] The photochemical aquation quantum yields of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ show similar pH profiles to the thermal rate constants, suggesting that thermal and photochemical reactions proceed through a common intermediate. A dissociative interchange nature regarding the photochemical aquation reaction has been invoked by Lilie et al.[4] There is still controversy concerning the nature of the aquation mechanism.

The volume of activation ($\Delta V^{\neq}$) determined from the effect of high pressure on the reaction rate has been applied to the elucidation of mechanistic problems.[5] The high-pressure study reported here was undertaken to determine the volumes of activation and to clarify the mechanism of the aquation reaction of the polypyridyl chromium(III) complexes. Recently, Kirk et al. have reported a small positive volume of activation of 2.9 cm³ mol⁻¹ for the photochemical reaction of $Cr(bpy)_3^{3+}$.[6] It is interesting to compare the volumes of activation for the ground-state reaction with the exited-state one.

Experimental

Materials. $[Cr(bpy)_3](ClO_4)_3 \cdot 1/2H_2O$ and $[Cr(phen)_3](ClO_4)_3 \cdot 2H_2O$ were prepared and purified as reported in the literature.[2c,7] The other chemicals used were guaranteed reagent-grade and doubly-distilled water.

Measurement. The reactions were conducted in a high-pressure vessel maintained at 50 °C by thermostated water circulated through channels in the body of the steel vessel. The pressure was monitored with a Heize Bourdon gauge. The complex concentration was 1.0×10^{-3} mol dm⁻³, ionic strength was maintained at 1.0 mol dm⁻³ with NaCl, and Britton–Robinson buffers 8×10^{-3} mol dm⁻³ were used throughout the following experiments. The kinetics of the aquation process were followed by the concentrations of the released polypyridine ligands. The released bipyridine or phenanthroline was extracted with *n*-heptane or chloroform, respectively, and analyzed spectrophotometrically, as described in the literature.[2]

Results and Discussion

No spectral changes were observed for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ at pH<4.5 and atmospheric pressure, and at pH<5.0 and a pressure of 300 MPa. In basic solutions, the spectra gradually changed and isosbestic points were observed at 307, 275, and 263 nm for $Cr(bpy)_3^{3+}$ and 302, 285, and 255 nm for $Cr(phen)_3^{3+}$, respectively; they were maintained until more than 50% of the reactant disappeared. The spectral changes were consistent with the formation of dihydroxy complexes and the free polypyridine ligand,[2] as given by

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

Here, NN is 2,2′-bipyridne or 1,10-phenanthroline. At pH 5—7, protonated products formed. After pressurerized reactions, the spectral changes recorded under atmospheric pressure showed the same isosbestic points for the ambient pressure reactions. The reaction stoichiometries at high pressure are also given by Eq. 2.

The values of the observed pseudo-first-order rate constants (k_{obsd}) for the polypyridyl complexes at different pressures and pH are summarized in Table 1. The pH dependencies of k_{obsd} are given in Fig. 1. At atmospheric pressure, the pH dependencies of k_{obsd} are consistent with early reports of Maestri et al.[2a] as well as

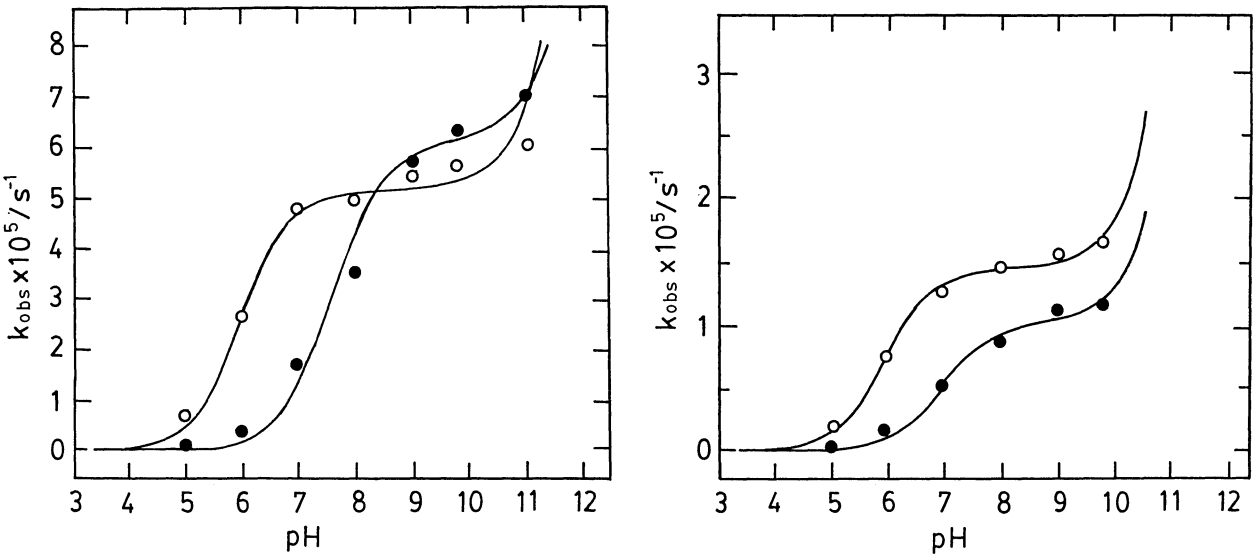


Fig. 1. pH dependence of the pseudo-first-order rate constants, k_{obsd}, for the aquation of $Cr(bpy)_3^{3+}$; a, and $Cr(phen)_3^{3+}$; b, at atmospheric pressure (○) and 300 MPa (●).

Table 1. Pressure and pH Dependence of Aquation Reaction Rate Constants for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ Ions[a)]

Pressure	pH	$Cr(bpy)_3^{3+}$	$Cr(phen)_3^{3+}$
P/MPa		10^5k_{obsd}/s^{-1}	10^5k_{obsd}/s^{-1}
0.1	5.0	0.68±0.02	0.18±0.02
	6.0	2.64±0.04	0.76±0.02
	7.0	4.82±0.05	1.23±0.02
	8.0	4.77±0.05	1.44±0.02
	9.0	5.47±0.07	1.55±0.02
	9.8	5.63±0.09	1.61±0.05
	11.0	5.84±0.11	—
	12.2	11.1 ±0.2	4.68±0.11
50	9.8	5.67±0.09	—
100		5.69±0.11	1.35±0.04
150		5.76±0.07	—
200		6.08±0.10	1.21±0.05
250		6.12±0.10	—
300	5.0	0.11±0.02	0.03±0.02
	6.0	0.37±0.02	0.16±0.02
	7.0	1.68±0.03	0.50±0.02
	8.0	3.54±0.08	0.85±0.03
	9.0	5.74±0.08	1.09±0.04
	9.8	6.32±0.10	1.12±0.07
	11.0	7.01±0.08	—
	12.2	9.18±0.20	4.55±0.13

a) At 50 °C; Britton-Robinson buffer; I=1.0 mol dm^{-3} with NaCl.

Table 2. Parameters of Eq. 1 for the pH Dependent Aquations of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ Ions, under Atmospheric Pressure and 300 MPa

Complex	P	$A^{-1}\times10^5$	$A\cdot B^{-1}\times10^{-7}$	$C\times10^2$
	MPa	s^{-1}	dm^3 mol^{-1}	dm^3 mol^{-1} s^{-1}
$Cr(bpy)_3^{3+}$	0.1	5.4 ±0.2	9.8 ±0.2	0.5±0.2
	300	6.1 ±0.2	0.25±0.03	1.0±0.2
$Cr(phen)_3^{3+}$	0.1	1.59±0.05	11.8 ±0.2	4.2±0.5
	300	1.05±0.05	1.07±0.03	2.9±0.5

Bolletta et al.[2c)] for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, respectively. Under high pressure (300 MPa), the inflection points shifted to higher pH for both complexes. In the pH 9—10 region the values of k_{obsd} reached plateaus. The pH dependencies of the pseudo-first-order rate constants were fitted with

$$k_{obsd}=\frac{[OH^-]}{B+A\cdot[OH^-]}+C[OH^-], \qquad (3)$$

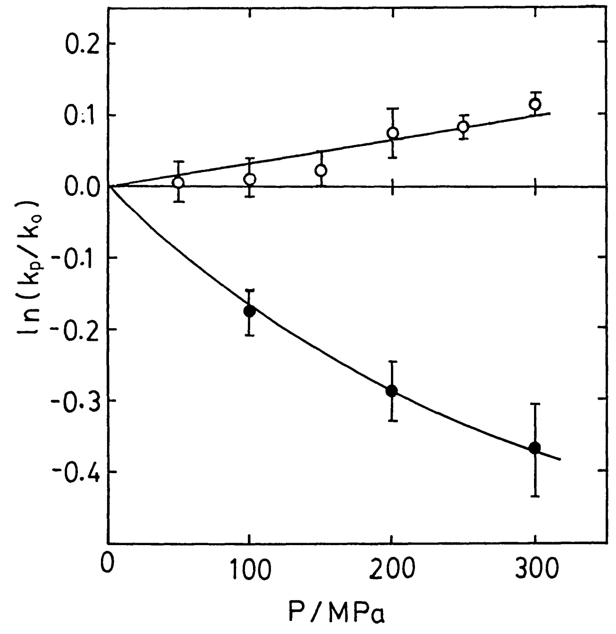


Fig. 2. Pressure dependence of ln k relative to atmospheric pressure for $Cr(bpy)_3^{3+}$ (○) and $Cr(phen)_3^{3+}$ (●) at 50.0 °C, I=1.0 mol dm^{-3} and pH 9.8.

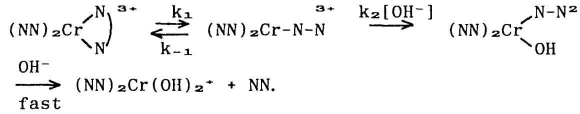
where $A \cdot B^{-1}$ gives the first inflection point, which corresponds to the acid-base equilibrium of the reaction intermediate; A^{-1} is the first-order rate constant at the plateau pH region, which is referred to the complete titration of the intermediate; C is a second-order rate constant corresponding to direct attacking of OH^-. Above pH 10.5, the second term of Eq. 3 contributes dominantly. A nonlinear least-squares curve fitting with Eq. 3 yielded parameters A, B, and C (Table 2). At the plateau region (pH 9.8), the rates of aquation for the complexes were measured under various pressures (Table 1 and Fig. 2). The rate constants for $Cr(phen)_3^{3+}$ markedly decreased upon the application of pressure. In contrast, only a small increase in the rate constant was observed for $Cr(bpy)_3^{3+}$.

The volume of activation ($\Delta V^{\neq}$) was evaluated from

$$-RT\ln(k_p/k_o) = \Delta V^{\neq}P + \Delta\beta^{\neq}P^2/2, \qquad (4)$$

where k_o and k_p are the rate constants at atmospheric pressure and the applied pressure (P), respectively, and $\Delta\beta^{\neq}$ is the compressibility of activation. The values of $\Delta V_A^{\neq}$ and $\Delta\beta_A^{\neq}$ for A^{-1} and ΔV_B for B^{-1} are summarized in Table 3.

We first consider the case in which the transition state is formed by a dissociative process. The dissociative mechanism involves an intermediate which is formed by one or both Cr–N bond rupture of the polypyridyl ligand. The elementary processes are given by



(5)

A steady-state treatment of the concentration of the intermediate leads to

$$k_{obsd} = \frac{k_1k_2[OH^-]}{k_{-1}+k_2[OH^-]}. \qquad (6)$$

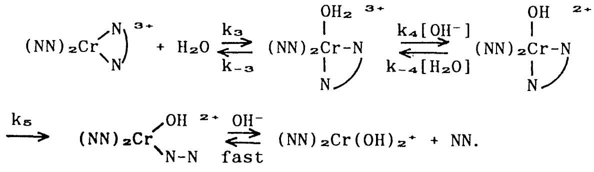
Each parameter in Eq. 1 is given by $A^{-1}=k_1$ and $B^{-1}=k_1 \cdot k_2/k_{-1}=K_1 \cdot k_2$. The volume of activation and the volume change are given by $\Delta V_A^{\neq}=\Delta V_1^{\neq}$ and $\Delta V_B=\Delta V_1+\Delta V_2^{\neq}$. The first bond rupture step (k_1) might be accompanied by a large positive volume of activation; a very large value of $\Delta V_1+\Delta V_2^{\neq}$ is expected because ΔV_1 is nearly equal to $\Delta V_1^{\neq}$; the second step involves charge neutralization. Indeed, aquation of $Fe(phen)_3^{3+}$ is associated with a large positive activation volume of +15.4 cm^3 mol^{-1},[8] which refers to the dissociation of a phen ligand. This limiting dissociative mechanism is not consistent with the observed small absolute values (+5.2 cm^3 mol^{-1} and −0.9 cm^3 mol^{-1} for $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$, respectively).

Table 3. Activation Volumes ($\Delta V_A^{\neq}$) and Compressibility Coefficients of Activation ($\Delta\beta_A^{\neq}$) and Volume Change ΔV_B for Aquations of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ Ions[a)]

Complex	$\Delta V_A^{\neq}$	$\Delta\beta_A^{\neq}$	ΔV_B
	cm^3 mol^{-1}	10^{-2} cm^3 mol^{-1} MPa	cm^3 mol^{-1}
$Cr(bpy)_3^{3+}$	−0.9±0.5[b)]	—	32±5[b)]
$Cr(phen)_3^{3+}$	5.2±0.4	1.3±0.2	21±4[b)]

a) At 50 °C; Britton-Robinson buffer; I=1.0 mol dm^{-3} with NaCl. b) Analyzed with linear relation; $\ln(k_p/k_o) = -(\Delta V^{\neq}/RT)P$.

On the other hand, the alternative associative mechanism assumes that the sevencoordinate complex obtained upon H_2O coordination undergoes an acid-base equilibrium:



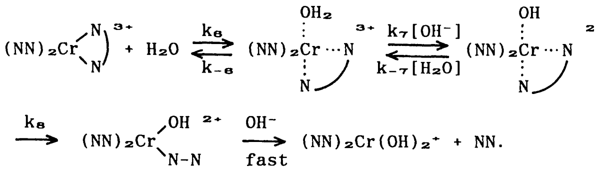
(7)

The pseudo-first-order rate constant is given by

$$k_{obsd} = \frac{k'_3k_4k_5[OH^-]}{k_{-3}(k_5+k'_{-4})+k_4k_5[OH^-]}, \qquad (8)$$

where $k'_1=k_1[H_2O]$; each parameter in Eq. 7 is $A^{-1}=k'_3$, and $B^{-1}=k'_3k_4k_5/k_{-3}(k_5+k'_{-4})$. It is assumed that rapid acid-base equilibrium is establish, $k_5 \ll k_4$ and k'_{-4}, since the proton transfer proess (k_4 and k_{-4}) should be faster than the bond-dissociation step (k_5). Then, $B^{-1}=K_3 \cdot K_4 \cdot k_5$. $\Delta V_A^{\neq}$ corresponds to $\Delta V_3^{\neq}$, and ΔV_B to $\Delta V_3+\Delta V_4+\Delta V_5^{\neq}$. The volume of activation of the k_3 step should have a large negative value, since a water molecule enters the coordination sphere to form a sevencoordinated intermediate during this step. For a purely associative mechanism one would expect a $\Delta V^{\neq}$ of approximately −16 cm^3 mol^{-1}.[9] ΔV_3 is expected to have a large negative value like that of $\Delta V_3^{\neq}$ since a water penetration reduces the volume of the system. ΔV_4, however, should have a large positive value, since an acid-base equilibrium involves charge neutralization. The volume change of acid-base equilibrium was estimated to be about 20 cm^3 mol^{-1} from the values measured for $Cr(H_2O)_6^{3+}$[10] and $Co(NH_3)_5(H_2O)^{3+}$[11] (17.5 cm^3 mol^{-1} and 20.6 cm^3 mol^{-1}, respectively). Since step k_5 involves bond breaking of the polypyridyl ligand, $\Delta V_5^{\neq}$ should have a large positive value. The sum of the volume changes of $\Delta V_3+\Delta V_4+\Delta V_5^{\neq}$ is expected to have a slightly positive value. The limiting associative mechanism is also not consistent with the observed volumes of activation.

The real situation proceeds between the two extremes. The interchange mechanism can be illustrated as follows:



(9)

This leads to

$$k_{\mathrm{obsd}}=\frac{k'_6k_7k_8[\mathrm{OH}^-]}{k_{-6}(k_8+k'_{-7})+k'_7k_8[\mathrm{OH}^-]},\qquad(10)$$

where $A^{-1}=k'_8$ and $B^{-1}=k'_6k_7k_8/k_{-6}(k_8+k'_{-7})$. If $k'_{-7}\gg k_8$ (for the same reason described above), then $B^{-1}=K_6\cdot K_7\cdot k_8$. $\Delta V_A^{\neq}$ corresponds to $\Delta V_6^{\neq}$ and ΔV_B to $\Delta V_6+\Delta V_7+\Delta V_8^{\neq}$. The k_6 step involves the association of a water molecule and an extension of one or both of the Cr–N bonds, simultaneously, in the transition state. The resultant volume of activatin for k_6 has a small absolute value, since both effects are compensating. The slightly positive $\Delta V_6^{\neq}$ for $\mathrm{Cr(phen)_3}^{3+}$ suggests that a more rigid phen ligand needs a large extension of the Cr–N bond. The absolute value of ΔV_6 is also small and the volume change for k_7 is expected to be very positive. The value of $\Delta V_7^{\neq}$ may have a small absolute value, since the k_8 step involves a neutral ligand exchange. The total of $\Delta V_6+\Delta V_7+\Delta V_8^{\neq}$ is expected to have a large positive value. This is consistent with the experimental results. The small positive value of $\Delta\beta_A^{\neq}$ for $\mathrm{Cr(phen)_3}^{3+}$ also provides evidence of an I_d mechanism.[5]

The volume of activation of the photochemical aquation reaction for $\mathrm{Cr(bpy)_3}^{3+}$ (Eq. 11) was determined to have a slightly positive value (2.9 $\mathrm{cm^3\,mol^{-1}}$):[6]

$$^{*}\mathrm{Cr(bpy)_3}^{3+}+2\mathrm{OH}^-\longrightarrow\mathrm{Cr(bpy)_2(OH)_2}^{+}+\mathrm{bpy}.\qquad(11)$$

The photoreactive excited state has been assigned to the lowest doublet excited state ($^2\mathrm{E}/^2\mathrm{T}_1$).[2c] The geometry of the doublet excited state should not change greatly from the ground state one, since both states are correlated with the same $\mathrm{t_{2g}}^3$ electronic configuration. In the transition state from the doublet state, the metal-bipyridine bond is more extended than in the ground state one.

We conclude that thermal and photochemical aquation mechanisms of polypyridyl chromium(III) complexes have an interchange character, and that the thermal aquation of $\mathrm{Cr(phen)_3}^{3+}$ and the photochemical aquation of $\mathrm{Cr(bpy)_3}^{3+}$ are more dissociative than the thermal aquation of $\mathrm{Cr(bpy)_3}^{3+}$.

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