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High Pressure Mechanistic Studies of the Photochemical Reactions of Transition Metal Complexes.
II. Ligand Field Photolysis of $Cr(NCS)_6^{3-}$, $Cr(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ in Aqueous Solution

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The photo-aquation reactions of $Cr(NCS)_6^{3-}$, $Cr(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ have been studied as a function of pressure up to 1500 bar. The apparent volumes of activation for these reactions, determined from the pressure dependence of the quantum yields, are +2.1 ± 0.3, +2.7 ± 0.2 and +1.3 ± 0.1 $cm^3 mol^{-1}$, respectively. These dataare discussed in detail in reference to partial molar volume data and are interpreted as evidence for a photo-aquation mechanism of the I_d type.

Introduction

In a recent study [1] we have reported the first high pressure mechanistic investigation of the ligand field photolysis of some cationic Cr(III) ammine complexes, *viz.* $Cr(NH_3)_5X^{2+}$ (X = Cl, Br and NCS) and $Cr(NH_3)_6^{3+}$. The apparent volumes of activation for the photo-substitution reactions, obtained from the pressure dependence of the quantum yields and volume equation calculations, led to a better understanding of the molecular processes involved in such reactions. We have now extended the latter study [1] to include the photo-aquation reactions of some anionic Cr(III) and Co(III) complexes.

Experimental

Materials

$K_3[Cr(NCS)_6]\cdot 4H_2O$ (Alfa Products) was recrystallized from ethanol. $K_3Cr(CN)_6$ and $K_3Co(CN)_6$ were prepared as described in the literature [2, 3]. The purity of the complexes was checked by chemical analyses. Analytical reagent grade chemicals and doubly distilled water were used in all solutions.

Instrumentation

As described in Part I of this series [1].

Measurements

In addition to the previously outlined measurements [1], the concentration of the cyanide ion released during the photolysis of $Cr(CN)_6^{3-}$ was determined following a potentiometric titration method [4, 5]. The photolysis of $Co(CN)_6^{3-}$ was followed spectrophotometrically since the photo-substitution process results in a significant change in absorption spectra [6].

Results and Discussion

During ligand field irradiation of the species ML_6^{3-} (M = Co(III), Cr(III) and L = CN, NCS) the observed photoreaction is [5–12]

$$ML_6^{3-} + H_2O \xrightarrow{h\nu} ML_5(OH_2)^{2-} + L^-$$

The corresponding thermal (dark) reactions of the parent complexes [7, 13–15] are sufficiently slow, so that they do not interfere with the determination of the photochemical conversions. But, depending on the experimental conditions, the $ML_5(OH_2)^{2-}$ photolysis product can undergo rapid thermal aquation to produce *cis*-$ML_4(OH_2)_2^-$ and in some cases even total loss of L^- [5]. However, it is possible to study the ligand field photolysis of the ML_6^{3-} species under conditions where the secondary reactions are reduced to a minimum, such that their contribution is negligible or can easily be corrected for [16].

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TABLE I. Comparison of the Quantum Yields Found in This Investigation with Those Reported in the Literature at Normal Pressure.

Complex	Absorption Maxima^a; nm	Irradiation Position, nm	$[H^+]$ *M*	ϕ_L^{b} mol/Einstein	Reference
$Cr(NCS)_6^{3-}$	416(L_1)	546	0.2	0.26	This work
	563(L_2)	545	0.06	0.26	7
		600	0.06	0.27	7
$Cr(CN)_6^{3-}$	307(L_1)	364.5	pH = 8.9	0.11	This work
	377(L_2)	L_2		0.12	5
		L_1		0.12	5
		L_2	pH = 6.9	0.09	9
		L_1		0.09	9
$Co(CN)_6^{3-}$	272(L_1)	316.5	pH = 6	0.32	This work
	314(L_2)	313		0.31	17–19
		313	pH = 2–7.5	0.31	6
		365		0.31	6

^{a}Measured in this study. ^{b}L = NCS, CN.

TABLE II. Pressure Dependence of the Quantum Yield for the Ligand Field Photolysis of Anionic Cr(III) and Co(III) Complexes in Aqueous Solution.^{a}

Complex	Irradiation Wavelength, nm	Temp. °C	$[H^+]$ *M*	Ionic strength *M*	Pressure bar	ϕ_L^{b} Mol/Einstein
$Cr(NCS)_6^{3-}$	546^c	15	0.1	0.5	1	0.256 ± 0.009
					250	0.242 ± 0.009
					500	0.241 ± 0.010
					750	0.235 ± 0.006
					1000	0.232 ± 0.008
$Cr(CN)_6^{3-}$	364.5^c	15	pH = 8.9	0.3	1	0.106 ± 0.003
					250	0.101 ± 0.005
					500	0.098 ± 0.007
					750	0.095 ± 0.004
					1000	0.094 ± 0.004
					1250	0.092 ± 0.005
					1500	0.088 ± 0.004
$Co(CN)_6^{3-}$	316.5^d	15	pH = 6	0	1	0.321 ± 0.011
					250	0.312 ± 0.013
					500	0.311 ± 0.018
					750	0.306 ± 0.013
					1000	0.303 ± 0.008
					1250	0.297 ± 0.008
					1500	0.293 ± 0.008

^{a}Reaction volume = 3.5 cm^3. ^{b}Mean value of at least five determinations, L = NCS, CN. ^{c}Hg lamp. ^{d}Argon ion laser.

The measured quantum yields of the photoaquation reactions are compared with literature values at normal pressure in Table I, and are reported as function of pressure in Table II. From Table I it follows that the quantum yields, ϕ_L, found in this study are in close agreement with those reported in the literature. In Table II it is shown that these decrease slightly with increasing pressure, which is exactly the opposite tendency than that observed for the photolysis of the cationic Cr(III) ammine complexes [1]. The plots of lnϕ_L *versus* p are linear for the three systems over the pressure range investigated,

TABLE III. Volumes of Activation for the Photo-aquation of Some Anionic Cr(III) and Co(III) Complexes.[a]

Complex	$\Delta V^{\neq}_{app}$ $cm^3\ mol^{-1}$	$\Delta V^{\neq}_r$ [b] $cm^3\ mol^{-1}$
$Cr(NCS)_6^{3-}$	+2.1 ± 0.4	+2.9 ± 0.6
$Cr(CN)_6^{3-}$	+2.7 ± 0.2	+3.0 ± 0.2
$Co(CN)_6^{3-}$	+1.3 ± 0.1	+2.0 ± 0.2

[a] For experimental conditions see Table II. [b] Calculated value – see Discussion.

and the thus calculated [1] apparent volumes of activation ($\Delta V^{\neq}_{app}$) are summarized in Table III. The individual volume of activation for the primary photochemical reaction ($\Delta V^{\neq}_r$) was calculated from the equation [1]

$$\Delta V^{\neq}_r = \Delta V^{\neq}_{app}/(1 - \phi^{o}_{L})$$

where ϕ^{o}_{L} is taken from Table II at normal pressure. The magnitude and sign of the values of $\Delta V^{\neq}_r$ (Table III) suggest the involved mechanism to be of the I_d type as a first approximation [20]. However, the data call for a more detailed analysis and discussion.

In a recent study [21] of the thermal aquation of $Co(CN)_5Cl^{3-}$ and $Co(CN)_5Br^{3-}$, the reported activation volumes are in agreement with a purely dissociative mechanism. Volume equation calculations [21] led to a partial molar volume of 114.2 ± 1.6 $cm^3\ mol^{-1}$ for the five-coordinate intermediate species, $Co(CN)_5^{2-}$. If we consider the possibility that a similar *dissociative* mechanism is operative during the ligand field photolysis of $Co(CN)_6^{3-}$, it may include the reaction

$$Co(CN)_6^{3-} \xrightarrow{h\nu} [Co(CN)_5^{2-} + CN^-]^{\neq} \rightarrow \text{products}$$

For the corresponding thermal process, the volume of activation, $\Delta V^{\neq}_D$, yields:

$$\Delta V^{\neq}_D = \bar{V}\{Co(CN)_5^{2-}\} + \bar{V}\{CN^-\} - \bar{V}\{Co(CN)_6^{3-}\}$$

$$= (114.2 \pm 1.6) + 28.0 - 132.8$$

$$= +9.4 \pm 1.6\ cm^3\ mol^{-1}$$

where the values for $\bar{V}\{CN^-\}$ and $\bar{V}\{Co(CN)_6^{3-}\}$ were obtained from density measurements [22].

Similar calculations for the photo-aquation of $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$ are more difficult due to a lack of partial molar volume data for the intermediate species, $Cr(CN)_5^{2-}$ and $Cr(NCS)_5^{2-}$, respectively. From a comparison of partial molar volume data [22, 23] of complexes of the type $M(NH_3)_6^{3+}$, $M(NH_3)_5OH_2^{3+}$ and $M(CN)_6^{3-}$ for M = Co(III) and Cr(III), it follows that a good approximation for the substitution of Co(III) by Cr(III) is given by the equation

$$\bar{V}\{Cr(CN)_5^{2-}\} = \bar{V}\{Co(CN)_5^{2-}\} + 15$$

$$= 129.2 \pm 1.6\ cm^3\ mol^{-1}$$

The estimation of $\bar{V}\{Cr(NCS)_5^{2-}\}$ is unfortunately more speculative. From a comparison of $\bar{V}\{Cr(CN)_6^{3-}\}$ and $\bar{V}\{Cr(NCS)_6^{3-}\}$, one can estimate that $\bar{V}\{Cr(NCS)_5^{2-}\}$ = 213.7 $cm^3\ mol^{-1}$. Alternatively from a comparison of $\bar{V}\{Co(CN)_6^{3-}\}$ and $\bar{V}\{Co(CN)_5^{2-}\}$, or $\bar{V}\{Cr(CN)_6^{3-}\}$ and $\bar{V}\{Cr(CN)_5^{2-}\}$, we predict that $\bar{V}\{Cr(NCS)_5^{2-}\}$ = 222.7 $cm^3\ mol^{-1}$. It follows that our estimated value for $\bar{V}\{Cr(NCS)_5^{2-}\}$ is between 213.7 and 222.7, with an average value of 218 ± 4 $cm^3\ mol^{-1}$. The latter value and the above estimated value for $\bar{V}\{Cr(CN)_5^{2-}\}$ were used to calculate $\Delta V^{\neq}_D$ for the photo-aquation of $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$ (in the way outlined for $Co(CN)_6^{3-}$), and the results are summarized in Table IV.

Although considerable errors are involved in the above outlined calculations, the values of $\Delta V^{\neq}_D$ in Table IV are remarkably constant for the three investigated systems. Furthermore, the average value of $\Delta V^{\neq}_D$, *viz.* +9.3 ± 0.1 $cm^3\ mol^{-1}$, is in very good agreement with the average value [24] of +9.7 ± 2.6 $cm^3\ mol^{-1}$ reported for the thermal aquation

TABLE IV. Volume Equation Calculations[a] for the Reactions $ML_6^{3-} + H_2O \xrightarrow{h\nu} ML_5(OH_2)^{2-} + L^-$.

Complex	$\bar{V}$[b]	$\Delta V^{\neq}_r$	$\bar{V}(ML_5^{2-})$	$\Delta V^{\neq}_D$	$\Delta V^{\neq}_A$ [c]	% Associative character
$Co(CN)_6^{3-}$	132.8	2.0 ± 0.2	114.2 ± 1.6[d]	+9.4 ± 1.6	−7.4 ± 1.8	46 ± 11
$Cr(CN)_6^{3-}$	147.8	3.0 ± 0.2	129.2 ± 1.6[e]	+9.4 ± 1.6	−6.4 ± 1.8	40 ± 11
$Cr(NCS)_6^{3-}$	249.2	2.9 ± 0.6	218.2 ± 4.5[e]	+9.2 ± 4.5	−6.3 ± 5.1	40 ± 31

[a] All volumes are given in $cm^3\ mol^{-1}$. [b] See ref. 22. [c] Calculated from $\Delta V^{\neq}_A = \Delta V^{\neq}_r - \Delta V^{\neq}_D$. [d] See ref. 21. [e] Estimated value – see Discussion.

reactions of $Co(CN)_5X^{3-}$ (X = Cl, Br and I), which are all dissociative processes. The values of $\Delta V_D^{\neq}$ in Table IV are, however, markedly more positive than the experimentally observed $\Delta V_r^{\neq}$ values, which indicates that the photo-aquation processes are rather of the I_d than of the D type. In the I_d mechanism partial bond formation with the entering solvent molecule occurs, and the associative contribution of this step towards the observed $\Delta V_r^{\neq}$ is given by

$$\Delta V_A^{\neq} = \Delta V_r^{\neq} - \Delta V_D^{\neq}$$

The negative contributions of $\Delta V_A^{\neq}$ are within expectation and are ascribed to the formation of the metal solvent bond. For the entrance of a water molecule into the first coordination sphere of an octahedral complex ion one would expect [1] $\Delta V_A^{\neq}$ to be of the order of -16 cm^3 mol^{-1}. It follows that the values of $\Delta V_A^{\neq}$ in Table IV favour a mechanism in which approx. 50% metal–solvent bond formation (associative character) occurs. This is in agreement with the general principle of interchange reactions: for an I_a mechanism the associative entrance of a solvent molecule is accompanied by partial bond breakage with the leaving group [1, 21, 23], whereas for an I_d mechanism the dissociative departure of the leaving group is accompanied by partial bond formation with the entering solvent molecule.

The reported $\Delta V_r^{\neq}$ value for the photo-aquation of $Cr(NCS)_6^{3-}$ is in excellent agreement with the value of +2.9 ± 0.8 cm^3 mol^{-1} reported [25] for the corresponding thermal reaction. The latter data was also considered as evidence for an I_d, rather than a D, mechanism.

Finally we would like to comment on the ability of Cr(III) complexes to undergo photo-substitution according to both I_a and I_d mechanisms. In our earlier study [1], we found that the cationic complexes $Cr(NH_3)_5X^{2+}$ (X = Cl, Br, NCS) and $Cr(NH_3)_6^{3+}$ undergo photo-aquation via an I_a mechanism, which is in contrast to the I_d mechanism now suggested for the photo-aquation of the negatively charged $Cr(CN)_3^{6-}$ and $Cr(NCS)_6^{3-}$. A similar switch over in mechanism was also observed by Cusumano and Langford [26] in the solvent dependence of the photolysis quantum yields: the cationic *trans*-Cr-$(en)_2(NCS)_2^+$ species showed associative, whereas the anionic *trans*-$Cr(NH_3)_2(NCS)_4^-$ species showed dissociative behavior. The concept of the interchange mechanism allows these effects to be seen as manifestations of one concerted process in which bond breaking and bond making occur simultaneously. In the cationic complexes the strong solute–solvent interactions cause the entering solvent molecules to dominate the reaction, while in the anionic complexes the columbic repulsion between the complex and the negatively charged ligand produces a more dissociatve transition state. It is interesting to note that a similar switch over in mechanism has also been observed [25] for the thermal aquation reactions of Cr(III) complexes which was ascribed to the *trans* labilizing effect of the ligands present in the complexes. However, the results for the mixed thiocyanate complexes [1, 26] illustrate that such *trans* labilizing effects can be ruled out in the photo-substitution processes.

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