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High-Pressure Mechanistic Studies of the Photochemical Reactions of Transition Metal Complexes. 1. Ligand Field Photolysis of Some Cationic Chromium(III) Ammine Complexes in Aqueous Solution¹

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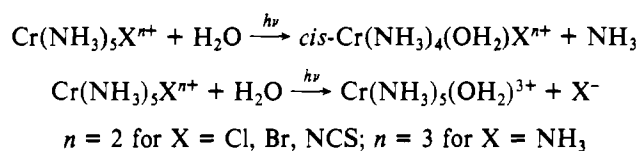
The photoaquation reactions of $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$) and $\text{Cr}(\text{NH}_3)_6^{3+}$ have been studied as a function of pressure up to 1500 bar. The pressure dependence of the quantum yields for the photosubstitution of X and NH_3 was utilized to estimate the corresponding apparent volumes of activation. ΔV_{app}^* for the substitution of X by H_2O in $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ has the values -13.0 ± 0.5 , -12.2 ± 0.3 , and $-9.8 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{X} = \text{Cl}, \text{Br},$ and NCS , respectively. ΔV_{app}^* values for the substitution of NH_3 by H_2O in the above-mentioned complexes are almost constant and independent of the charge on the complex species, with an average value of $-6.4 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$. These data are discussed in detail in reference to the activation volumes reported in the literature for the corresponding thermal aquation reactions. Volume equation calculations suggest the photoaquation mechanism to be of the I_a type.

Introduction

It has been the general objective of our group in the past years to contribute toward the better understanding of the intimate mechanisms involved in chemical reactions. For this purpose high-pressure kinetic measurements were performed to determine the volumes of activation, and partial molar volumes were measured in order to be able to construct reaction volume profiles. A large variety of chemical reactions have been studied in this manner, viz., substitution, isomerization, and redox reactions of inorganic complexes,³⁻¹⁰ as well as Menshutkin, cycloaddition, and photochemical reactions of organic compounds.¹¹⁻¹⁶ These studies clearly illustrated the usefulness of high-pressure kinetic measurements in the elucidation of reaction mechanisms and motivated us to expand our studies to the photochemical reactions of transition metal complexes.

Since this is to our knowledge the first study of photo-

chemical reactions of transition metal complexes at elevated pressures, we have chosen a well-documented system,¹⁷⁻²⁰ viz. the ligand field photolysis of chromium(III) ammine complexes. In general two photoreactions occur:



For the pentaammine complexes the loss of NH_3 is the predominant photoreaction, whereas the loss of X^- occurs to a much smaller extent and in addition is the only observable thermal reaction. The two photoreactions given above are thought to occur via different electronic excited states^{17,21,22} in contrast to earlier suggestions.²³

Quenching studies in connection with measurements of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ phosphorescence demonstrated that chromium(III) complexes react by two pathways.²⁴⁻²⁶ About two-thirds of the photoreaction of $\text{Cr}(\text{NH}_3)_6^{3+}$ is quenched by typical doublet quenchers, whereas the remaining part is unquenchable. The quenchable part either originates from the lowest doublet state ${}^2\text{E}^{27,28}$ or passes it prior to the reaction.²⁴⁻²⁶

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- (2) Institut für Anorganische Chemie der Universität Köln.
- (3) Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1976**, *19*, 117.
- (4) Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1977**, *16*, 3139.
- (5) Hyde, K.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1978**, *17*, 1647.
- (6) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.
- (7) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 1520.
- (8) Mares, M.; Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1978**, *27*, 153.
- (9) Palmer, D. A.; van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1978**, *30*, 83.
- (10) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1978**, *29*, 253.
- (11) Walper, M.; Brauer, H.-D.; Kelm, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30B*, 561.
- (12) von Jouanne, J.; Kelm, H. *High Temp.—High Pressures* **1977**, *9*, 515.
- (13) Swieton, G.; Kelm, H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 519.
- (14) von Jouanne, J.; Kelm, H.; Huisgen, R. *J. Am. Chem. Soc.* **1979**, *101*, 151.
- (15) Schmidt, R.; Kelm, H.; Brauer, H.-D. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 402.
- (16) Schmidt, R.; Brauer, H.-D.; Kelm, H. *J. Photochem.* **1978**, *8*, 217.

- (17) Zinato, E. *Concepts Inorg. Photochem.* **1975**, 143.
- (18) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.
- (19) Adamson, A. W.; Waltz, W. L.; Zinato, E.; Watts, D. W.; Fleischauer, P. D. *Chem. Rev.* **1968**, *68*, 541.
- (20) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.
- (21) Wong, C. F. C.; Kirk, A. D. *Can. J. Chem.* **1974**, *52*, 3384.
- (22) Wong, C. F. C.; Kirk, A. D. *Can. J. Chem.* **1975**, *53*, 419.
- (23) Balzani, V.; Carassiti, V.; Scandola, F. *Gazz. Chim. Ital.* **1966**, *96*, 1213.
- (24) Langford, C. H.; Tipping, L. *Can. J. Chem.* **1972**, *50*, 887.
- (25) Chen, S.; Porter, G. B. *Chem. Phys. Lett.* **1970**, *6*, 41.
- (26) Ballardini, R.; Varani, G.; Wasgestian, H. F.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2947.

Whatever the photoactive states may be,²⁹⁻³¹ the reactants must go through transition states which may be either dissociative or associative.^{32,33} Information concerning the latter may be inferred from the pressure dependence of the photochemical quantum yields.

Experimental Section

Materials. The following complexes were prepared as described in the literature: $[\text{Cr}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$,³⁴ $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)(\text{N}-\text{O}_3)_3 \cdot \text{NH}_4\text{NO}_3$,³⁵ $[\text{Cr}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$,²⁹ $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$,³⁶ *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]\text{SO}_4$,³⁷ *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Br}]\text{Br}_2$.³⁸ Chemical analyses were in agreement with the theoretically expected values. Analytical reagent grade chemicals and doubly distilled water were used in the preparation of all test solutions.

Instrumentation. Test solutions were irradiated in a high-pressure optical cell³⁹ with use of a mercury lamp (Osram HBO 100/2) at 436 and 546 nm and an argon ion laser (Spectra Physics) at 476.5 and 488 nm, respectively.⁴⁰ UV-visible absorption spectra were recorded on a Zeiss DMR 10 spectrophotometer. Partial molar volumes were calculated from density measurements with a Paar DMA 02/C digital precision density apparatus at 25.000 ± 0.002 °C.

Measurements. The quantum yield of the photochemical reactions was measured according to standard procedures.⁴⁰ Corrections for the inner light filter effects⁴¹⁻⁴³ were found to be within the experimental error limits of the quantum yield values and were, therefore, omitted. The photochemical conversions were kept very small ($\leq 5\%$) throughout this investigation in order to minimize the influence of secondary reactions. The progress of the reaction was determined by analyzing for the individual reaction products. The NH_3 concentration was determined from a potentiometric acid-base titration,⁴⁰ the thiocyanate ion concentration spectrophotometrically by the addition of ferrinirate,²⁹ the chloride ion concentration potentiometrically with use of an Ag/AgCl electrode,⁴⁴ the bromide ion concentration with an Ag/AgBr electrode, and the formation of $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ during the photolysis of $\text{Cr}(\text{NH}_3)_6^{3+}$ by spectrophotometry (using diphenylcarbazide after separation and oxidation of Cr(VI)⁴⁵) under well-controlled pH and ionic strength conditions.⁴⁶

Results

The complex species $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ undergoes photosubstitution during ligand field irradiation to produce $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ and *cis*- $\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^{2+}$.^{21,22,44,47-49} During

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

complex	abs max, ^a nm	irradn posi- tion, nm	Φ_{NH_3} , mol/ einstein	Φ_{X} , ^b mol/ einstein	ref
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	374 (L ₂)	476.5 ^c	0.36	0.007	this work
	510 (L ₁)	L ₂	0.38		47
		L ₁	0.36		47, 49
			0.48		24
		406		0.007	44
		546		0.005	44
$\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$	377 (L ₂)	476.5 ^c	0.36	0.009	this work
	523 (L ₁)	L ₂	0.37		54
		L ₁	0.35		54
		405		0.011	54
		546		0.009	54
		511		0.004	74
$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$	365 (L ₂)	488 ^c	0.44	0.010	this work
	502 (L ₁)	546 ^d	0.42	0.02	this work
		L ₂	0.46	0.03	29
		L ₁	0.48	0.021	29, 62
		401		0.0002	21, 22
		461		0.004	74
$\text{Cr}(\text{NH}_3)_6^{3+}$	352 (L ₂)	436 ^d	0.47		this work
	461 (L ₁)	436 ^d	0.47 ^e		this work
		L ₁	0.26		45
		L ₁	0.32		69
		366		0.43	72
				0.51	24

^a Measured in this study. ^b X = Cl⁻, Br⁻, and NCS⁻ for the first three complex entries, respectively. ^c Argon ion laser. ^d Mercury lamp. ^e Spectrophotometric analysis.

the thermal (dark) aquation of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ and *cis*- $\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^{2+}$, the only observable reaction is the exchange of Cl⁻ for H₂O, such that $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ and $\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ are produced, respectively.^{50,51} These reactions can apparently contribute significantly to the quantum yield of the photolysis process and have to be corrected for (as described before⁴⁴) by utilizing the available rate and activation parameters reported for the thermal aquation reactions.⁵⁰⁻⁵³ The so obtained corrected values for Φ_{Cl} (formation of $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$) and Φ_{NH_3} (formation of *cis*- $\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^{2+}$) are compared to literature values in Table I. These are in general agreement with previously reported values, especially with our earlier determination of Φ_{Cl} ,⁴⁴ which is 1 order of magnitude larger than the value of Wong and Kirk.^{21,22} These authors suggested that in our previous experiments contamination by short-wavelength light might have caused the apparently higher quantum yield. Using laser light, however, confirmed our earlier measurements, and the difference is probably due to different ionic media. The pressure dependence of the quantum yields is summarized in Table II.

The ligand field photolysis of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ was studied in the same manner as described above for the $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ species. The photolysis products⁵⁴ are $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ and *cis*- $\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Br}^{2+}$, and the measured quantum yields (Φ_{Br} and Φ_{NH_3} in Tables I and II) were corrected for the thermal (dark) aquation reactions by using the appropriate kinetic data.^{51,52,53,56}

- (27) Adamson, A. W.; Walters, R. T.; Fukuda, R.; Gutierrez, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 5241.
 (28) Fukuda, R.; Walters, R. T.; Mäcke, H.; Adamson, A. W.; *J. Phys. Chem.* **1979**, *83*, 2097.
 (29) Zinato, E.; Lindholm, R. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1969**, *91*, 1076.
 (30) Adamson, A. W. *J. Phys. Chem.* **1967**, *71*, 798.
 (31) Adamson, A. W.; Martin, J. E.; Diomeddi-Camassei, F. *J. Am. Chem. Soc.* **1969**, *91*, 7530.
 (32) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions"; Wiley: New York, 1967.
 (33) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1966.
 (34) Christensen, O. T. *Z. Anorg. Allg. Chem.* **1893**, *4*, 227.
 (35) Mori, M. *Inorg. Synth.* **1957**, *5*, 132.
 (36) Linhard, M.; Weigel, M. *Z. Anorg. Allg. Chem.* **1951**, *266*, 49.
 (37) Mori, M. *J. Inst. Polytech., Osaka City Univ., Ser. C* **1952**, *3*, 41.
 (38) Benrath, A.; Steinrath, H. *Z. Anorg. Allg. Chem.* **1930**, *194*, 351.
 (39) Fleischmann, F. K.; Conze, E. G.; Kelm, H.; Stranks, D. R. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
 (40) Angermann, K. Ph.D. Dissertation, University of Frankfurt, 1977; p 17.
 (41) Wasgestian, H. F.; Schläfer, H. L. *Ber. Bunsenges. Phys. Chem.* **1967**, *71*, 489.
 (42) Kling, O.; Nikolaiski, E.; Schläfer, H. L. *Z. Elektrochem.* **1963**, *67*, 883.
 (43) Riccieri, P.; Zinato, E. *Z. Phys. Chem. (Wiesbaden)* **1972**, *79*, 28.
 (44) Wasgestian, H. F.; Schläfer, H. L. *Z. Phys. Chem. (Wiesbaden)* **1968**, *62*, 127.
 (45) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.
 (46) Reference 40, p 31.

- (47) Wasgestian, H. F.; Schläfer, H. L. *Z. Phys. Chem. (Wiesbaden)* **1968**, *57*, 282.
 (48) Moggi, L.; Bolletta, F.; Balzani, V. *Ric. Sci.* **1966**, *36*, 1228.
 (49) Manfrin, M. F.; Moggi, L.; Balzani, V. *Inorg. Chem.* **1971**, *10*, 207.
 (50) Levine, M. A.; Jones, T. P.; Harris, W. E.; Wallace, W. J. *J. Am. Chem. Soc.* **1961**, *83*, 2453.
 (51) Guastalla, G.; Swaddle, T. W. *Can. J. Chem.* **1973**, *51*, 821.
 (52) Jackson, W. G.; Vowels, P. D.; Fee, W. W. *Inorg. Chim. Acta* **1976**, *19*, 221.
 (53) Reference 40, 36.
 (54) Riccieri, P.; Schläfer, H. L. *Inorg. Chem.* **1970**, *9*, 727.

Table II. Pressure Dependence of the Quantum Yield for the Ligand Field Photolysis of Chromium(III) Ammine Complexes in Aqueous Solution^a

complex	irradn wavelength, nm	T, °C	[H ⁺], M	ionic strength, M	P, bar	$\Phi_{\text{NH}_3}^b$, mol/einstein	$10^2 \Phi_X^b$, mol/einstein
Cr(NH ₃) ₅ Cl ²⁺	476.5	20	0.01	0.5	1	0.355 ± 0.007	0.65 ± 0.04 ^c
					500	0.404 ± 0.020	0.85 ± 0.06 ^c
					1000	0.468 ± 0.017	1.19 ± 0.04 ^c
					1500	0.513 ± 0.017	1.52 ± 0.08 ^c
Cr(NH ₃) ₅ Br ²⁺	476.5	5	0.01	0.5	1	0.358 ± 0.016	0.85 ± 0.06
					500	0.410 ± 0.014	1.12 ± 0.04
					1000	0.475 ± 0.019	1.43 ± 0.08
					1500	0.540 ± 0.019	1.91 ± 0.09
Cr(NH ₃) ₅ NCS ²⁺	488	15	0.01	0.5	1	0.444 ± 0.017	1.04 ± 0.05
					500	0.511 ± 0.012	1.26 ± 0.02
					1000	0.583 ± 0.027	1.55 ± 0.07
					1500	0.668 ± 0.013	1.93 ± 0.08
Cr(NH ₃) ₆ ³⁺	436	15	0.01	0.015	1	0.470 ± 0.010	
					250	0.514 ± 0.020	
					500	0.559 ± 0.013	
					750	0.583 ± 0.013	
					1000	0.629 ± 0.015	

^a Reaction volume 3.4–3.5 cm³. ^b Mean value of between four and six determinations. ^c T = 2 °C; [H⁺] = 0.001 M.

The thermal aquation of Cr(NH₃)₅NCS²⁺ produces^{57–60} Cr(NH₃)₅OH₂³⁺, whereas the ligand field photolysis produces Cr(NH₃)₅OH₂³⁺ and *cis*-Cr(NH₃)₄(OH₂)NCS²⁺.^{29,61,62} No corrections for the thermal (dark) reactions were made since these can be disregarded⁶³ at low pH, i.e., at [H⁺] ≥ 0.01 M. The obtained values for the quantum yields Φ_{NCS} and Φ_{NH_3} are also included in Tables I and II.

In the well-studied Cr(NH₃)₆³⁺ system stepwise thermal^{64–68} and photochemical^{24,45,69–72} aquation occurs, during which NH₃ is exchanged for H₂O, to produce species of the type Cr(NH₃)_{6-n}(OH₂)_n³⁺. Fortunately, the quantum efficiency of the first photosubstitution reaction, i.e., Cr(NH₃)₆³⁺ $\xrightarrow{h\nu}$ Cr(NH₃)₅OH₂³⁺ + NH₃, is larger than that of the subsequent reactions and decreases along the reaction sequence. Preliminary experiments⁷³ illustrated that the quantum yield (Φ_{NH_3}) for the ligand field irradiation of Cr(NH₃)₆³⁺ had exactly the same value whether it was determined by a potentiometric titration of NH₃ or a spectrophotometric analysis for Cr(NH₃)₅OH₂³⁺ (see Experimental Section). This was considered as evidence that, under the experimental conditions of this investigation, only the primary photoaquation step is observed. In a similar way it was proved that no interference of any thermal (dark) aquation reaction occurred during irradiation. The relevant data for the photoaquation of Cr(NH₃)₆³⁺ are included in Tables I and II.

Table III. Volumes of Activation (in cm³ mol⁻¹) for the Thermal and Photochemical Aquation of Chromium(III) Ammine Complexes

complex	$\Phi_{\text{NH}_3}^a$		Φ_X^a	thermal ΔV^\ddagger
	$\Delta V_{\text{app}}^\ddagger$	ΔV_r^\ddagger		
Cr(NH ₃) ₅ Cl ²⁺	-6.0 ± 0.4	-9.4	-13.0 ± 0.5	-10.8 ± 0.3 ^c
Cr(NH ₃) ₅ Br ²⁺	-6.5 ± 0.1	-10.2	-12.2 ± 0.3	-10.2 ± 0.3 ^c
Cr(NH ₃) ₅ NCS ²⁺	-6.4 ± 0.1	-11.4	-9.8 ± 0.2	-8.6 ± 1.0 ^d
Cr(NH ₃) ₆ ³⁺	-6.7 ± 0.5	-12.6		

^a For experimental conditions see Table II. ^b Calculated according to eq 4. ^c T = 25 °C, ionic strength 0.1 M; ref 51. ^d T = 80 °C, ionic strength 0.1 M; ref 60.

Table IV. Volume Equation Calculations^a for the Photoaquation of Cr(NH₃)₅X²⁺ According to the Reaction

X	Cr(NH ₃) ₅ X ²⁺ + H ₂ O $\xrightarrow{h\nu}$ Cr(NH ₃) ₅ OH ₂ ³⁺ + X ⁻			
	\bar{V}_{RX}	\bar{V}_X	ΔV_r^\ddagger	ΔV_D^\ddagger
Cl	83.2	21.75	-13.0	7.15
Br	91.9	29.4	-12.2	6.1
NCS	102.6	40.2	-9.8	6.2

^a All volumes are given in cm³ mol⁻¹.

The data in Table I clearly illustrate that the quantum yields (Φ_{NH_3} and Φ_X) found in this study are in good agreement with those reported in the literature especially when the differences in experimental conditions, which are not included in this table for simplicity reasons, are taken into consideration. It is very obvious that Φ_{NH_3} is considerably larger than Φ_X for the Cr(NH₃)₅X²⁺ (X = Cl, Br, NCS) species and fairly constant for all the studied systems.

Discussion

The quantum yields of the photolysis processes increase significantly with increasing pressure (Table II) for the substitution of both NH₃ and X⁻ in the studied systems. If we consider a chemical reaction with rate constant *k*, the following expression for the volume of activation for this reaction can be derived from the transition state theory:

$$\Delta V^\ddagger = -RT(\partial \ln k / \partial P)_T \quad (1)$$

In the case of a photochemical reaction the situation is more complex. In general the photochemical quantum yield depends

- (55) Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1932**, 95.
 (56) Reference 40, p 41.
 (57) Adamson, A. W.; Wilkins, R. G. *J. Am. Chem. Soc.* **1956**, *78*, 1820.
 (58) Parris, M.; Wallace, W. J. *Inorg. Chem.* **1964**, *3*, 1133.
 (59) Gay, D. L.; Lalor, G. C. *J. Chem. Soc. A* **1966**, 1179.
 (60) Gay, D. L.; Nalepa, R. *Can. J. Chem.* **1970**, *48*, 910.
 (61) Lindholm, R. D.; Zinato, E.; Adamson, A. W. *J. Phys. Chem.* **1967**, *71*, 3713.
 (62) Zinato, E.; Riccieri, P. *Inorg. Chem.* **1973**, *12*, 1451.
 (63) Reference 40, p 43.
 (64) Bjerrum, J.; Lamm, C. G. *Acta Chem. Scand.* **1955**, *9*, 216.
 (65) Jørgensen, E.; Bjerrum, J. *Acta Chem. Scand.* **1958**, *12*, 1047.
 (66) Bjerrum, J.; Jørgensen, E. *J. Inorg. Nucl. Chem.* **1958**, *8*, 313.
 (67) Guastalla, G.; Swaddle, T. W. *Inorg. Chem.* **1974**, *13*, 61.
 (68) Mønsted, L.; Mønsted, O. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 569.
 (69) Edelson, M. R.; Plane, R. A. *J. Phys. Chem.* **1959**, *63*, 327.
 (70) Edelson, M. R.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 231.
 (71) Zinato, E.; Tulli, P.; Riccieri, P. *J. Phys. Chem.* **1971**, *75*, 3504.
 (72) Krause, H. H.; Wasgestian, F. *Inorg. Chim. Acta* **1978**, *29*, 231.
 (73) Reference 40, pp 49, 119.
 (74) Wehry, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 2137.

Table V. Overall Volume Changes^a during the Photoaquation of Chromium(III) Ammine Complexes

complex (RX)	\bar{V}_{RX}	\bar{V}_X	$\bar{V}_{Cr(NH_3)_5OH_2^{3+}}$	$\Delta\bar{V}_X^b$	\bar{V}_{NH_3}	$\bar{V}_{Cr(NH_3)_4(OH_2)X^{2+}}$	$\Delta\bar{V}_{NH_3}^c$
$Cr(NH_3)_5Cl^{2+}$	83.2	21.75	70.6	-8.85	24.85	84.3 ^d	7.95
$Cr(NH_3)_5Br^{2+}$	91.9	29.4	70.6	-9.9	24.85	89.6 ^d	4.55
$Cr(NH_3)_5NCS^{2+}$	102.6	40.2	70.6	-9.8	24.85	102.6 ^e	6.85
$Cr(NH_3)_6^{3+}$	68.6				24.85	70.6 ^f	8.85
mean				-9.5 ± 0.6			7.1 ± 1.9

^a All volumes are given in $cm^3 mol^{-1}$. ^b Calculated from $\Delta\bar{V}_X = \bar{V}_{Cr(NH_3)_5OH_2^{3+}} + \bar{V}_X - \bar{V}_{RX} - \bar{V}_{H_2O}$. ^c Calculated from $\Delta\bar{V}_{NH_3} = \bar{V}_{Cr(NH_3)_4(OH_2)X^{2+}} + \bar{V}_{NH_3} - \bar{V}_{RX} - \bar{V}_{H_2O}$. ^d Data measured in this study. ^e Estimated value—see Discussion. ^f Partial molar volume of $Cr(NH_3)_5OH_2^{3+}$.

on the various processes that populate and deactivate the photoactive state. As a first approximation we assumed that the quantum yield depends on the efficiency of the primary photochemical step with respect to all deactivating processes,⁷⁵ such that

$$\Phi = \frac{k_r}{k_r + k_{nr}} \quad (2)$$

where k_r is the rate constant of the primary photochemical reaction and k_{nr} represents the sum of the rate constants of all photophysical deactivating processes. Differentiation of the above expression with respect to pressure results in

$$\begin{aligned} \Delta V_{app}^* &= \text{apparent volume of activation} \\ &= -RT(\partial \ln \Phi / \partial P)_T \\ &= -(1 - \Phi^\circ)RT(\partial \ln k_r / \partial P)_T + \\ &\quad (1 - \Phi^\circ)RT(\partial \ln k_{nr} / \partial P)_T \\ &= (1 - \Phi^\circ)(\Delta V_r^* - \Delta V_{nr}^*) \end{aligned} \quad (3)$$

where ΔV_r^* and ΔV_{nr}^* are the volumes of activation for the primary photochemical reaction and the photophysical deactivating processes, respectively. It was recently⁷⁶ shown that the excited-state lifetimes of some Ru(II) and Cr(III) complexes decrease only slightly by increase in pressure ($\Delta V^* \approx 0.5 cm^3 mol^{-1}$). Furthermore, the electronic and vibrational absorption spectra of various complexes have in general been observed^{77,78} to be independent of pressure up to 1500 bar. We, therefore, assume that the photophysical deactivation processes are far less pressure dependent over the limited pressure range concerned and that $|\Delta V_{nr}^*| \ll |\Delta V_r^*|$. Equation 3 can then be simplified to

$$\Delta V_{app}^* = (1 - \Phi^\circ)(\Delta V_r^*) \quad (4)$$

ΔV_{app}^* can be calculated in the normal way from the pressure dependence of $\ln \Phi$, such that ΔV_r^* can be estimated since Φ° is known at normal pressure.

It follows from the data in Table II that $\ln \Phi$ depends linearly on P in all cases, and no meaningful curvature can be observed in such plots. Values for the so calculated apparent volumes of activation are summarized in Table III and compared with the corresponding available volumes of activation for the thermal aquation reactions.

From the values of Φ_X in Table II it follows that $\Phi_X \ll 1$, such that $\Delta V_{app}^* \approx \Delta V_r^*$ for the photoaquation of $Cr(NH_3)_5X^{2+}$ to produce $Cr(NH_3)_5OH_2^{3+}$ and X^- . Table III further shows that ΔV_{app}^* (i.e., ΔV_r^*) decreases along the series $Cl > Br > NCS$ and closely parallels the similar sequence and order of magnitude reported for the thermal aquation reac-

tions.^{51,60} The latter data have been discussed in detail elsewhere⁴ and were interpreted as evidence for an I_a mechanism. We have repeated such volume equation calculations for the photoaquation process and the results are summarized in Table IV.

For a purely associative mechanism one would expect a ΔV_A^* of approximately $-16 cm^3 mol^{-1}$ for the entrance of a water molecule into the first coordination sphere^{4,79} of such complex species. However our mean value of $-11.7 \pm 1.7 cm^3 mol^{-1}$ for ΔV_r^* (Φ_X) is significantly more positive than the latter value, and this difference is ascribed to a dissociative contribution from the expulsion of the leaving group. For a purely dissociative mechanism of the type



$\Delta V_D^* = \bar{V}_R - \bar{V}_{RX} + \bar{V}_X$, where $R = Cr(NH_3)_5^{3+}$. It is assumed as before^{4,79} that $\bar{V}_{Cr(NH_3)_5^{3+}} \approx \bar{V}_{Cr(NH_3)_6^{3+}} = 68.6 cm^3 mol^{-1}$, so that ΔV_D^* can be calculated from the known^{4,80} values of \bar{V}_{RX} and \bar{V}_X (Table IV). ΔV_D^* turns out to be almost constant for various X and has an average value of $+6.5 \pm 0.6 cm^3 mol^{-1}$. Since ΔV_r^* is a composite of ΔV_A^* and ΔV_D^* ,⁵¹ the positive value of the latter causes the deviation of ΔV_r^* from that for a purely associative mechanism (ΔV_A^*). It follows that this photoaquation process is of the I_a type, during which the $Cr-X$ bond is partially dissociated in the transition state.

The ΔV_{app}^* values for Φ_{NH_3} in Table III are almost constant, with an average value of $-6.4 \pm 0.3 cm^3 mol^{-1}$. They are independent of the charge on the complex species. However, the values of Φ_{NH_3} in Table II are such that $\Delta V_{app}^* \neq \Delta V_r^*$, and the latter has to be calculated in the manner outlined above. The values for ΔV_r^* (included in Table III) are of the same order of magnitude as those for the release of X^- . However, it is important to note that no change in charge occurs during the overall substitution of NH_3 or during the formation of the transition states $[H_2O \cdots Cr(NH_3)_4X^{2+} \cdots NH_3]^*$ for $X = Cl, Br, NCS$ or $[H_2O \cdots Cr(NH_3)_5^{3+} \cdots NH_3]^*$. During the substitution of X^- , a markedly negative contribution of ΔV_{sol}^* (i.e., the solvation component of ΔV^* due to changes in electrostriction) toward the observed value of ΔV^* is expected since partial charge creation occurs during the formation of the transition state $[H_2O \cdots Cr(NH_3)_5^{3+} \cdots X^-]^*$. This effect also shows up very significantly in the calculated overall volume changes summarized in Table V, where $\Delta\bar{V}_X$ is approximately $16 cm^3 mol^{-1}$ more negative than $\Delta\bar{V}_{NH_3}$. In the latter calculations the partial molar volume of $Cr(NH_3)_4(OH_2)NCS^{2+}$ could not be measured, due to our inability to isolate pure samples of this species, and it was assumed to be close to that of $Cr(NH_3)_5NCS^{2+}$ (compare the partial molar volumes of the *cis*- $Cr(NH_3)_4(OH_2)X^{2+}$ and $Cr(NH_3)_5X^{2+}$ species for $X = Cl$ and Br). We, therefore, must interpret the negative values of ΔV_r^* for the photosubstitution

(75) Reference 20, p 9.

(76) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* 1980, 84, 2998.

(77) Whalley, E. "High Pressure Chemistry"; Kelm, H., Ed.; Reidel: Dordrecht, 1978; p 127.

(78) Brauer, H.-D.; Schmidt, R. Kelm, H. "High Pressure Chemistry"; Kelm, H., Ed.; Reidel: Dordrecht, 1978; p 512.

(79) Stranks, D. R. *Pure Appl. Chem.* 1974, 38, 303.

(80) Horne, R. A., Ed. "Water and Aqueous Solutions: Structure, Thermodynamics and Transport Properties"; Wiley-Interscience: London, 1972; Chapter 13.

of NH_3 to a mechanism which is basically *more associative* than that suggested above for the photosubstitution of X^- .

The associative character is furthermore in good agreement with the conclusions drawn^{72,81} from the stereochemical effects generally observed in the photochemistry of chromium(III) ammine complexes. For a purely associative mechanism we would once again expect a ΔV_A^* value of approximately $-16 \text{ cm}^3 \text{ mol}^{-1}$, which is more negative than our mean value of $-10.9 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$ for ΔV_A^* (Φ_{NH_3}). The difference is ascribed to a counteracting dissociative contribution from the expulsion of the leaving group (NH_3). The dissociative character is in line with the theoretical foundations^{82,83} for Adamson's first rules,³⁰ which in general correctly predict the leaving group in mixed-ligand complexes. Since no change in charge occurs during this process, ΔV_D^* is expected to be of the order of $+24.8 \text{ cm}^3 \text{ mol}^{-1}$, i.e., the partial molar volume of NH_3 . This is, however, substantially more positive than

ΔV_D^* calculated for the release of X^- , with the result that a smaller dissociative contribution will cause the same effect. In an overall consideration the photoaquation of NH_3 is indeed more associative (less dissociative) in character than the corresponding photoaquation of X as mentioned above. Hydrogen bonding may partially stabilize the $\text{Cr}-\text{NH}_3$ bond in the transition state and account for the observed decrease in dissociative character for the photoaquation of NH_3 . It follows that an I_a mechanism also described the photosubstitution of NH_3 in the studied complexes.

We conclude that the results of this first high-pressure mechanistic study of photosubstitution reactions are very encouraging. They can lead to a better understanding of the molecular nature of such photoreactions and enable us to make meaningful suggestions regarding the intimate mechanisms involved.

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Registry No. $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$, 14482-76-9; $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$, 22289-65-2; $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$, 16884-60-9; $\text{Cr}(\text{NH}_3)_6^{3+}$, 14695-96-6.

(81) Kirk, A. D. *Mol. Photochem.* 1973, 5, 127.

(82) Zink, J. I. *J. Am. Chem. Soc.*, 1972, 94, 8039; 1974, 96, 4464.

(83) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* 1977, 99, 2208; 1978, 100, 475.

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Circularly Polarized Luminescence Studies of Terbium(III) Complexes of Hydroxycarboxylic Acids

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Circularly polarized luminescence (CPL) spectroscopy has been used to study the binding of L-lactic (LAC), L-mandelic (MAN), and L-phenyllactic (PLA) acids by Tb(III). Complexes having the general formulas $\text{Tb}(\text{L})_3$, $\text{Tb}(\text{DPA})(\text{L})_2$, and $\text{Tb}(\text{DPA})_2(\text{L})$ were studied (DPA = pyridine-2,6-dicarboxylate), and these complexes were used to evaluate the relative contributions of vicinal, conformational, and configurational effects to the overall chirality of the Tb(III) complex. It was found that both the line shape and magnitude of the CPL spectra could be used to deduce the major source of optical activity in the complexes and that the results could also be used to deduce modes of ligand bonding to the metal ion in these and other related complexes.

Introduction

Since the earliest work^{1,2} involving the binding of trivalent lanthanide ions by proteins and enzymes, considerable effort has been expended in the development of these ions as structural probes.^{3,4} One of the most useful methods that has been developed involves the use of Tb(III) as a luminescence probe, and it has been demonstrated that Tb(III) will substitute for Ca(II) almost without exception.⁵ A considerable enhancement of Tb(III) emission is found when one irradiates the aromatic residues of phenylalanine, tyrosine, or tryptophan, and these in turn sensitize the Tb(III) luminescence by means of a radiationless energy transfer.

To obtain a higher degree of information regarding the stereochemistry of the Tb(III) site, various workers have employed circular polarization of luminescence (CPL) as a chiroptical tool.⁵⁻¹⁰ Strong CPL was found in many cases,

but it was found that CPL was not observed in a considerable fraction of Tb(III)-substituted proteins.⁵ When CPL was observed, however, one generally obtained one mirror image or the other of a particular line shape. These features led to the suggestion that a dissymmetric arrangement of donor atoms about the Tb(III) ion (such as would exist at the interior of a protein chain) was responsible for the CPL and that binding at exterior protein sites might not lead to observable CPL.⁴

In order to understand these effects in greater detail, we have undertaken a study of model Tb(III) complexes which mimic the metal-binding site of a protein. Mixed-ligand complexes of Tb(III), pyridine-2,6-dicarboxylic acid (DPA), and an asymmetric ligand have proved especially useful, since the DPA ligand acts both as a luminescence sensitizer and as an achiral portion of the Tb(III) coordination sphere (thus enabling a study of isolated metal-ligand interactions). In an effort to understand the various mechanisms by which optical activity may be induced in a Tb(III) ion, we have examined the CPL spectra of mixed-ligand Tb/DPA complexes containing monodentate carboxylic acids,¹¹ α -amino acids,¹² and

(1) Birnbaum, E. R.; Gomez, J. E.; Darnall, W. W. *J. Am. Chem. Soc.* 1970, 92, 5287.

(2) Luk, C. K. *Biochemistry* 1971, 10, 2838.

(3) Nieboer, E. *Struct. Bonding (Berlin)* 1975, 22, 1.

(4) Martin, R. B.; Richardson, F. S. *Q. Rev. Biophys.* 1979, 12, 181.

(5) Brittain, H. G.; Richardson, F. S.; Martin, R. B. *J. Am. Chem. Soc.* 1976, 98, 8255.

(6) Gafni, A.; Steinberg, I. Z. *Biochemistry* 1974, 13, 800.

(7) Donato, H., Jr.; Martin, R. B. *Biochemistry* 1974, 13, 4575.

(8) Miller, T. L.; Nelson, D. J.; Brittain, H. G.; Richardson, F. S.; Martin, R. B.; Kay, C. M. *FEBS Lett.* 1975, 58, 262.

(9) Brittain, H. G.; Richardson, F. S.; Martin, R. B.; Burtnick, L. D.; Kay, C. M. *Biochem. Biophys. Res. Commun.* 1976, 68, 1013.

(10) Duportail, G.; LeFever, J.-F.; Lestienne, P.; Dimicoli, J.-L.; Bieth, J. G. *Biochemistry* 1980, 19, 1377.

(11) Brittain, H. G. *Inorg. Chim. Acta* 1981, 53, L7.