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Photochemical Chloride Anation and Aquation of Hexammine Chromium(III) in Acid Solution

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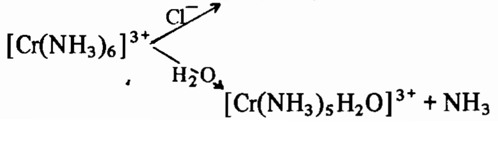
Photolysis of aqueous solutions of $[Cr(NH_3)_6]^{3+}$ *(pH = 2.0) containing chloride ions produces* $[Cr(NH_3)_5H_2O]^{3+}$ *and* $[Cr(NH_3)_5Cl]^{2+}$*. The competition between photoanation and photoaquation was studied as a function of* Cl^- *concentration (0–8* M *LiCl). The quantum yield for ammonia release remained constant over the whole concentration range* (ϕ = *0.41). Comparable efficiency of anation and aquation was found between 2–3* M Cl^-*. A mechanism assuming a trigonal prismatic transition state is proposed for photosubstitution reactions of Cr(III) complexes.*

Introduction

Thermal anation reactions played an important role in clarifying the mechanisms of thermal reactions. If the rate depended on the entering anion, an association mechanism was assumed. In chromium(III) photochemistry interest was mainly focused on the leaving ligand [1, 2]. To our knowledge, only two papers appeared on photoanation reactions of chromium(III) complexes: in 1960 Adamson [3] studied the systems $[Cr(H_2O)_6]^{3+}/Cl^-$; SCN^- and $[Cr(NH_3)_5H_2O]^{3+}/SCN^-$, whereas in a recent publication Langford and Tong [4] reported on the system $[Cr(dmso)_6]^{3+}/N_3^-$; SCN^- (dmso = dimethylsulfoxide). In this case quantum yields for N_3^- anation were significantly larger than those for SCN^- anation. This fact was taken to support an associative mechanism.

In order to get further information on the mechanism of the photosubstitution we decided to study a system where aquation and anation quantum yields could be determined simultaneously as a function of anion concentration. In this paper we report our results of the competing reactions



$$[Cr(NH_3)_6]^{3+} \begin{cases} \xrightarrow{Cl^-} [Cr(NH_3)_5Cl]^{2+} + NH_3 & (1a) \\ \xrightarrow{H_2O} [Cr(NH_3)_5H_2O]^{3+} + NH_3 & (1b) \end{cases}$$

The hexammine chromium(III) ion is thermally sufficiently stable, so that the corresponding thermal reactions could be neglected. Both reaction products could be prepared easily and their properties could be compared with those of the irradiated solutions.

Experimental

Materials

$[Cr(NH_3)_6]^{3+}$ was prepared, according to the procedure of Oppegard and Bailar [5], by treating anhydrous $CrCl_3$ with a solution of sodium in liquid NH_3. The complex was used as the perchlorate. Spectral characteristics: λ_{max} (ϵ_{max}): 464 nm (39.7 M^{-1} cm^{-1}); 352 nm (32.6 M^{-1} cm^{-1}).

$[Cr(NH_3)_5H_2O]^{3+}$ was prepared, according to the method of Mori [6], by heating $KCr(SO_4)_2 \cdot 12H_2O$ in a solution of NH_4NO_3 in concentrated aqueous NH_3. The nitrate was converted into the perchlorate by precipitation with concentrated perchloric acid. Spectral characteristics: λ_{max} (ϵ_{max}): 481 nm (35.6 M^{-1} cm^{-1}); 360 nm (31.3 M^{-1} cm^{-1}).

$[Cr(NH_3)_5Cl]^{2+}$ was obtained, according to the procedure of Christensen [7], by treating anhydrous $CrCl_3$ with liquid NH_3. The product was recrystallized as the chloride with concentrated HCl. Spectral characteristics: λ_{max} (ϵ_{max}): 512 nm (36.2 M^{-1} cm^{-1}); 376 nm (37.1 M^{-1} cm^{-1}). The purity of these compounds was checked by their visible and infrared spectra. All the other chemicals used were of reagent grade.

Techniques

Equipments: Irradiations were carried out as described previously [8], using a 100 W mercury high pressure lamp (Osram HBO 100 W/2) in combination with a Bausch and Lomb 250 mm grating monochromator. Absorption spectra were recorded on a Cary 14 or taken point by point on a Zeiss PMQ II photometer. The pH changes were measured with a Schott micro glass electrode N 59 and a Knick digital pH-meter 641.

TABLE I. Photoaquation[a] Quantum Yields of $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5OH_2]^{3+}$.

Complex	Time of Irradiation (min)	Conversion (%)[b]	Molar Absorption (einst/mol)	Apparent Quantum Yield (mol/einst)		
				ϕ'_{NH_3}	ϕ'_{OH_2}	"ϕ'_{Cl}"
$[Cr(NH_3)_6]^{3+}$ [c]	2	8.5	0.209	. . .	0.40	0.001
	2	8.5	0.199	. . .	0.42	0.010
	3	12.5	0.298	. . .	0.40	0.019
	3	13.1	0.307	. . .	0.42	0.009
	3	13.6	0.312	. . .	0.44	−0.007
	5	19.2	0.497	0.49	0.37	0.019
	5	19.9	0.539	0.40	0.35	0.016
	10	35.3	1.104	0.41	0.31	0.034
	10	36.1	1.071	0.43	0.32	0.034
	. . .	. . .	. . .	0.43[e]	0.41[f]	0.006[f]
$[Cr(NH_3)_5OH_2]^{3+}$ [d]	3	3.7	0.167	0.19	0.22	. . .
	3	3.9	0.194	0.20	0.20	. . .
	4	5.1	0.255	0.20	0.20	. . .
	5	6.4	0.284	0.17	0.23	. . .
	5	7.1	0.324	0.19	0.22	. . .
	7	7.8	0.353	0.20	0.22	. . .
	6	8.4	0.386	0.21	0.22	. . .
	7	8.4	0.396	0.20	0.21	. . .
	7	9.9	0.451	0.19	0.22	. . .
	10	10.4	0.503	0.22	0.21	. . .
	8	11.2	0.519	0.20	0.22	. . .
	. . .	. . .	. . .	0.20[e]	0.21[e]	. . .

[a] Conditions of photolysis: wavelength of irradiation = 366 nm; temperature = 15 °C; medium = 0.01 N $HClO_4$. [b] Percent of initial complex concentration. [c] Initial concentration $[Cr(NH_3)_6]^{3+}$ 8×10^{-3} *M*. [d] Initial concentration $[Cr(NH_3)_5OH_2]^{3+}$ 20×10^{-3} *M*. [e] Average value. [f] Value extrapolated to zero % conversion.

Determination of the Photochemical Conversions

The amount of liberated ammonia was obtained from pH changes in .01 N acid (HCl or $HClO_4$). The concentrations of the three main constituents ($[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5H_2O]^{3+}$, $[Cr(NH_3)_5Cl]^{2+}$) were calculated by a linear regression analysis [9] of the optical densities of the irradiated solutions at 20 wavelengths in the range of 600–410 nm. A test with known concentrations reproduced the concentrations of the aquo complex within 10% and of the chloro complex within 5% relative error. In experiments, which produced small conversions (≤15%), difference spectra were recorded (*versus* the non irradiated solutions), using tenfold scale expansion in optical density.

Results

Photoaquation of Hexamminechromium(III) Ion and Aquopentammine Chromium(III) Ion

Aqueous solutions of $[Cr(NH_3)_6]^{3+}$, irradiated in the absence of Cl^-, were analysed for $[Cr(NH_3)_5H_2O]^{2+}$ as well as for $[Cr(NH_3)_5Cl]^{2+}$. The calculated quantum yields of the latter provided a further test for the reliability of our computer program. Table I shows that on the average the quantum yields of this imaginary anation are .02 mol/einst, indicating an experimental error of this order of magnitude. The apparent aquation quantum yields, determined spectrophotometrically, depended on the molar absorption. At high conversions secondary photolysis adulterated the measured quantum yields. The quantum yield for zero % conversion was calculated by a least squares treatment of the expression:

$$\phi' = \phi^o + \alpha\left(\frac{Q_{abs}}{c_o}\right)^2$$

(Q_{abs}: quanta absorbed by unit volume, c_o: initial concentration of hexamminechromium(III), α: constant). The quadratic form was chosen because it produces a zero slope at $Q_{abs}/c_o = 0$.

The data of Table I further show that deviations due to secondary reactions are within experimental error at conversions less than 15%. The quantum

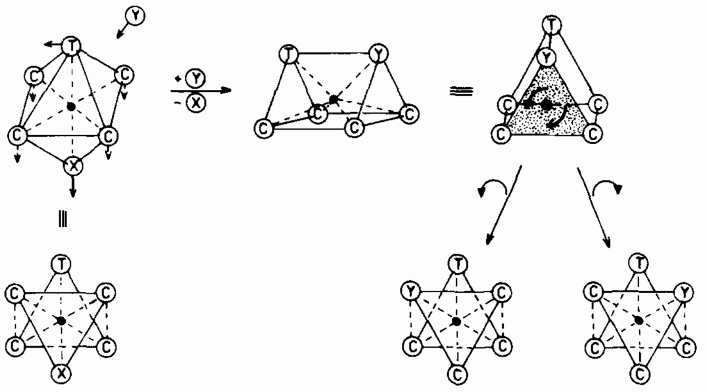


Figure 5. Mechanism proposed for the photosubstitution of Cr(III) complexes.

which has been identified as the lowest excited quartet state [14–16]. Since this state is very short lived ($\tau < 10^{-10}$ sec) [17], only those molecules present in the second coordination sphere will be able to compete with the reentry of the labilized NH_3. That is, only ion pairs or higher associates should be able to photoanate.

At the wavelengths of irradiation (excitation of the ligand field states) the ion associate and the free complex have the same optical density. Therefore, the distribution of the excited species will be equal to that of the ground state molecules. If the associates produce the chloro complex exclusively, the ratio ϕ_{Cl}/ϕ_{NH_3} should be equal to the degreee of association. The data presented in Fig. 3 yield a portion of ion paired complexes of 27% and 70% in 1 *M* and 4 *M* Cl^-, respectively.

For the $[Cr(NH_3)_6]^{3+}/Cl^-$ system the equilibrium constant for ion pairing has been determined for dilute solutions only [18]. Since ion association equilibria are highly dependent on ionic strength this value cannot be used to describe the situation in our experiments. On the other hand, Johansson [19] studied the similar system $[Co(NH_3)_6]^{3+}/Br^-$ at the ionic strengths 1 *M* and 4 *M*. According to his results a solution of $[Co(NH_3)_6]^{3+}$ in 1 *M* Br^- should contain 29% of the cobalt complex as ion pair and 3% as higher associates. The corresponding values in 4 *M* solution are 63% and 28%. The photochemically estimated values agree with this result in order of magnitude. Therefore, ion association is necessary for photoanation of chromium complexes. The floating ionic strength of our experiments forbids a more detailed analysis in terms of ion association.

The competition between anation and aquation requires the same mechanism for both reactions. Therefore, any mechanism to be proposed must be consistent with the experimental facts observed in the aquation reactions of Cr(III). As for instance the stereomobility involved in the photoaquation of *trans*-diacidoamminechromium ions [2] and the complete racemisation concomitant with aquation of trisethylenediaminechromium(III) [20].

Kirk [21] stressed the point that an associative mechanism is necessary to explain the stereochemical specifity in the photoaquation of substituted ammine complexes. We want to propose an interchange mechanism characterized by a six coordinate activated complex, which is reached after the labilized ligand has been expelled.

Excitation from a nonbonding t_{2g} to a σ-antibonding e_g orbital weakens the bond of both ligands on that labilized axis (T–X in Fig. 5). X may be expelled, the other (T) will give way in direction to the deserted t_{2g}-orbital, thus leaving space for the incoming ligand Y, which probably approaches a face trans to X. In this way a trigonal prismatic transition state is formed. This configuration can turn into a new octahedron by rotating its triangle faces by $\pi/3$ either to the left or to the right. This mechanism leads to the following predictions:

i) one triangle face with T at one corner will be unchanged;

ii) the new ligand Y will always be *cis* to the ligand T, which has been *trans* to the leaving ligand X;

iii) of the non labilized ligands, two will remain *trans* to each other, while the others will become *trans* to Y and T;

iv) the decay of the trigonal prismatic transition state leads to racemisation.

Trans attack is necessary to explain the stereochemical rearrangement. In a *cis* attack the entering ligand just should replace the leaving one.

For anation of $[Cr(NH_3)_6]^{3+}$ *trans* attack implies that in a 1:1 ion pair either the anion determines on which side the ammonia is expelled or, if labilisation is statistical, only half of the leaving ligands will be *trans* to the anion. In this case the ion pair should lead to 50% anation, because only half of the leaving

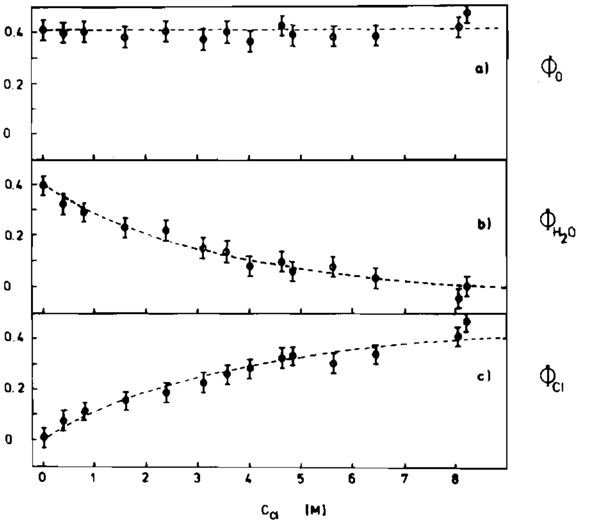


Figure 3. Quantum yields of $[Cr(NH_3)_6]^{3+}$ photolysis as function of chloride concentration. a) Sum of anation and aquation quantum yields; b) aquation; c) anation. Conditions: λ_{irr} = 366 nm, T_{irr} = 15 °C, pH = 2, complex concentration ≈ 0.8×10^{-2} M. All quantum yields are average values of at least 3 determinations.

remained constant. No significant difference in quantum yield was observed between irradiation at 366 and 436 nm. Cooling down from 25 °C to 5 °C produced a slight decrease in the aquation quantum yield at chloride concentrations $c_{Cl} < 1$ M. At higher concentrations this difference gradually disappeared. The anation did not exhibit any significant temperature effect.

In this set of experiments the Cl^- concentration was limited to 3 M because in higher concentrated solutions the photochemically produced $[Cr(NH_3)_5Cl]^{2+}$ precipitated as the chloride salt.

Dependence of the quantum yields on chloride concentration

Extension to higher chloride concentrations became possible by reducing the degree of conversion. Samples, in which 10% of the starting complex was photolyzed, could contain up to 8 M Cl^- without interference of a precipitate. Furthermore, the small conversions made any extrapolation to zero % conversion unnecessary. For the analysis of those runs, the difference spectra had to be recorded on tenfold scale expansion in optical density.

As the preliminary experiments had revealed that neither the excitation wavelength nor the temperature had large effects on the quantum yields, we confined ourselves to one wavelength (366 nm) and one temperature (15 °C). We studied the quantum yields as a function of Cl^- concentration up to 8 M by addition of LiCl. It was not possible to keep the ionic strength constant, for the high Cl^- concentrations of this study would have required still higher concentrations of inert salt to balance the ionic strength. The usually applied perchlorate could not be used, because it precipitates the starting material $[Cr(NH_3)_6]^{3+}$. Besides, addition of another compound would have complicated the reaction system.

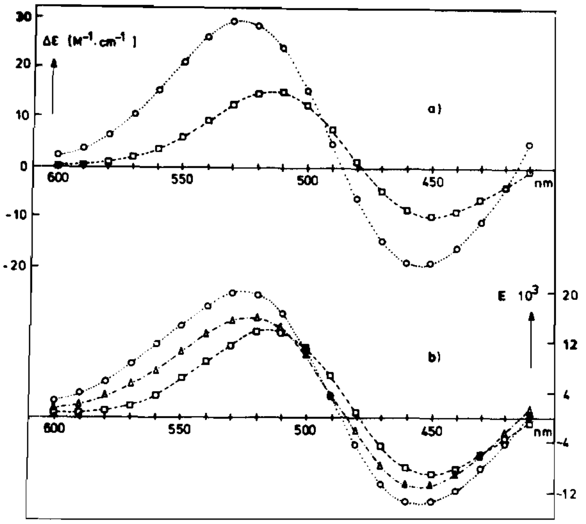
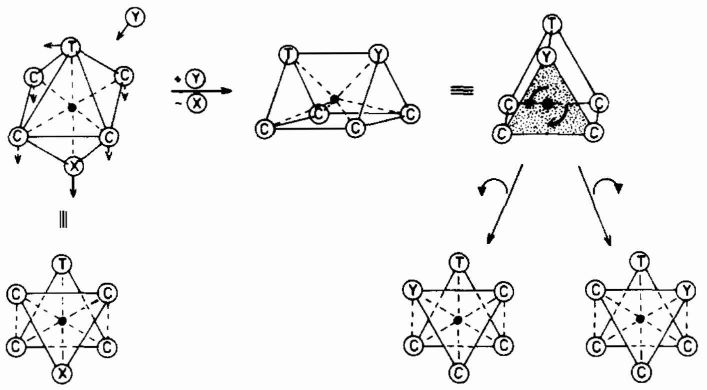


Figure 4. Difference spectra. a) Difference of extinction coefficients: ------ between $[Cr(NH_3)_5H_2O]^{3+}$ and $[Cr(NH_3)_6]^{3+}$; ······ between $[Cr(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_6]^{3+}$; b) difference in optical density of irradiated and non irradiated solutions of 3 photolysis runs with different chloride concentrations (C_{Cl}), 9×10^{-3} M $[Cr(NH_3)_6]^{3+}$, irradiation wavelength 366 nm: ------ C_{Cl} = 0, ϕ_{H_2O} = 0.42; ...·-·- C_{Cl} = 3.22 M, ϕ_{H_2O} = 0.15, ϕ_{Cl} = 0.23; ······ C_{Cl} = 6.44 M, ϕ_{H_2O} = 0.004, ϕ_{Cl} = 0.37.

Fig. 3 shows the results. The aquation quantum yield decreased to the same amount as the chloride quantum yield increased. The total quantum yield remained constant over this extended concentration range, too. Due to the floating ionic strength the anation quantum yield did not show a linear dependence on the Cl^- concentration. An initial slope of .2 $einst^{-1}$ was found. At very high concentrations the photoaquation could be completely quenched ($\phi \leqslant$ .02 mol/einst). The difference spectrum (Fig. 4), obtained with a solution containing 6.4 M Cl^-, showed the production of $[Cr(NH_3)_5Cl]^{2+}$ only. Whether under those conditions the anation quantum yield had reached its limiting value, could not yet be decided.

Discussion

In the region of 0–8 M Cl^- the total quantum yield does not depend on addition of chloride. Anation and aquation only compete with each other. This indicates that the physical deactivation processes are not affected by the presence of chloride and that both reactions originate from the same excited state,



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Acknowledgment

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