

Doublet Versus Quartet Reactivity in the Photoanation of Hexammine Chromium(III) Ion

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The photoanation of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ by Cl^- and Br^- was studied in acid solution. No difference in quantum yields was found for both anions. The photoanation by Cl^- was further studied in alkaline solution and in acid solution containing Co(II) . In those solutions the ${}^2\text{E}_g$ state of Cr(III) is quenched. The limiting quantum yield for complete doublet quenching (unquenchable part of the photoreaction) is identical in acid and alkaline solution and has the same value as for the aquation ($\phi_{\text{na}} = 0.14$). The quenchable part of the photoreaction depends on the Co(II) concentration the same way as the phosphorescence. The probable photochemical pathways are discussed.

Introduction

In a recent series of publications [1–3], A. W. Adamson and coworkers advanced the idea, that in Cr(III) photosubstitution reactions two excited states (${}^4\text{T}_{2g}$ and ${}^2\text{E}_g$) are photoactive. In laser flash studies they observed two pathways of product formation: one part of the reaction appeared immediately after the flash, the other was delayed. The rate of the second part equalled that of the disappearance of the ${}^2\text{E}_g$, as obtained by the excited state absorption. These observations are in accordance with quenching studies [4–6], which demonstrated that one part of the reaction can be quenched by typical doublet quenchers (OH^- , Co^{2+}) the same way as the ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ phosphorescence (quenchable part), while the other part is unquenchable. Following A. W. Adamson, the unquenchable or immediate part originates in the ${}^4\text{T}_{2g}$ and the quenchable or delayed part reacts from the ${}^2\text{E}_g$.

If both states are photoactive, they should differ in reactivity, because they are of different electronic configurations ($t_{2g}^2 e_g$ and t_{2g}^3). If the excited complex gets the choice between different reaction partners, differences in the quenchable and unquenchable parts should be observed.

Aqueous solutions containing halide ions provide suitable systems. In these solutions photoaquation

competes with photoanation [7]. We therefore measured the photochemical quantum yields of the two competing reactions for both, the quenchable and the unquenchable part. We varied the incoming ligand and compared the photochemical quantum yields with the phosphorescence data. The phosphorescence gives information on the ${}^2\text{E}_g$ state.

Experimental

Materials

The chromium complexes used were prepared by standard procedures.

The purity was checked by chemical analyses, visible and infrared spectroscopy (absorption maxima λ [nm] (ϵ [$M^{-1} \text{cm}^{-1}$]) are given in brackets).

$[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_3$ [8] (464 (39.7); 352 (32.6))
 $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ [9] (481 (35.6); 360 (31.3))
 $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ [10] (515 (44.1); 392 (40.4))
 $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ [11] (512 (36.2); 376 (37.1))
 $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ [12] (520 (36.4); 469 sh (23.8); 378 (37.0)).

All other chemicals were of reagent grade.

Photolysis

The solutions of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ were irradiated by a high pressure mercury lamp (Osram HBO 100 W/2) in combination with a Bausch and Lomb 250 mm grating monochromator. The optical cells were thermostatted to $\pm 0.2^\circ\text{C}$. The quanta absorbed were determined by the bolometer technique described elsewhere [13].

Photochemical conversion

The photochemically liberated ammonia was obtained from H^+ consumption in 0.01 N acid (HCl , HBr or HClO_4). The pH-changes were measured with a Schott micro glass electrode N 59 and a Knick digital pH-meter 641.

The main photoproduct or in case of competing reactions the two main photoproducts were calculated by linear regression analysis [14] of the difference spectra (optical densities of irradiated versus

non-irradiated solution). Optical densities at 20 wavelengths in the range of 350–600 nm were employed for the computation. The spectra were recorded on a Cary 14 spectrophotometer under tenfold scale expansion. Tests with known concentrations reproduced the data within 10% relative error for evaluation of two products and within 5% relative error for a single product.

The photochemical conversion of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ was kept below 10% to minimize the influence of secondary photolysis, which could be neglected up to 10% conversion [7].

Phosphorescence decay times were measured by exciting with a frequency doubled ruby laser (104 TRG; Control Data Corp.). The equipment used has been described elsewhere [15]. All measurements were performed at room temperature.

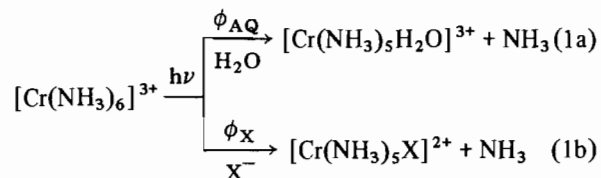
Phosphorescence intensity

The excitation wavelengths ($\lambda_{\text{irr}} = 366; 436 \text{ nm}$) were isolated from a high pressure mercury lamp (Osram HBO 100 W/2) by means of interference filters (Schott UV-PIL and PIL 1). The cells were standard fluorescence cuvettes (thickness 1 cm) in a right angle arrangement. The emission spectra were analysed by a scanable grating monochromator (GCA/Mc Pherson EU 700-2) with a Peltier cooled photomultiplier (RCA C31034) as detector. The relative intensities were determined at the phosphorescence maxima by comparison with a standard solution (0.01 M $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 0.01 M HClO_4). The experimental emission intensities were corrected for quanta absorbed as well as for the inner light filter effects caused by the quencher, which absorbed at irradiation and emission wavelengths.

Results

$[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{Cl}^-; \text{Br}^-$ in Acid Media

Aqueous $[\text{Cr}(\text{NH}_3)_6]^{3+}$ solutions containing halide ions ($X = \text{Cl}; \text{Br}$) undergo the competing photosubstitutions (1a, 1b):



These reaction pathways have been previously demonstrated for $[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{Cl}^-$ [7] using LiCl as Cl^- adjusting agent ($c_{\text{Cl}} = 0\text{--}8 \text{ M}$; pH = 2).

In this study the Cl^- photoanation was reinvestigated extending the accessible Cl^- concentration range up to 12 M, by using HCl. Further, we varied the anion and turned to the $[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{Br}^-$ system. The competition of Br^- photoanation

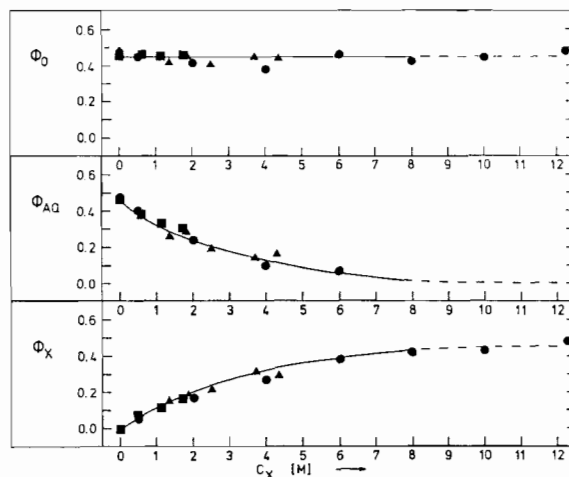


Fig. 1. Quantum yields of $[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{X}^-$ photolysis in acid solution. $\phi_{\text{O}} = \phi_{\text{AQ}} + \phi_{\text{X}}$ (total quantum yield); ϕ_{AQ} : quantum yield of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ formation; ϕ_{X} : quantum yield of $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$ formation; \bullet : $\text{X}^- = \text{Cl}^-$ (HCl solution); \blacksquare : $\text{X}^- = \text{Br}^-$ (pH = 2; NaBr); \blacktriangle : $\text{X}^- = \text{Br}^-$ (pH = 3; NaBr); —: $\text{X}^- = \text{Cl}^-$ (pH = 2; LiCl) [7]; - - -: $\text{X}^- = \text{Cl}^-$ (pH = 2; LiCl) extrapolated; experimental conditions: $\lambda_{\text{irr}} = 366; 436 \text{ nm}$, $t_{\text{irr}} = 1\text{--}3 \text{ min}$, $T = 15^\circ \text{C}$, $c_{\text{Cr}} \approx 0.01 \text{ M}$.

and photoaquation (1a, 1b) was studied between 0 and 4.3 M Br^- (NaBr; pH = 2 or 3). This concentration range was limited by precipitation of $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$.

The difference spectra, obtained from the photolysis runs at various X^- concentrations, were analysed for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$. At low Br^- concentrations the pH-method was also employed to determine the total NH_3 loss.

Figure 1 shows the quantum yields ϕ_{AQ} , ϕ_{X} , ϕ_{O} as a function of X^- concentration. The solid line represents the results of the previous experiments [7] performed in LiCl solutions (pH = 2). The dashed line results from extrapolation to higher Cl^- concentrations. Figure 1 demonstrates that in both Cl^- containing media the same results were obtained, although they strongly differ in viscosity ($\eta_{8\text{M HCl}} = 1.48$, $\eta_{8\text{M LiCl}} = 3.22$ centipoise (at 23°C)).

In general the photochemical behaviour of the $[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{Br}^-$ system paralleled that of the Cl^- system. The total quantum yield ϕ_{O} for NH_3 loss remained constant over the whole X^- concentration range ($\phi_{\text{O}} = 0.45 \pm 0.04 \text{ mol/einst.}$). The aquation quantum yield ϕ_{AQ} decreased to the same extent as the X^- anation ϕ_{X} increased. Within experimental accuracy the initial slope of $\phi_{\text{Br}} \text{ vs. } c_{\text{Br}}$ (0.08 l/einst.) was the same as that of $\phi_{\text{Cl}} \text{ vs. } c_{\text{Cl}}$ (0.09 l/einst.).

At high Cl^- concentrations ($c_{\text{Cl}} \geq 8 \text{ M}$) only Cl^- photoanation occurred, while photoaquation is com-

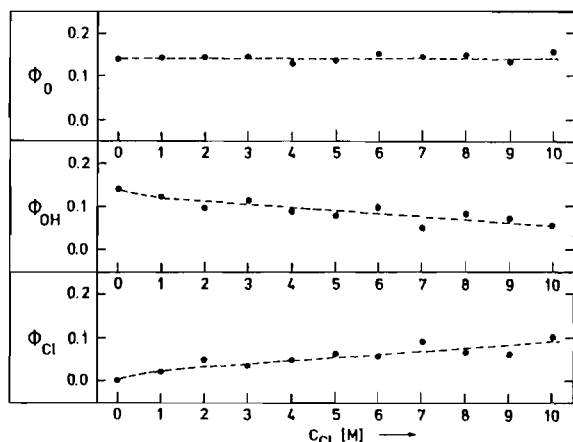


Fig. 2. Quantum yields of $[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{Cl}^-$ photolysis in alkaline solution ($\text{pH} = 13$). $\phi_{\text{O}} = \phi_{\text{OH}} + \phi_{\text{Cl}}$ (total quantum yield); ϕ_{OH} : quantum yield of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ formation; ϕ_{Cl} : quantum yield of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ formation; experimental conditions: $\lambda_{\text{irr}} = 366; 436 \text{ nm}$, $t_{\text{irr}} = 2-4 \text{ min}$, $T = 15^\circ \text{C}$, $c_{\text{Cr}} \approx 0.01 \text{ M}$; media: 0.1 N NaOH , LiCl .

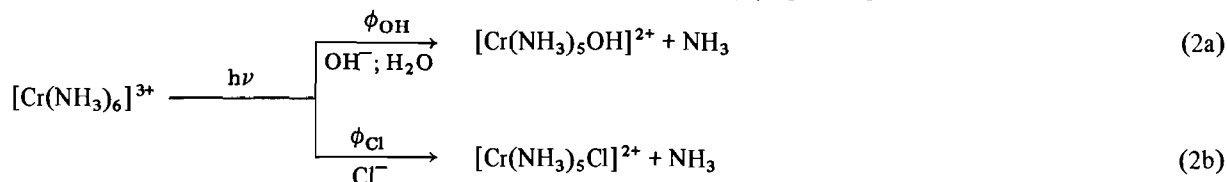
pletely quenched. We found no difference in quantum yields on irradiation in either of the two absorption bands ($\lambda_{\text{irr}} = 436$ and 366 nm).

$[\text{Cr}(\text{NH}_3)_6]^{3+}$ Photolysis in Alkaline Solution

The doublet state of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is completely quenched in alkaline solution [4]. The remaining photochemical NH_3 loss originates directly from the excited quartet state ${}^4\text{T}_{2g}$ (unquenchable part of quantum yield ϕ_{NQ}). We reexamined the photolysis of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in alkaline solution ($\text{pH} = 13$). The photochemical formation of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ was determined by the difference spectra technique. The photolysis quantum yield was found to be $\phi_{\text{OH}} = 0.14 \pm 0.01 \text{ mol/einst.}$ (at 20°C). This is equivalent to 30% of photoaquation observed in acid media.

$[\text{Cr}(\text{NH}_3)_6]^{3+}/\text{Cl}^-$ in Alkaline Solution

In alkaline solution ($\text{pH} = 13$) containing Cl^- the competing photosubstitutions (2a, 2b) take place:



The Cl^- concentration was varied in the range of $c_{\text{Cl}} = 0-10 \text{ M}$ by adding LiCl . The concentrations of the photolysis products were simultaneously determined by the difference spectra technique.

The quantum yields obtained by this procedure are given in Fig. 2. The total NH_3 loss remained constant over the whole Cl^- concentration range ($\phi_{\text{O}} = 0.14 \pm 0.02 \text{ mol/einst.}$). The slope of ϕ_{Cl} vs. c_{Cl} was significantly lower (0.007 l/einst.) in alkaline solution than in acid media. At $c_{\text{Cl}} = 8 \text{ M Cl}^-$ photoanation amounted to only 50% of the total quantum yield, whereas in acid solutions Cl^- photoanation was approximately complete at this Cl^- concentration.

To clarify whether these differences are due to the doublet quenching or to a special reactivity of the OH^- ion, we decided to study the effect of doublet quenching in acid media, too.

$[\text{Cr}(\text{NH}_3)_6]^{3+}$ Phosphorescence Quenching by Co(II) Complexes

The phosphorescence and the photolysis quenching of the similar $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complex was described by Ballardini *et al.* [5, 6]. They used CoCl_2 as quenching agent in acid Cl^- solutions.

The relative abundances of the various Co(II)-species ($[\text{Co}(\text{H}_2\text{O})_6]^{2+}$; $[\text{CoCl}(\text{H}_2\text{O})_5]^+$; $[\text{CoCl}_2(\text{H}_2\text{O})_4]$; $[\text{CoCl}_3(\text{H}_2\text{O})_3]^-$; $[\text{CoCl}_4]^{2-}$), which are present in Cl^- solutions, strongly depend on the total Cl^- concentration c_{Cl} (complexed and free Cl^-). At constant c_{Cl} the relative abundances of the Co(II) complexes remain constant. Under these conditions a linear Stern-Vollmer-plot was obtained.

We investigated the quenching effect on $[\text{Cr}(\text{NH}_3)_6]^{3+}$ by Co(II) species in 8 M Cl^- solution using HCl as Cl^- adjusting agent. The phosphorescence quenching was measured in the Co(II) concentration range of $c_{\text{Co}} = 0-5 \cdot 10^{-3} \text{ M}$. The phosphorescence life time of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 0.01 N HClO_4 was found to be $\tau = 1.90 \mu\text{sec}$ in good agreement with recently published data of other research groups [2, 16, 17]. In 8 M HCl the life time is slightly reduced to $\tau = 1.61 \mu\text{sec}$.

In the Stern-Vollmer-equation (i)

$$\frac{I^{\circ}}{I} = \frac{\tau^{\circ}}{\tau} = 1 + K_{\text{SV}}^{\text{eff}} \cdot c_{\text{Co}} \quad (i)$$

$K_{\text{SV}}^{\text{eff}}$ is defined as effective quenching constant of the Co(II) species present in 8 M Cl^- solutions. I,

I° and τ , τ° are the phosphorescence intensities and decay times with and without added quencher,

*en = 1,2-diaminoethane.

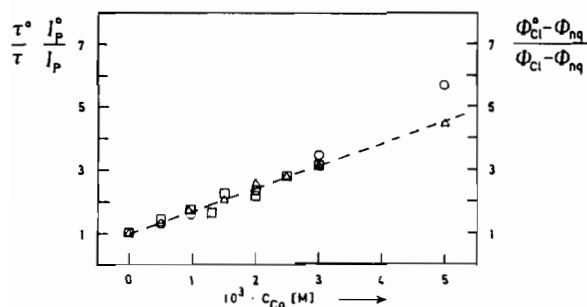


Fig. 3. Stern-Vollmer-plot of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ photolysis and phosphorescence quenching by $\text{Co}(\text{II})$ in 8 M HCl . \square : I_P^0/I_P ; \circ : τ^0/τ ; Δ : $(\phi_{\text{Cl}}^0 - \phi_{\text{nq}})/(\phi_{\text{Cl}} - \phi_{\text{nq}})$; I_P : phosphorescence intensity; τ : phosphorescence decay time; ϕ_{Cl} : quantum yield of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ formation; ϕ_{nq} : quantum yield of the non quenchable part (calculated by extrapolation of ϕ_{Cl} to $1/c_{\text{Co}} \rightarrow 0$); index 0 : values at $c_{\text{Co}} = 0$. Experimental conditions: intensity: $\lambda_{\text{irr}} = 366\text{ nm}$, $T = 23^\circ\text{C}$, $c_{\text{Cr}} \approx 0.01\text{ M}$; decay time: $\lambda_{\text{irr}} = 346.7\text{ nm}$, $T = 22^\circ\text{C}$, $c_{\text{Cr}} \approx 0.01\text{ M}$; quantum yield: as in Fig. 4.

respectively. Figure 3 shows the Stern-Vollmer-plot of the phosphorescence quenching by $\text{Co}(\text{II})$ species in solutions 8 M in total Cl^- . The data obtained by lifetime measurements and those calculated from intensity quenching coincide very well. The experimental results yielded an effective Stern-Vollmer-constant of $K_{\text{SV}}^{\text{eff}} = 700\text{ M}^{-1}$. From $K_{\text{SV}}^{\text{eff}}$ the effective bimolecular quenching constant is obtained by $k_q^{\text{eff}} = K_{\text{SV}}^{\text{eff}}/\tau^0$.

In 8 M Cl^- a value of $k_q^{\text{eff}} = 4 \cdot 10^8\text{ M}^{-1}\text{ sec}^{-1}$ was determined, while 4 M Cl^- (KCl ; $\text{pH} = 2$) produced a lower value of $3 \cdot 10^6\text{ M}^{-1}\text{ sec}^{-1}$. Similar results were previously reported for the $[\text{Cren}_3]^{3+}$ system [5, 6].

The stronger quenching efficiency of $\text{Co}(\text{II})$ in the 8 M Cl^- media is caused by the larger amount of negative charged $\text{Co}(\text{II})$ species formed in the more concentrated Cl^- solution [18, 19].

$[\text{Cr}(\text{NH}_3)_6]^{3+}$ Photolysis Quenching by $\text{Co}(\text{II})$ Complexes

The $[\text{Cr}(\text{NH}_3)_6]^{3+}$ photolysis in 8 M HCl was quenched by $\text{Co}(\text{II})$ complexes under the same experimental conditions as the emission. The quencher concentration was extended to $c_{\text{Co}} = 5 \cdot 10^{-2}\text{ M}$. The total Cl^- concentration was kept constant at 8 M by adding HCl . Under these experimental conditions complete anation occurred; this was verified by analysing the difference spectra for both possible reaction products $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$.

Figure 4 presents the quantum yields of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ formation as a function of added $\text{Co}(\text{II})$.

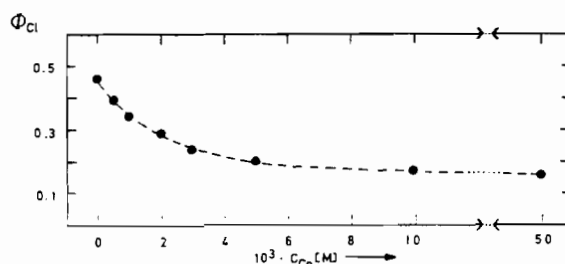


Fig. 4. Influence of the doublet quenching by $\text{Co}(\text{II})$ on the Cl^- photoanation quantum yield of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 8 M HCl ; ϕ_{Cl} : quantum yield of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ formation; experimental conditions: $\lambda_{\text{irr}} = 366\text{ nm}$, $t_{\text{irr}} = 2\text{--}5\text{ min}$, $T = 20^\circ\text{C}$, $c_{\text{Cr}} \approx 0.01\text{ M}$.

ϕ_{Cl} decreases with increasing quencher concentration. At high $\text{Co}(\text{II})$ concentrations ϕ_{Cl} approximately reaches a limiting value. Extrapolation of the ϕ_{Cl} vs. $1/c_{\text{Co}}$ plot to infinite quencher concentration $1/c_{\text{Co}} \rightarrow 0$ produced the unquenchable part of photoreaction $\phi_{\text{nq}} = 0.14\text{ mol/einst.}$ The quenchable part ($\phi_{\text{Cl}} - \phi_{\text{nq}}$) has the same Stern-Vollmer dependence as the phosphorescence. The photochemical data are included in Fig. 3.

The unquenchable part of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ photolysis determined by $\text{Co}(\text{II})$ as quencher in acid media is identical with that obtained in alkaline solution by OH^- quenching. But the extent of Cl^- photoanation differs significantly in acid and in alkaline solution. In 8 M HCl complete Cl^- photoanation occurs, while in alkaline 8 M Cl^- solution the Cl^- photoanation reaches only 50% of total $[\text{Cr}(\text{NH}_3)_6]^{3+}$ photolysis.

Discussion

If in solution deactivation of the 2E_g takes place by chemical reaction, the quantum yields of the quenchable and non quenchable part are given by

$$\phi_q = 0.3 = \phi_{\text{ISC}} \eta_{\text{D}} \quad (\text{ii})$$

$$\phi_{\text{nq}} = 0.14 = (1 - \phi_{\text{ISC}}) \eta_{\text{Q}} \quad (\text{iii})$$

where ϕ_{ISC} is the quantum yield for intersystem crossing and η_{D} , η_{Q} the efficiencies for reaction from the doublet and quartet, respectively.

In the following the discussion will be based in part on data obtained from $[\text{Cren}_3]^{3+}$, because its photophysical and photochemical properties are very similar to that of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ [20, 21].

Fukuda *et al.* [1] reported $\phi_{\text{ISC}} = 0.3$ for $[\text{Cren}_3]^{3+}$. If this value also applies to $[\text{Cr}(\text{NH}_3)_6]^{3+}$ than η_{D} must be close to unity. In that case the quantum yield should increase on direct excitation of the doublet state. This is in contrast to observa-

tions of Wegner and Adamson [22] and Chen and Porter [23]. (An older report [24] claiming $\phi(^2E_g) = 1$ is less reliable.) Besides, the total quantum yield should be wavelength dependent in the red region of the spectrum, because $\eta_D > \eta_Q$ and ϕ_Q was found to decrease at irradiation wavelengths above 500 nm, while the total quantum yield remained constant [25].

Balzani and coworkers [5, 26] reported a value of $\phi_{\text{ISC}} = 0.7$ for $[\text{Cr}(\text{NH}_3)_6]^{3+}$. This value was obtained by two different methods. In our opinion, it is more reliable. Equation (ii) and (iii) yield $\eta_D = 0.44$ and $\eta_Q = 0.45$. This result means that doublet and quartet have equal reactivity.

This result is compatible with the experimental facts. However it is rather difficult to imagine, how two electronic states, which differ in multiplicity, electronic configuration and decay time, should have exactly the same reactivity. Therefore we are still convinced that in those experiments which we report here, the doublet state is substitutional inert and only acts as reservoir for excitation energy.

If no quencher is added, the efficiency of back-intersystem crossing is supposed to be one. In that case:

$$\phi_O = \eta_Q \quad (\text{iv})$$

$$\phi_{\text{nq}} = (1 - \phi_{\text{ISC}})\eta_Q \quad (\text{v})$$

yielding $\eta_Q = 0.45$ and $\phi_{\text{ISC}} = 0.7$ in good agreement with the values obtained for $[\text{Cr}(\text{NH}_3)_6]^{3+}$.

The ${}^2E_g \rightarrow {}^4A_{2g}$ phosphorescence appears within picoseconds after pulsed excitation [27, 28]. This and the fact that fluorescence cannot be detected, render it improbable that $[\text{Cr}(\text{NH}_3)_6]^{3+}$ passes a thermally equilibrated ${}^4T_{2g}$ state (hexi state), which is higher in energy than the lowest doublet state. After excitation into the orbitally degenerated ${}^4T_{2g}$ immediate Jahn-Teller distortion will follow, leading first to a crossing with the potential surfaces of the doublet states and reaching an area close to the ground state potential surface. This area will be assumed to be the photoactive state. From there the molecule either reacts or returns to the thermally equilibrated ground state.

When the photoactive state is reached from the 2E_g , the molecule again must be distorted. That means the deactivation of the doublet state proceeds in solution by a strong coupling mechanism [29]. Strong coupling is in accordance with the small isotope effect found in solution [2, 16] relative to the pronounced effect observed in solid matrices [30–32]. The deactivation probably is solvent assisted, because room temperature phosphorescence was found to be solvent dependent [2, 33, 34] but does not correlate with the solvent effect of the photochemical quantum yields [35].

Cationic chromium complexes have solvolysis quantum yields, depending on the donicity of the solvent [35]. This dependence indicates a rate determining effect of the entering ligand (associative mechanism). The same conclusions arise from the stereochemical course of the photosubstitution reactions [36] and from high pressure studies [37].

These observations seem to be opposed to our findings of equal reactivity of Cl^- , Br^- and H_2O towards excited $[\text{Cr}(\text{NH}_3)_6]^{3+}$. One way to explain the discrepancy may be seen in the fact that even at the highest anion concentrations water molecules still dominate the second coordination sphere. The anions can only move, when a neighbouring H_2O molecule makes room for them. The ligand to be expelled can only get out, when there is room in the solvation layer.

Conclusions

Photoanation and photoaquation are supposed to take place from one photoactive state. This state is highly distorted and situated in a crossing or near crossing region between the ground and the excited quartet potential surfaces.

Acknowledgement

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References

- 1 R. Fukuda, R. T. Walters, H. Mäcke and A. W. Adamson, *J. Phys. Chem.*, **83**, 2097 (1979).
- 2 R. T. Walters and A. W. Adamson, *Acta Chem. Scand.*, **A33**, 53 (1979).
- 3 A. W. Adamson, H. Mäcke, J. P. Puaux, E. Zinato, R. Ricciari and C. K. Poon, *Abstr. XXI Intern. Conf. Coord. Chem.*, p. 270, Toulouse (1980).
- 4 C. H. Langford and L. Tipping, *Can. J. Chem.* **50**, 887 (1972).
- 5 R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi and V. Balzani, *J. Phys. Chem.*, **77**, 2947 (1973).
- 6 H. F. Wasgestian, R. Ballardini, G. Varani, L. Moggi and V. Balzani, *J. Phys. Chem.*, **77**, 2614 (1973).
- 7 H. H. Krause and F. Wasgestian, *Inorg. Chim. Acta*, **29**, 231 (1978).
- 8 A. L. Oppegard and J. C. Bailar, *Inorg. Synth.*, **3**, 153 (1950).
- 9 M. Mori, *Inorg. Synth.*, **5**, 131 (1957).
- 10 S. C. Chan and K. Y. Hui, *Austral. J. Chem.*, **21**, 3061 (1968).
- 11 O. T. Christensen, *Z. Anorg. Allg. Chem.*, **4**, 229 (1893).
- 12 M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **226**, 49 (1951).
- 13 F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankf.)*, **51**, 208 (1966).

- 14 E. Weber, 'Grundriss der Biologischen Statistik', Fischer Verlag, Jena (1964).
- 15 W. Geis, H. F. Wasgestian and H. Kelm, *Ber. Bunsenges. Phys. Chem.*, **76**, 1093 (1972).
- 16 N. A. P. Kane-Maguire, R. C. Kerr and J. R. Walters, *Inorg. Chim. Acta*, **33**, L163 (1979).
- 17 G. B. Porter and A. D. Kirk, *III. Microsymp. on Photochem. and Photophys. Coord. Comp.*, Poster 14, Cologne (1978).
- 18 A. H. Zeltmann, N. A. Matwyoff and L. O. Morgan, *J. Phys. Chem.*, **72**, 121 (1968).
- 19 A. H. Zeltmann, N. A. Matwyoff and L. O. Morgan, *J. Phys. Chem.*, **73**, 2689 (1969).
- 20 V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds', Academ. Press, London (1970).
- 21 A. W. Adamson and P. D. Fleischauer, 'Concepts of Inorganic Photochemistry', J. Wiley, New York (1975).
- 22 E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
- 23 S. N. Chen and G. B. Porter, *Abstr. X. Informal Conference on Photochemistry*, p. 155, Stillwater, Oklahoma (1972).
- 24 R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964).
- 25 N. A. P. Kane-Maguire, J. E. Phifer and C. G. Toney, *Inorg. Chem.*, **15**, 593 (1976).
- 26 F. Boletta, M. Maestri and V. Balzani, *J. Phys. Chem.*, **80**, 2499 (1976).
- 27 A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley and M. W. Windsor, *Chem. Phys. Letters*, **37**, 199 (1976).
- 28 S. C. Pyke and M. W. Windsor, *J. Am. Chem. Soc.*, **100**, 6518 (1978).
- 29 R. Englman and J. Jortner, *J. Molec. Phys.*, **18**, 145 (1970).
- 30 C. D. Flint and A. P. Matthews, *Chem. Comm.*, 954 (1971).
- 31 I. B. Neporent, E. B. Sveshnikova and A. P. Serov, *Izv. Akad. Nauk. SSSR, Ser. Fiz.*, **39**, 1959 (1975).
- 32 N. A. P. Kane-Maguire, G. M. Clonts and R. C. Kerr, *Inorg. Chim. Acta*, **44**, L157 (1980).
- 33 R. Dannöhl-Fickler, H. Kelm and F. Wasgestian, *J. Luminescence*, **10**, 103 (1975).
- 34 S. R. Allsopp, A. Cox, T. J. Kemp and W. J. Reed, *J. Chem. Soc., Faraday I*, **76**, 162 (1980).
- 35 M. Cusumano and C. H. Langford, *Inorg. Chem.*, **17**, 2222 (1978).
- 36 A. D. Kirk, *Mol. Photochem.*, **5**, 127 (1973).
- 37 K. Angermann, R. van Eldik, H. Kelm and F. Wasgestian, *Inorg. Chem.*, in press.