Photolysis of Aminechromium(III) Complexes with CrN_6 Skeletons in Acid Solution

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Sterically modified molecules have been found very useful in clarifying the mechanisms of thermal reactions [1, 2]. Therefore it is remarkable that analogous studies on the photoreactions of chromium(III) complexes are rather scarce, although their photosubstitution reactions have been extensively studied [3]. In CrN_6 complexes the spectral features are very similar. However, photochemical quantum yields vary considerably.

In this paper, we report photosubstitution quantum yields of some chromium complexes and discuss their stereochemical aspects**.

Experimental

The chromium complexes were prepared using standard methods. The following compounds were synthesized: $[Cr(meam)_6](ClO_4)_3$ [4]; $[Cr(pn)_3](ClO_4)_3$ [5]; $[Cr(t\text{-}Chx)_3]Cl_3$ [5]; $[Cr(ditn)_2](ClO_4)_3$ [6]; $[Cr\ cyclam\ en](ClO_4)_3$ [7]; $[Cr(9\text{-}AneN_3)_2](ClO_4)_3$ [8].

Purity was checked by IR, visible spectroscopy, and chromium analysis. The visible spectra were recorded with a Cary 14 instrument.

Absorbed quanta were measured by a thermostatted bolometer apparatus described elsewhere [9]. pH-changes were determined with a Schott N59 microglasselectrode connected to a Knick 641 digital pH-meter. Solutions were irradiated with light from a high pressure mercury lamp (Osram HBO 100 W/2) passing a 250 mm Bausch and Lomb grating monochromator. All samples were thermostatted to 20 ± 0.10 °C and contained 0.01 M complex/0.01 M $HClO_4$ if not stated otherwise.

Results and Discussion

In acid solution, non-coordinated amino groups are protonated. Therefore, in weakly acid solution, the degree of aquation can be followed by the pH change. For complexes with monodentate ligands, the decrease in H^+ concentration equals the photochemical conversion. In chelates, more than one coordinative bond may be broken, either photochemically, or thermally in a postirradiation reaction. Despite this complication, we used the quantum yields of H^+ consumption to determine the extent of the photoreaction. Up to now, there is only one report where complete photochemical separation of a bidentate ligand has been observed. This is the photolysis of $[Cr(tn)_3]^{3+}$ [10]. The quantum yield for simultaneous bond breaking however, was found to be considerably smaller ($\Phi = 0.04$) than that for the formation of the monodentate product ($\Phi = 0.14$). For polydentate ligands, complete detachment may be assumed to be even less probable. A secondary thermal reaction can be recognized by its postirradiation effect. It can be suppressed by lowering the temperature [11].

All complexes studied were stable in acid solution for at least 2 h. Therefore thermal aquation did not interfere. With the exception of $[Cr(t\text{-}Chx)_3]^{3+}$, no postirradiation reactions were observed. Solutions of $[Cr(t\text{-}Chx)_3]^{3+}$ decreased slightly in absorptivity at 520 nm. However, the error introduced by the secondary reaction was less than 5% of the photochemical reaction.

Whereas the other complexes were subject to consecutive photolysis indicated by the disappearance of the isosbestic points upon prolonged exposure, $[Cr\ cyclam\ en]^{3+}$ (Fig. 1) formed a photostable product with absorption maxima at 483(108) and 365(67)

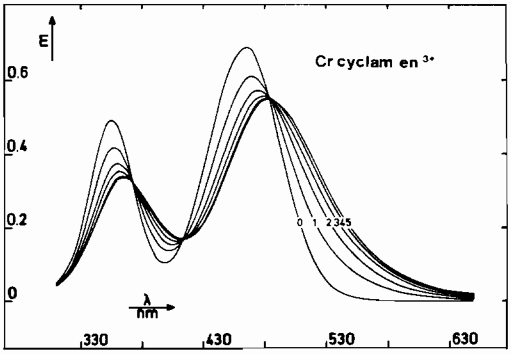

Fig. 1. Spectral changes upon irradiation (366 nm) of 0.005 M $[Cr\ cyclam\ en](ClO_4)_3$ in 0.01 N $HClO_4$ at 20 °C. Exposure times for curves 0 to 5: 0, 5, 10, 15, 20, and 25 min.

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**Abbreviations: meam; methylamine; en, 1,2-diaminoethane; pn, 1,2-diaminopropane; t-Chx, *trans*-1,2-diaminocyclohexane; tn, 1,3-diaminopropane; ditn, 1,5,9-triazanonane; cyclam, 1,4,8,11-tetraazacyclotetradecane; (9-AneN$_3$), 1,4,7-triazacyclonane; sep, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6.]eicosane; diamsar, 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6.]eicosane.

TABLE I. Quantum Yields for H^+ Consumption of Hexaaminechromium(III) Complexes in 0.01 N $HClO_4$

Complex	Φ_{H^+}[a]	Reaction conditions[b]	Reference
$[Cr(NH_3)_6]^{3+}$	0.43	15 °C	13
$[Cr(meam)_6]^{3+}$	0.42 ± 0.04 (7)	5 °C	this work[d]
$[Cr(en)_3]^{3+}$	0.37	10 °C/0.01 N $HClO_4$/0.5 N $NaClO_4$	11
$[Cr(pn)_3]^{3+}$	0.39 ± 0.04 (3)	15 °C	this work[e]
$[Cr(\textit{trans}\text{-}Chxn)_3]^{3+}$	0.37 ± 0.02 (22)[c]		this work
$[Cr(tn)_3]^{3+}$	0.22 ± 0.01 (22)[c]		10
$[Cr(ditn)_2]^{3+}$	0.16 ± 0.01 (23)[c]		this work
$[Cr\ cyclam\ en]^{3+}$	0.21 ± 0.02 (22)[c]		this work
cis$[Cr\ cyclam(NH_3)_2]^{3+}$	0.2		14
trans-$[Cr\ cyclam(NH_3)_2]^{3+}$	~0		14
$[Cr(9\text{-}AneN_3)_2]^{3+}$	$\leqslant$0.001 ± 0.001 (4)[c]		this work
$[Cr(sep)]^{3+}$	<0.03	25 °C, H_2O	15
$[Cr(diamsar)]^{3+}$	2×10^{-5}	22 °C, pH 5	16

[a] Average deviation, number of independent runs in brackets. [b] 20 °C, 0.01 N $HClO_4$ if not stated otherwise. [c] Average values from excitations at 366 and 436 nm. [d] Determined in a graduate training course by C. Tomuschat and F. Salzer. [e] Determined in a graduate training course by A. Sauer.

nm (1 mol^{-1} cm^{-1}). Assuming that only one-ended species were formed, we calculated the product spectrum from the spectral changes and the H^+ consumption, and obtained absorption maxima at 488(112) and 370(65) nm (1 mol^{-1} cm^{-1}).

The photoproduct is similar to *cis*-$[Cr\ cyclam(H_2O)_2]^{3+}$ (483(126); 370(38)) [12]. The quantum yields for H^+ consumption are presented in Table I, together with values from other CrN_6 complexes. Excitation at 436 nm and at 366 nm gave identical results.

If the approach of the entering ligand was rate determining, increasing steric hindrance should lead to decreasing quantum yields. Table I shows that tris complexes of en, pn, and t-Chx have the same quantum yields, although the ligands differ in size and structure.

Table I further shows that complexes of monodentate amines have quantum yields of about 0.5. Chelates with five-membered rings (en, pn, and t-Chx) aquate with quantum yields close to 0.4. The tris tn complex containing three six-membered chelate rings is significantly less photosensitive. The smaller quantum yield of $[Cr(ditn)_2]^{3+}$ can be rationalized if one considers the two central Cr–N bonds as photochemically inert. Then the quantum yield of $[Cr(ditn)_2]^{3+}$ should be 4/6 of that of $[Cr(tn)_3]^{3+}$. The cyclic tridentate ligand in $[Cr(9\text{-}AneN_3)_2]^{3+}$ is not photodissociated. In $[Cr\ cyclam\ en]^{3+}$, only the ethylenediamine is photosubstituted. The quantum yield has the same value as that of *cis*-$[Cr\ cyclam(NH_3)_2]^{3+}$. These facts point to a dissociative photoactive state in agreement with conclusions from anation studies [13] and theoretical models [17].

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