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Increased Reactivity of SCN⁻ in the Photoanation of Chromium(III) Hexammine Ion

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In our studies of the photoanation of hexammine chromium(III) by halide ions [1, 2], we observed a reaction pattern which differed from that found [3] in the photoanation of hexakis dimethylsulfoxide chromium(III) by SCN^- and N_3^-. In our system the total quantum yield, *i.e.* the sum of the quantum yields of photoanation and photosolvation, was independent of the halide concentration, whereas Langford and Tong [3] reported the anation quantum yield to increase on adding pseudo halides (SCN^- and N_3^-), without observing any photochemical solvent exchange.

In order to check whether the difference in reaction behaviour is caused by a special reactivity of Langford and Tong's anions, we studied the photoreaction of haxammine chromium(III) in the presence of thiocyanate.

Two pathways of photosubstitution reactions take place:

$$[Cr(NH_3)_6]^{3+} \xrightarrow[h\nu,\ H_2O,\ SCN^-]{\Phi_{AQ}} [Cr(NH_3)_5H_2O]^{3+} + NH_3$$

$$[Cr(NH_3)_6]^{3+} \xrightarrow[h\nu,\ H_2O,\ SCN^-]{\Phi_{SCN}} [Cr(NH_3)_5NCS]^{2+} + NH_3$$

Using the difference spectra technique [1, 2] Φ_{AQ} and Φ_{SCN} could be determined simultaneously.

Experimental

Hexamminechromium(III) perchlorate was prepared according to literature methods [4]. 2 ml samples were irradiated at 436 nm at 20° ± 0.2 °C. The quanta absorbed were determined by means of a bolometer [5]. Concentrations of the photoproducts generated by the two competing reactions were calculated by linear regression analysis of the difference spectra [2]. The photochemical conversion was kept below 10%. Under these conditions secondary photolysis could be neglected. Phosphorescence decay times were determined by excitation with a Lambda Physics dye laser (POPOP) (λ_{exc} = 410–445 nm) in combination with a PAR 162/164 boxcar averager.

Results

Photoanation in 0.01 M *$HClO_4$ and Dimethylsulfoxide (DMSO)*

In 0.01 $HClO_4$ protonation of SCN^- is negligible (only 0.01% of the thiocyanate is protonated, estimated from $K_a = 70$ [6]), and decomposition of HSCN [7, 8] did not interfere. The total quantum yield $\Phi_o = \Phi_{AQ} + \Phi_{SCN}$ increased from 0.49 ± 0.04 moles/einst. to 0.70 ± 0.07 moles/einst. at $c_{SCN} = 0$

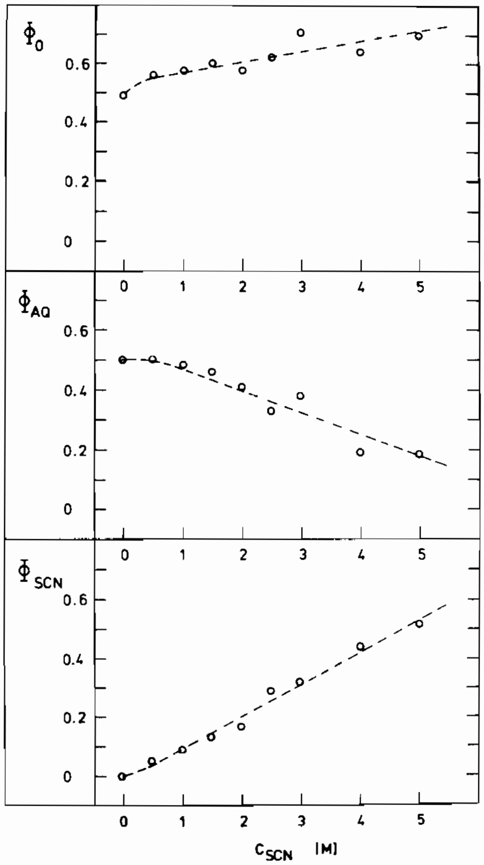

Fig. 1. Quantum yields for SCN^- anation of 0.01 *M* $[Cr(NH_3)_6]^{3+}$ in aqueous solution pH = 2 ($HClO_4$), 20 °C; Φ_o: total quantum yield; Φ_{AQ}: quantum yield for formation of $[Cr(NH_3)_5H_2O]^{3+}$; Φ_{SCN}: quantum yield for formation of $[Cr(NH_3)_5NCS]^{2+}$.

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to 5 *M* (Fig. 1). The same effect was observed in DMSO. In this solvent Φ_0 increased from 0.43 ± 0.04 to 0.59 ± 0.04 in 5 *M* NH_4SCN.

Photoanation in 0.1 M *NaOH*

In alkaline solution however the total quantum yield remained constant over the whole concentration range (Fig. 2). The photoanation increased to the same extent, and the formation of $[Cr(NH_3)_5OH]^{2+}$ was quenched. The slope of Φ_{SCN} *versus* c_{SCN} was 0.008 l/einst, significantly lower than that for acid medium. It equals the data which we obtained for the anation of hexammine chromium(III) by Cl^- and Br^- in alkaline solution [2].

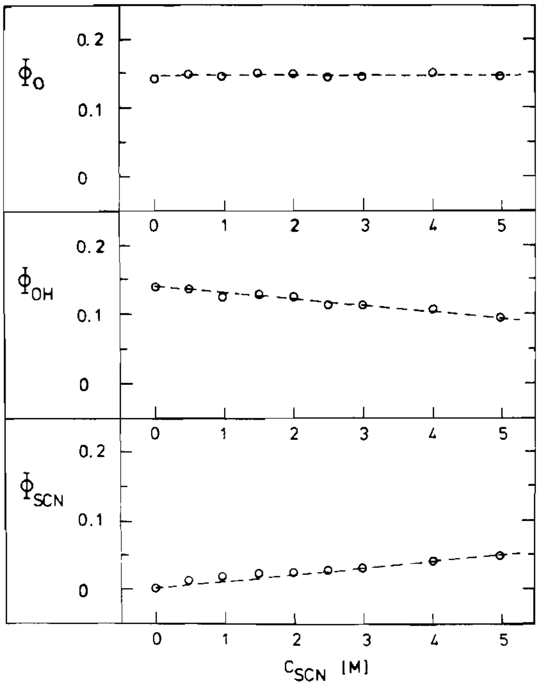

Fig. 2. Quantum yields for SCN^- anation of 0.01 *M* $[Cr(NH_3)_6]^{3+}$ in aqueous 0.1 *M* NaOH, 20 °C; Φ_0: total quantum yield; Φ_{OH}: quantum yield for formation of $[Cr(NH_3)_5OH]^{2+}$; Φ_{SCN}: quantum yield for formation of $[Cr(NH_3)_5NCS]^{2+}$.

Phosphorescence

In order to test whether the increased photoreaction occurring in acid solution is caused by a doublet reaction, we studied the effect of SCN^- on the phosphorescence decay time of $[Cr(NH_3)_6]^{3+}$ under photolysis conditions. Table I shows that SCN^- did not affect the life time of the ^2E_g state. The decrease observed in DMSO on addition of NH_4SCN is caused by the ammonium ion. Therefore we have to rule out that SCN^- reacts directly with the doublet state, though the additional photoreaction disappears in alkaline solution, where the doublet state is completely quenched.

TABLE I. Phosphorescence Decay Times of $[Cr(NH_3)_6]^{3+}$ in Different Media, 22 °C.

medium	μsec
0.01 *M* $HClO_4$	1.8
8 *M* HCl	1.6
4 *M* KCl, pH = 2	2.5
4 *M* NH_4SCN, pH = 2	1.5
0.1 *M* NaOH	phosphorescence not detectable
DMSO	3.6
2 *M* NH_4SCN/DMSO	2.6
4 *M* NH_4SCN/DMSO	1.3
2 *M* NH_4Cl/DMSO	2.6

Conclusion

Comparison with the $[Cr(NH_3)_6]^{3+}/Cl^-$ system [2] shows that for low anion concentrations ($c_X < 1$ *M*) $\Phi_{SCN} \approx \Phi_{Cl}$, and $\Phi_{AQ}(SCN) > \Phi_{AQ}(Cl)$, while for higher concentrations $\Phi_{SCN} > \Phi_{Cl}$. This indicates a catalytic effect of SCN^-, perhaps due to a Cr^{2+} intermediate, produced by photoreduction of $[Cr(NH_3)_6]^{3+}$ by thiocyanate. The difference in reaction behavior between Langford and Tong's system [3] and that we have previously studied [2] has to be attributed to a special reaction pattern with SCN^-. Therefore its mechanism cannot be regarded as typical for photosubstitution reaction of Cr(III) compounds.

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