Ligand Field Photochemistry of $Co(en)_3{}^{3+}$; the Reaction with $Fe(CN)_6{}^{4-}$ in NaCl Solutions

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Summary The photoreaction of $Co(en)_3{}^{3+}$ with $Fe(CN)_6{}^{4-}$ is shown to originate in an excited state of Co^{III} and hence to be the first example of efficient photoreaction of a cobalt–amine complex in a ligand field (L.F.) excited state.

IN contrast with the photochemistry of Rh^{III},[1] Pt^{IV},[2] and Cr^{III} [3] complexes under L.F. excitation, that of d^6 Co^{III} has seemed disappointing in view of the very low quantum yields.[4] This has led to the suggestion that the ^1T excited states of Co^{III} are unreactive because of an efficient relaxation to the $^1A_{1g}$ ground state.[5] But, there is an alternative possibility.

A hint that this might be so is provided by the reaction between $Co(en)_3{}^{3+}$ and $Fe(CN)_6{}^{4-}$ noted briefly by Larsson.[6] When such solutions were illuminated (wavelength unspecified) a cherry-red colour developed. Reaction was described as redox mediated, and tentatively assigned to a charge transfer (c.t.) transition from $Fe(CN)_6{}^{4-}$ to $Co(en)_3{}^{3+}$ in an ion-pair, on the grounds that the increased intensity of the L.F. band implied c.t. mixing. We have re-examined and quantified the study of the photoreaction, this report being concerned with our results in 4M NaCl solution. The advantage of the NaCl is that the high ionic strength minimizes formation of the ion-pair, the spectrum for example of an 0·004M $Co(en_3)^{3+}$—0·01M $Fe(CN)_6{}^{4-}$ solution now being nearly normal; ϵ (465 nm) = 95 [compared with ϵ (465 nm) = 91 in the absence of $\mathrm{Fe(CN)_6}^{4-}$ and 180 in the absence of NaCl, about 95% of the ion-pairing enhancement is eliminated]. Thus, any high yield photoreaction *must follow* from an L.F. excitation of the $\mathrm{Co^{III}}$ complex. [There are no available low lying $\mathrm{Fe(CN)_6}^{4-}$ states.]

Irradiations were done at 436 nm employing a 1000 W Hg-Xenon lamp or using the 457·9, 476·5, or 496·5 nm lines available on the argon ion laser. Reaction was monitored by following the loss in optical activity (quantum yields calculated from the estimated product absorptivity were in good agreement) of the (+)589-$\mathrm{Co(en)_3}^{3+}$ starting material. At present we have only been able to examine the reaction product *in situ*. An identical quantum yield and final spectrum is obtained in the presence or absence of oxygen. The cherry-red colour is associated with an absorption maximum at 440 nm (ϵ = 1060). The product is negatively charged on the basis of its ion-exchange behaviour, while the n.m.r. spectrum confirms the presence of 2 (en) ligands bound to $\mathrm{Co^{III}}$. The negative charge suggests the presence of ferrocyanide in a bridged species, and the absence of either line-broadening or a contact shift for the methylene resonance signal provides additional support for the presence of diamagnetic $\mathrm{Fe^{II}}$ and $\mathrm{Co^{III}}$.

TABLE. *Quantum yield at* 436 *nm for photolysis of* $\mathrm{Co(en)_3}^{3+}$–$\mathrm{Fe(CN)_6}^{4-}$ *system*

$\mathrm{Co(en)_3}^{3+}$ (10^3M	$\mathrm{Fe(CN)_6}^{4-}$ (10^2M)	NaCl (M)	$I/10^{-8\,b}$ (einsteins $\mathrm{l^{-1}\,s^{-1}}$)	ϕ^{a} (±0·03)
2·0	6·0	4·0	2·2	0·19
4·0	3·0	4·0	1·7	0·15
4·0	3·0	4·0	0·10	0·19
4·0	6·0	4·0	2·5	0·17
8·0	6·0	4·0	2·2	0·19

[a] Temperature 25°. [b] Light intensity gauged by ferrioxalate actinometry.

There is, however, evidence for the intermediacy of $\mathrm{Co^{II}}$ during the reaction. For instance, when equimolar $\mathrm{O_2}$-free solutions of $\mathrm{Co(en)_3}^{2+}$ and $\mathrm{Fe(CN)_6}^{3-}$ were mixed in the presence of excess $\mathrm{Fe(CN)_6}^{4-}$ (to simulate photochemical conditions), the visually instantaneous formation of the cherry-red photolysis product was confirmed spectrally (λ_{max} 440 nm; ϵ 900). Further, L.F. irradiation of the $\mathrm{Co(en)_3}^{3+}$–$\mathrm{Fe(CN)_6}^{4-}$ system at pH 0 [where the ferrocyanide exists predominantly as $\mathrm{H_2Fe(CN)_6}^{2-}$] results in a green coloured colloidal solution. This is similar to the green precipitate formed during the rapid thermal electron transfer reaction between $\mathrm{Co(NH_3)_5H_2O^{3+}}$ and $\mathrm{Fe(CN)_6}^{4-}$.[8] Also, the course of the photoreaction is drastically altered in cyanide solutions. The cherry-red product is not observed, the absorbance instead declining at 440 nm. Quantum yields were considerably higher than for the analogous cases with excess NaCl, and were sensitive to the presence of $\mathrm{O_2}$. These results indicate the intermediacy of the reaction chain-carrier $\mathrm{Co(CN)_5}^{3-}$. [The n.m.r. spectrum of irradiated solutions indicates the release of all **3 (en)** groups originally bound to $\mathrm{Co^{III}}$]. Excess reaction may be quenched by the addition of $\mathrm{Fe(CN_6)}^{3-}$. This reaction will be described in detail elsewhere.

We consider now our results in NaCl solution. The absorption spectra indicate suppression of the $\mathrm{Co(en)_3}^{3+}$, $\mathrm{Fe(CN)_6}^{4-}$ ion pair. However, photoreduction still occurs readily (Table). The quantum yield is hardly sensitive to the initial $\mathrm{Co(en)_3}^{3+}$ and $\mathrm{Fe(CN)_6}^{4-}$ concentrations which suggests strongly that ion-pairs do not play a significant role in the photo process.

We conclude then that reaction is a consequence of L.F. excitation (${}^1A_{1g} \rightarrow {}^1T_{1g}$). This requires that the ${}^1T_{1g}$ state does not relax completely to the ground state. The reaction is probably photoreduction of excited $\mathrm{Co^{III}}$ by $\mathrm{Fe(CN)_6}^{4-}$. The $\mathrm{Fe(CN)_6}^{4-}$ concentration independence, coupled with a quantum yield less than unity, would seem to preclude the ${}^1T_{1g}$ state as the reactive level. We suggest the possibility of intersystem crossing (ISC) to a lower L.F. excited state (X) occurring in competition with return to the ground state; reaction with $\mathrm{Fe(CN)_6}^{4-}$ then occurring out of the state X (or its relaxation successor) with near unit efficiency. Earlier failures to observe efficient LF photochemistry may imply only that the wrong reaction partners were supplied to the excited states and not to the extraordinarily facile relaxation of $\mathrm{Co^{III}}$ states.

$$\begin{tikzcd} {}^1A_{1g} \arrow[r, rightleftharpoons, "h\nu"] & {}^1T_{1g} \arrow[r, "\text{intersystem crossing}", "\phi\ ca.0{\cdot}2"'] & \mathrm{X} \arrow[d, dash, "\mathrm{Fe(CN)_6}^{4-}\ \phi\ ca.\ 1"] \\ & & \text{Products} \end{tikzcd}$$

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