Redox Photochemistry of Bromopenta-amminechromium(III)

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Summary The continuous photolysis of $[Cr(NH_3)_5Br]^{2+}$ in the charge transfer to metal region leads to reduction of Cr^{III} and oxidation of Br^-, *e.g.*, producing Br_2^- in flash photolysis studies; the redox quantum yield was obtained as a function of irradiation wavelength and the redox threshold was found to be in the second ligand field quartet absorbtion band.

WHILE oxidation–reduction photochemistry is common to most trivalent transition-metal complexes,[1,2] reports of photoredox processes in chromium(III) complexes are scattered[3–6] and rarely substantiated. As a consequence photoredox processes have come to be regarded as not important for chromium(III) complexes. In contrast, consideration of oxidation–reduction energetics have indicated a relatively low threshold energy for photoredox processes in these complexes.[7] However the investigation of such photoredox processes is complicated by the fact that Cr^{2+} is a powerful reductant[8] so that one would expect relatively ready solvent cage recombination of the primary redox products as well as bulk solution reactions of Cr^{2+} with oxidized ligand species, O_2, *etc.*

We have found that flash photolyses at $\lambda \geqslant 300$ nm of solutions 1×10^{-4}M in $[Cr(NH_3)_5Br]^{2+}$, $1{\cdot}0 \times 10^{-3}$M in NaBr, and 0·01M in $HClO_4$ produced the Br_2^- radical anion. This is in concordance with reported observations of $(NCS)_2^-$ following flash photolyses of $[Cr(NCS)_6]^{3-}$, $[Cr(NH_3)_2(NCS)_4]^-$, and $[Cr(NH_3)_5NCS]^{2+}$.[5,6]

Irradiated solutions of $[Cr(NH_3)_5Br]^{2+}$ do not exhibit significant reducing properties when treated with oxidant following the irradiations. However, reducing properties are developed when the oxidant is contained in the solution during irradiation. When weakly absorbing cobalt(III) complexes, *e.g.*, $[Co(NH_3)_5F]^{2+}$, $[Co(NH_3)_5OH_2]^{3+}$, and $[Co(NH_3)_5CN]^{2+}$, are present in solution during irradiation of $[Cr(NH_3)_5Br]^{2+}$ an appreciable amount of Co^{2+} is formed. Of these complexes, $[Co(NH_3)_5F]^{2+}$ is the most efficient scavenger for Cr^{2+}.[9] Accordingly we have photolysed solutions of 5×10^{-3}M $[Cr(NH_3)_5Br]^{2+}$ and $4{\cdot}0 \times 10^{-3}$M $[Co(NH_3)_5F]^{2+}$ in 0·01M $HClO_4$ at 25 °C at several excitation wavelengths. A low-pressure mercury lamp or a xenon lamp coupled with monochromator and band pass filters were used for the photolyses. The relative absorptivity of $[Co(NH_3)_5F]^{2+}$ is sufficiently small that it absorbed $<5\%$ of the light at most excitation wavelengths; corrections were made as necessary for larger absorptions by cobalt(III). Cobalt(II) was determined spectrophotometrically by the thiocyanate method;[10] ferrioxalate was used as the reference actinometer.[11] The quantum yield of Co^{2+} resulting from such irradiations increased with increasing concentration of $[Co(NH_3)_5F]^{2+}$ and was equal to 0·02 at the highest scavenger concentrations; such yields did not represent complete scavenging of Cr^{2+} owing to the limitations imposed by $[Co(NH_3)_5F]^{2+}$ absorptivity and photosensitivity. Based on this and the yield of 0·2 for ammonia[12] from the 254 nm irradiations of $[Cr(NH_3)_5Br]^{2+}$ we would set $0{\cdot}02 \leqslant \phi\,(Cr^{2+}) \leqslant 0{\cdot}04$ for 254 nm irradiations.

A most striking feature of the present study is the determination that the photoredox threshold energy, E_{th}, lies at *ca.* 28,000 cm^{-1} for $[Cr(NH_3)_5Br]^{2+}$ (Figure). This lies roughly in the middle of the second *d–d* quartet, an absorption band whose irradiation has previously been thought to give rise only to photoaquation processes.[1,13,14] Such a low threshold energy for photoredox is consistent with a model[7] which proposed that the lowest-energy channel for redox decomposition of charge-transfer excited states of chromium(III) would not be correlated smoothly with the lowest-energy charge transfer to metal absorptions in these complexes.

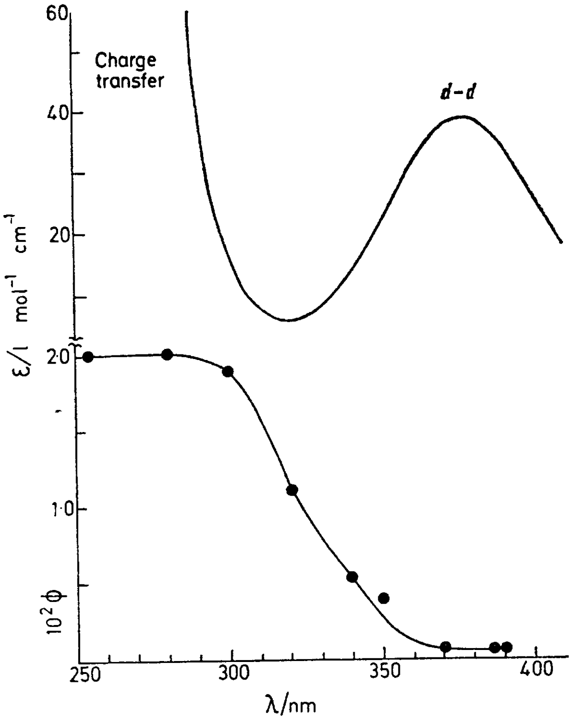

FIGURE. Absorption spectrum (upper curve) and wavelength dependence of the redox quantum yield (lower curve) for irradiations of $[Cr(NH_3)_5Br]^{2+}$.

It should be emphasized that we have only determined the net redox yields, not the primary redox yield of $\{Cr(HN_3)_5^{2+}, \cdot Br\}$ species trapped in a solvent cage.[1,2,13] Since $Cr(NH_3)_5^{2+}$ is a far more powerful reductant than $Co(NH_3)_5^{2+}$,[2,8,16] the roughly 10-fold smaller redox yield for $[Cr(NH_3)_5Br]^{2+}$ than for $[Co(NH_3)_5Br]^{2+}$ may only reflect an increased probability of cage recombination. Clearly, claims that redox photochemistry is insignificant in chromium(III) were premature.

Preliminary studies have shown that similar redox processes and yields are obtained for u.v. irradiations of other acidopenta-amminechromium(III) complexes. Of these it is somewhat ironic that the redox yield for 254 nm irradiations of $[Cr(NH_3)_5N_3]^{2+}$ is found to be *ca.* 0·02 and for

350 nm irradiations to be *ca.* 10^{-4}. The very large yields (0·3—0·4) for near-u.v. photodecomposition of this complex have been reported to be accompanied by production of N_2;[4] however, the 'redox' process involved at the longer wavelengths is more likely to involve nitrene, $Cr(NH_3)_5N^{2+}$, intermediate formation[16] rather than formation of $\{Cr(NH_3)_5^{2+}, \cdot N_3\}$.

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