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PHOTOCHEMICAL PRODUCTION OF CHROMATE(VI) IONS FROM SOME CHROMIUM(III) COMPLEXES[1]

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Abstract—Complexes of the type $[Cr(CN)_{6-x}(OH)_x]^{3-}$ were found to produce the chromate(VI) ions upon exposure to UV radiation in alkaline medium. The quantum yields are reported and possible mechanism is discussed.

Chromium(III) complexes are generally known to undergo substitution and substitution-related photoreactions. Photoredox reactions of these compounds are apparently rare. Only in few cases such processes were reported and then reduction to chromium(II) species was concluded.[2–9]

The cyanide complex, $[Cr(CN)_6]^{3-}$, has received perhaps more detailed study than that of any other ligand and photosubstitution of the CN^- ligand was inferred as the only mode by all authors[5,10–17] except Fleischauer[4] who suggested also a redox behaviour from his flash experiments. Our previous study[18] has revealed that under special conditions photosubstitution has been accompanied by a redox process in the case of hexacyanochromate(III) and hydroxocyanochromates(III).

We now report details of the redox photodecomposition of chromium(III) complexes with CN^- and OH^- ligands.

RESULTS AND DISCUSSION

Spectral changes recorded upon exposure of aerated alkaline solutions of cyanochromates(III) were found to depend strongly on the energy of radiation. This is illustrated in Fig. 1(a) and 1(b) for $[Cr(CN)_6]^{3-}$ and $[Cr(CN)_5OH]^{3-}$, respectively. Other hydroxocyanochromates(III) could not be studied photochemically due to their high thermal instability. However, similar photochemical behaviour was also detected in the case of the $[Cr(CN)_3(OH)_3]^{3-}$, the most stable member of this group. In all these systems exposure to radiation within LF bands (see Table 1) resulted only in absorption changes characteristic of substitution products (see Ref. 18), whereas irradiation within LMCT bands (Table 1) generated also another species absorbing at $26.8 \times 10^3\,cm^{-1}$ and $36.6 \times 10^3\,cm^{-1}$.

This new photochemical mode was observed not only in the case of cyanochromates(III) but also in highly alkaline solutions of other chromium(III) salts. These were characterized by two LF bands at $16.8 \times 10^3\,cm^{-1}$ ($\epsilon = 29\,dm^3\,mole^{-1}\,cm^{-1}$) and $23.3 \times 10^3\,cm^{-1}$ ($\epsilon = 30\,dm^3\,mole^{-1}\,cm^{-1}$) and a continuous increasing absorption towards higher wave numbers (Fig. 1c). Species prevailing in such a solution were as yet not fully defined, among others it was formulated earlier as $[CrO_2(H_2O)_n]^-$.[29] For the sake of convenience, the complexes studied here are formulated as $[Cr(CN)_{6-x}(OH)_x]^{3-}$, where $x = 0, 1, 3$ or 6.

Spectral characteristic of the product generated upon exposure to radiation from CT bands in all systems studied fitted that of the CrO_4^{2-} ions (see Fig. 1d). This conclusion was confirmed also by chemical analysis. The rate of the chromate(VI) production was found to depend on concentration of the OH^- ions and molecular oxygen in solution.

However, considerable amounts of CrO_4^{2-} were

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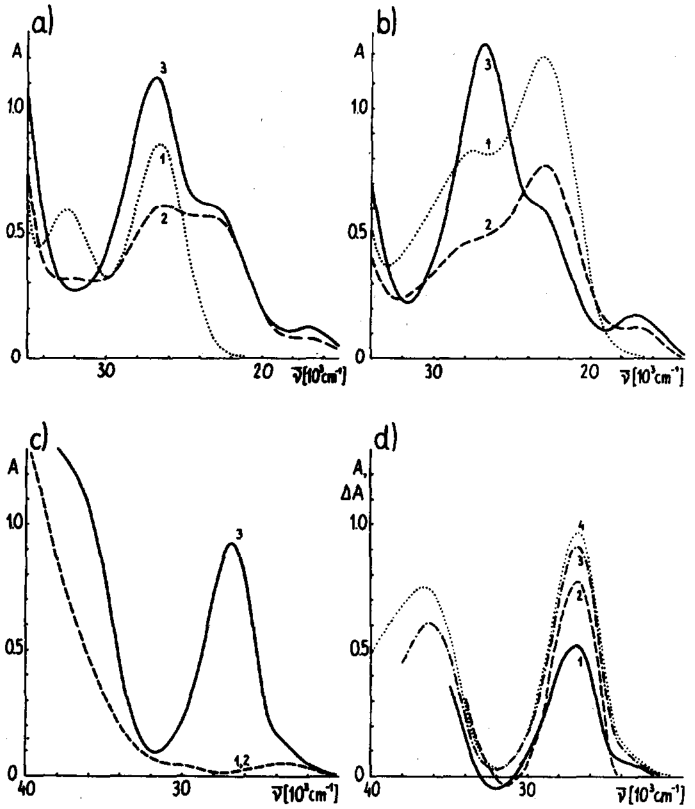

Fig. 1. Absorption changes observed in continuous photolysis of oxygenated alkaline (1 M KOH) solutions of: (a) $[Cr(CN)_6]^{3-}$ (10^{-2} M, $t_{irr} = 2$ min); (b) $[Cr(CN)_5OH]^{3-}$ (10^{-2} M, $t_{irr} = 5$ min); and (c) $[CrO_2(H_2O)_n]^-$ (10^{-3} M, $t_{irr} = 20$ min). Curves 1, in Figs. 1(a–c), refer to unirradiated solutions, curves 2—to solutions irradiated within LF bands ($\bar{\nu} \leqslant 32 \times 10^3\,cm^{-1}$); and curves 3—to solutions irradiated within both, LF and CT, ranges (up to $\bar{\nu} \approx 37 \times 10^3\,cm^{-1}$). In Fig. 1(d) the difference spectra, $(A_3 - A_2)$ from Fig. 1(a) (curve 1), Fig. 1(b) (curve 2) and Fig. 1(c) (curve 3) are compared with the spectrum of 10^{-4} M CrO_4^{2-} in 1 M KOH (curve 4).

observed also in aqueous unbuffered aerated solutions of $[Cr(CN)_6]^{3-}$ due to increase in pH in consequence of photoaquation. Some traces of Cr(VI) were also detected in de-aerated* alkaline solutions of $[Cr(CN)_{6-x}(OH)_x]^{3-}$.

Quantum yields of the CrO_4^{2-} production (Table 2) were found to depend strongly on the number of the CN^- ligands in the complex. The redox process at 265 nm was observed in the case of cyanochromates(III) to be accompanied by substitution. Its quantum yield could not be, determined however, with sufficient precision due to significant overlap of the product spectra with dominating absorption from the CrO_4^{2-} ions (see curves 3 in Figs. 1a, b). For hexacyanochromate(III) the substitution quantum yield under conditions quoted in Table 2 was roughly estimated as 0.06 ± 0.03.

Flash photolysis (time resolution 20 μs, detection within $14 < \bar{\nu} < 35 \times 10^3\,cm^{-1}$) did not reveal any transient product preceding substitution in de-aerated as well as in aerated alkaline solutions of cyanochromates (see Fig. 2a). Since the experiments were carried out under conditions appropriate to detect transient absorption characteristic of hydrated electron (e.g. Ref. 31), its generation in the system seems to be improbable.

Chromate(VI) absorption was recorded not earlier than within seconds upon flashing of aerated samples (Figs. 2a and b) indicating that the CrO_4^{2-} ions are generated in secondary thermal processes at the expense of intermediates(I) absorbing weakly in the visible region, according to overall reaction

$$[Cr(CN)_{6-x}(OH)_x]^{3-} \xrightarrow{h\nu(CT)} \mathbf{I} \xrightarrow[OH^-,\,O_2]{kT} CrO_4^{2-} + (6-x)CN^-. \qquad (1)$$

The intermediate species, I, could be observed only upon flashing of the $[Cr(CN)_6]^{3-}$ complex in the

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*The presence of traces of oxygen in the system cannot be excluded.

Table 1. Electronic spectra of cyanochromates(III) in alkaline solution

Complex	$\tilde{\nu}$ max $[10^3\ cm^{-1}]$	$\epsilon\ [dm^3\ mole^{-1}\ cm^{-1}]$	Assignment [d]		
$[Cr(CN)_6]^{3-}$ pH 5.8 - 14	26.5 [a,b]	86	$^4A_{2g} \rightarrow {}^4T_{2g}$	d - d	$t_{2g} \rightarrow e_g$
	32.6 [a,b]	60	$^4A_{2g} \rightarrow {}^4T_{1g}$		
	38.1 [a]	5400	$^4A_{2g} \rightarrow {}^4A_{1u}$ $^4A_{2g} \rightarrow {}^4E_{1u}$ $^4A_{2g} \rightarrow {}^4T_{1u}$ $^4A_{2g} \rightarrow {}^4T_{2u}$	CTL→M	$t_{1u} \rightarrow t_{2g}$
	43.5	1700	$^4A_{2g} \rightarrow {}^4A_{1g}$ $^4A_{2g} \rightarrow {}^4E_{1g}$ $^4A_{2g} \rightarrow {}^4T_{1g}$ $^4A_{2g} \rightarrow {}^4T_{2g}$	CTL→M	$t_{1g} \rightarrow t_{2g}$
	45.8	3100			
	48.4	3900			
$[Cr(CN)_5OH]^{3-}$ pH 14	23.0 [c]	120			
	27.5 [c]	78			
	41.2	4100			

[a] see also Refs. 19, 20; [b] see also Refs. 11, 21 - 24; [c] see also Ref. 25;

[d] based on SINDO/FEMP calculations [26,27]; the assignment of d - d bands is consistent with other reports [11,19, 21-23], whereas CTL→M character of the more energetic transitions was suggested earlier by Schläfer et al [28], although Alexander and Gray [19], basing on SCCC MO method, assigned the band at $38.1 \times 10^3\ cm^{-1}$ to $t_{2g}\ [M] \rightarrow t_{1u}\ \pi^*\ [L]$.

Table 2. Quantum yields of chromate(VI) production at 265 nm (1 M KOH, saturated with oxygen, T = 295 ± 0.5 K)

Complex	Concentration, [M]	Quantum yield, $[mole\ Einstein^{-1}]$
$[Cr(CN)_6]^{3-}$	2×10^{-3}	0.057 ± 0.002
$[Cr(CN)_5OH]^{3-}$	2×10^{-3}	0.025 ± 0.002
$[CrO_2(H_2O)_n]^-$	1×10^{-2}	0.007 ± 0.002

presence of an excess of the CN^- ions. Then, a short-lived absorption with a maximum at $\sim 30.5 \times 10^3\ cm^{-1}$ was recorded (Fig. 2c) that fitted into that characteristic of the $[Cr(CN)_6]^{4-}$ complex in solution.[25,30] Rapid decay of the $[Cr(CN)_6]^{4-}$ absorption when the $[OH^-]/[CN^-]$ ratio in solution is higher than 5[25] would be responsible for the lack of any transient absorption in our experiments carried out in absence of the excess CN^-.

These results have led us to believe that CT photochemistry of the $[Cr(CN)_{6-x}(OH)_x]^{3-}$ complexes proceeds through photoreduction pathway. This conclusion is consistent with the LMCT character of the transitions (see Table 1) and is supported by the quantum yield values (Table 2) corresponding with the reported earlier[25] tendency of the chromium(III) complexes to be reduced to the Cr(II) ones in alkaline medium.

Subsequent fate of chromium(II) species generated photochemically would depend on the presence of oxygen in the system. In aerated solution, chromium(III) complexes should be rapidly regenerated. However, chromium(II) compounds are known[32] to be oxidized by molecular oxygen not only to chromium(III) but also to chromium(VI) with presumable generation of O_2^- and/or O_2^{2-} ions. The latter are used to oxidize Cr(III) compounds in alkaline medium to the CrO_4^{2-} ions for analytical purposes. Hydrogen peroxide was

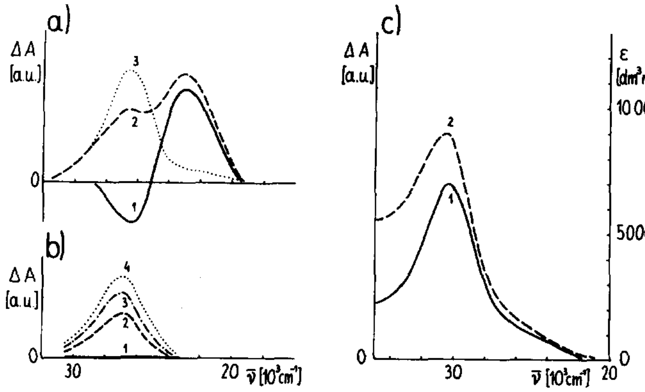

Fig. 2. Absorption changes recorded upon flashing of: (a) $[Cr(CN)_6]^{3-}$ (2×10^{-4} M) in oxygenated 0.01 M NaOH: curves 1 and 2—difference spectra ($A_t - A_o$), recorded at delay times, t, between 20 μs and 0.2 s (curve 1) and at 200 s (curve 2), curve 3—difference spectrum ($A_{200\,s} - A_{20\,\mu s}$); (b) $[CrO_2(H_2O)_n]^-$ (2×10^{-3} M) in oxygenated 1 M NaOH: curves 1–4—difference spectra ($A_t - A_o$) for t between 20 μs and 1 s (no changes), 22, 120 and 600 s, respectively; (c) $[Cr(CN)_6]^{3-}$ (2×10^{-4} M) in de-aerated 0.02 M NaOH and 0.05 M KCN curve 1 (left scale)—difference spectrum ($A_{10\,\mu s} - A_{300\,\mu s}$), curve 2 (right scale)—spectrum of the $[Cr(CN)_6]^{4-}$ complex according to Ref. 25.

reported[30] also to produce chromate(VI) from alkaline cyanochromates(II). We have found that the $[Cr(CN)_{6-x}(OH)_x]^{3-}$ complexes are transformed to the CrO_4^{2-} ions by an excess of H_2O_2 at room temperature (with the exception of $[Cr(CN)_6]^{3-}$ that needs to be heated).

Thus, reductive properties of generated photochemically chromium(II) species would be responsible for chromium(VI) production in secondary thermal processes.

On the other hand, chromium(II) complexes were reported[25] to catalyze substitution of hexacyanochromate(III) in aqueous alkaline cyanide media. Thus, the substitution proceeding upon exposure of the $[Cr(CN)_6]^{3-}$ complex to CT radiation would be a consequence of the catalytic properties of chromium(II) species generated photochemically, although population of the $^4T_{2g}$ level could not be excluded as well.

The photoreduction pathway should be accompanied by generation of ligand or/and solvent radical. In aqueous solution of the $[Cr(CN)_{6-x}(OH)_x]^{3-}$ complexes, where $x \neq 6$, these could be the ·CN and ·OH radicals, whereas for $x = 6$, the only one possible would be ·OH.

Unfortunately, due to the high concentration of OH^- ions and relatively high radiation energy necessary for the redox process to proceed, our scavenging experiments did not lead to unequivocal detection of any radical in aqueous solution.

On the other hand, use of ESR spin trapping technique in methanolic solution of $K_3[Cr(CN)_6]$/crown ether has revealed that photochemical decay of the $[Cr(CN)_6]^{3-}$ signal ($g = 1.992$, 43.3 G linewidth) was accompanied by generation of spin adducts of the $\cdot OCH_3$ and $\cdot CH_2OH$ radicals (Table 3). This would be consistent with the intermolecular pathway

$$[Cr(CN)_6]^{3-} \xrightarrow[CH_3OH]{h\nu(CT)} [Cr(CN)_6]^{4-} + \cdot OCH_3 + H^+ \tag{2}$$

Table 3. Hyperfine splitting constants of spin adducts (in mT) generated in photolyzed solutions of $K_3[Cr(CN)_6]$/18-crown-6

Radical	Spin trap	Solvent	a_N	a_H
$\cdot OCH_3$	DMPO	CH_3OH / NaOH	1.36 ± 0.02	0.76 ± 0.02 /1H/
$\cdot CH_2OH$	DMPO	CH_3OH / NaOH	1.60 ± 0.02	2.27 ± 0.02 /1H/
$\cdot CH_2OH$	ND	CH_3OH / CH_2Cl_2 (5 : 1 v/v)	1.37 ± 0.02	0.79 ± 0.02 /2H/

Abbreviations : DMPO = 5,5-dimethylpyrroline-1-oxide; ND = nitrosodurene.

followed by

$$\cdot OCH_3 + CH_3OH \longrightarrow \cdot CH_2OH + CH_3OH \quad (3)$$

although the $\cdot OCH_3$ radical production in a secondary thermal process cannot be excluded, as well. Besides the $\cdot OCH_3$ and $\cdot CH_2OH$ radicals, other signals were also detected which could be assigned to radicals generated from spin trap and crown ether in reaction with reducing or oxidizing species.

The results obtained in methanolic medium as well as those from aqueous solutions induced us to postulate that CT photochemistry of the $[Cr(CN)_{6-x}(OH)_x]^{3-}$ complexes proceeds through intermolecular reduction

$$[Cr(CN)_{6-x}(OH)_x]^{3-} \xrightarrow[SH]{h\nu(CT)} [Cr(CN)_{6-x}(OH)_x]^{4-} + \cdot S + H^+ \quad (4)$$

where $SH = H_2O$ or CH_3OH. Secondary thermal reactions of the chromium(II) complexes would be responsible for the chromate(VI) production in aerated alkaline solutions and (at least in part) for aquation accompanying the redox process.

EXPERIMENTAL

Materials. Cyano- and hydroxo-cyanochromates(III) were prepared according to the methods described earlier.[18] The $[CrO_2(H_2O)_n]^-$ complex was obtained in solution from chromium potassium alum, $KCr(SO_4)_2 \cdot 12H_2O$, using an excess of KOH or NaOH. The solution was irradiated not before stopping its spectral changes. Alkalis were purified from carbonates, other chemicals were best available commercial reagents without further purification. For flash experiments water was purified adequately to observe the absorption of hydrated electron.

Apparatus and procedure. Techniques used for flash and continuous irradiations were described elsewhere.[18,33]

ESR spectra were recorded at room temperature using a JEOL JES-3BQ spectrometer. Irradiations were performed directly within the ESR cavity by a 200-W high pressure mercury lamp (HBO 200, Narva, Berlin). The light $\bar{\nu} < 28 \times 10^3\ cm^{-1}$ was cut off by means of 1 cm of saturated $NiSO_4$ solution and 2 mm of the Schott glass UG 5.

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