Some Reactions of Pentacyanosulphitoferrate(II) with Oxidising Agents

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Oxidation of the species $[Fe^{II}(CN)_5(SO_3)]^{5-}$ by one equivalent of the oxidising agents $[Ir^{IV}Cl_6]^{2-}$ and $[Fe^{III}(CN)_6]^{3-}$ leads rapidly to the formation of the complex $[Fe^{III}(CN)_5(SO_3)]^{4-}$ which reacts with an excess of $[Ir^{IV}Cl_6]^{2-}$ to form $[Fe^{III}(CN)_5(OH_2)]^{2-}$ and $[SO_4]^{2-}$. Further oxidation of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ by Br_2 gives a red complex ($\lambda_{max.}$ 490 nm). The observed first-order rate constants for the reactions of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ with the different oxidants are the same, and are independent of the concentration of the oxidant.

It has been reported[1] that the oxidation of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ by Br_2 in aqueous solution leads to the formation of a red sulphato-complex, and more recently Swinehart showed[2] that the reaction of solutions of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ with one equivalent of several oxidising agents gave the green complex $[Fe^{III}(CN)_5(SO_3)]^{4-}$, the visible spectrum of which is typical[3] of complexes of the type $[Fe^{III}(CN)_5X]$, where X is a reducing agent. It was found that the iron(III) complex could be further oxidised by Cl_2, although the products of this reaction were not established.

We report the results of an investigation of the stoicheiometries and kinetics of the reactions of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ with Br_2 and $[Ir^{IV}Cl_6]^{2-}$.

EXPERIMENTAL

All the chemicals were AnalaR grade with the exception of $Na_2[Ir^{IV}Cl_6]$ (Johnson, Matthey and Co. Ltd.). Water was distilled twice. Buffers were prepared from $Na_2[HPO_4]$ and Na[OH] (pH 6.8) and $K[O_2CC_6H_4CO_2H]$ (pH 3.8), and constant ionic strength was maintained using NaCl. Samples of $Na_5[Fe^{II}(CN)_5(SO_3)]\cdot 4H_2O$ were prepared by the method previously[4] reported. The product was recrystallised twice from water–methanol {Found: C, 14.3; H, 1.7; Fe, 12.2; S, 7.2. $Na_5[Fe^{II}(CN)_5(SO_3)]\cdot 4H_2O$ requires C, 13.3; H, 1.8; Fe, 12.3; S, 7.1%}.

The methods used for potentiometric and absorbance measurements have been reported[5] previously. Sephadex G 25 columns were used[5] to separate reaction products chromatographically. Estimates of the concentrations of solutions of $[Fe^{III}(CN)_5(SCN)]^{3-}$ were made spectrophotometrically[5] at 590 nm (ε 2 680 dm³ mol⁻¹ cm⁻¹).

RESULTS AND DISCUSSION

Oxidation of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ *by* $[Ir^{IV}Cl_6]^{2-}$.—The stoicheiometry of the rapid oxidation of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ by $[Ir^{IV}Cl_6]^{2-}$ to give $[Fe^{III}(CN)_5(SO_3)]^{4-}$ was determined spectrophotometrically at 660 nm, 10 °C, pH 7.5, and $I = 1.00$ mol dm^{-3}. Maximum absorption occurred after the addition of 1.00 ± 0.05 equivalents of $[Ir^{IV}Cl_6]^{2-}$. Solutions of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ were sufficiently stable in the absence of excess of $[Ir^{IV}Cl_6]^{2-}$ to allow an investigation of its properties; the half-time for the decay in absorbance at 660 nm was *ca.* 20 min at 30 °C, pH 6.8, and $I = 1.0$ mol dm^{-3}.

A potentiometric titration of a solution of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ with $[Ir^{IV}Cl_6]^{2-}$ at 0 °C, pH 6.8, and $I = 1.0$ mol dm^{-3} gave a reduction potential[3] for the $[Fe^{III}(CN)_5(SO_3)]^{4-}$–$[Fe^{II}(CN)_5(SO_3)]^{5-}$ couple of 0.44 V. A titration with $[Ir^{IV}Cl_6]^{2-}$ at pH 4 gave a value of 0.57 V, and similar values of the reduction potentials at pH 6.8 and 4 were obtained with Br_2 as the oxidant. The increased value at the lower pH is probably due to protonation of the iron(II) complex; a pH titration of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ with HCl at $I = 1.0$ mol dm^{-3} gave a pK for this species of 6.85 ± 0.05. Both K_1 and K_2 have been shown[3] to be $\geqslant 10^3$ dm³ mol⁻¹ at 0 °C.

$$[Fe^{III}(CN)_5(OH_2)]^{2-} + [SO_3]^{2-} \overset{K_1}{\rightleftharpoons} [Fe^{III}(CN)_5(SO_3)]^{4-} + H_2O \quad (1)$$

$$[Fe^{II}(CN)_5(OH_2)]^{3-} + [SO_3]^{2-} \overset{K_2}{\rightleftharpoons} [Fe^{II}(CN)_5(SO_3)]^{5-} + H_2O \quad (2)$$

When four or more equivalents of $[Ir^{IV}Cl_6]^{2-}$ were added to solutions of $[Fe^{II}(CN)_5(SO_3)]^{5-}$, 2.9 ± 0.15 equivalents of oxidising agent were consumed with simultaneous conversion of the original iron(II) complex into a species with a spectrum identical to $[Fe^{III}(CN)_5(OH_2)]^{2-}$. In accordance with this stoicheiometry we can write (3).

$$[Fe^{II}(CN)_5(SO_3)]^{5-} + 3[Ir^{IV}Cl_6]^{2-} + 2H_2O \longrightarrow [Fe^{III}(CN)_5(OH_2)]^{2-} + [SO_4]^{2-} + 2H^+ + 3[Ir^{III}Cl_6]^{3-} \quad (3)$$

In titrations where $[Ir^{IV}Cl_6]^{2-}$ was added in portions so that the concentration of this species was always much less than the concentration of the iron species, stoicheiometries of more than 2.5 but less than 3 : 1 were observed although complete conversion into $[Fe^{III}(CN)_5(OH_2)]^{2-}$ still occurred. Stoicheiometries of less than 2 : 1 have been observed[6] for the oxidation of sulphite ion by $[Ir^{IV}Cl_6]^{2-}$ when the latter was not in large excess, and have been attributed to the formation of $[S_2O_6]^{2-}$.

Reactions of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ *with* Br_2.—Spectrophotometric titrations of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ with Br_2 at 10 °C, pH 6.8, and $I = 1.0$ mol dm^{-3}, where absorbance measurements were made at 660 and 490 nm, showed that the maximum concentration of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ occurred after the addition of 2.1 ± 0.1 equivalents of Br_2. (Potentiometric titrations of the complex with Br_2 gave metastable end-points after the

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[1] K. A. Hoffman, *Annalen*, 1900, **312**, 27.

[2] J. H. Swinehart, *J. Inorg. Nuclear Chem.*, 1967, **27**, 2313.

[3] A. D. James and R. S. Murray, *J.C.S. Dalton*, 1975, 1530.

[4] 'Gmelins Handbuch der organischen Chemie,' 1932, vol. **B59**, p. 903.

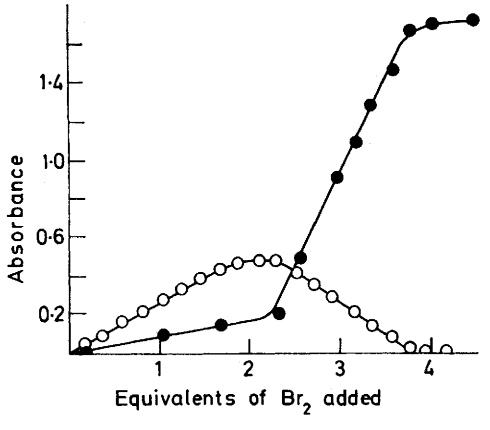
[5] A. D. James and R. S. Murray, *J.C.S. Dalton*, 1974, 1273.

[6] A. Brown and W. C. E. Higginson, *Chem. Comm.*, 1967, 725; *J.C.S. Dalton*, 1972, 166.

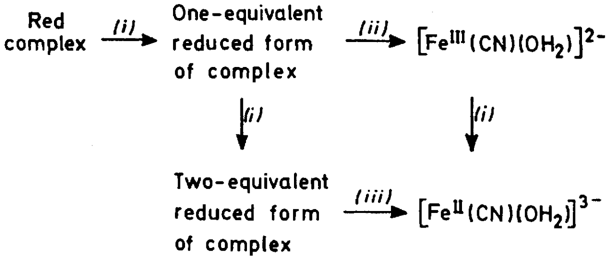
addition of *ca.* 2 equivalents of Br_2.) Further addition of Br_2 led to an increase in absorbance at 490 nm with a corresponding decrease at 660 nm and the solutions became red (Figure). The absorbance at 490 nm reached a maximum after the addition of a total of 4.3 ± 0.3 equivalents of Br_2 to the $[Fe^{II}(CN)_5(SO_3)]^{5-}$. The apparent absorption coefficient of the red complex at 490 nm was calculated to be 510 ± 50 dm^3 mol^{-1} cm^{-1} assuming that complete conversion of the original $[Fe^{II}(CN)_5(SO_3)]^{5-}$ into this species had occurred. When a solution of $[Fe^{III}(CN)_5(SO_3)]^{4-}$, prepared by oxidation of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ by excess of $[Fe^{III}(CN)_6]^{3-}$, was oxidised by Br_2 the absorption coefficient at 490 nm was found to be 632 dm^3 mol^{-1} cm^{-1}, indicating that there was only $80 \pm 10\%$ conversion into the red species in the titrations of $[Fe^{II}(CN)_5(SO_3)]^{4-}$ with Br_2.

The reaction of the red complex with $[SCN]^-$ (0.1 mol dm^{-3}) gave 1.04 ± 0.05 mol of $[Fe^{III}(CN)_5(SCN)]^{3-}$ per mol of iron complex present indicating that the iron was present as a pentacyano-species in the red complex. Its visible and infrared spectra are typical of pentacyanoiron(III) complexes, and in particular[3] $[Fe^{III}Br(CN)_5]^{3-}$ which also absorbs strongly at 490 nm. However, this latter species has ε 902 dm^3 mol^{-1} cm^{-1} at 490 nm compared with the above value for the red complex.

A solution of the red complex could be reduced with ascorbic acid, and complete reduction to $[Fe^{II}(CN)_5(OH_2)]^{3-}$ (which was identified by its absorption maximum[5] at 440 nm, ε 700 dm^3 mol^{-1} cm^{-1}) required 2.18 ± 0.18 equivalents of reductant per mol of the complex. The red colour was completely removed after the addition of 1.02 ± 0.04 mol of ascorbic acid. This one-equivalent reduction was partly reversible when reoxidation with Br_2 was carried out within several minutes at 0 °C. However, when the reduced solution was allowed to stand for a few minutes at room temperature regeneration of the red complex was not possible, and the ultraviolet and visible spectrum of the solution became similar to that[5] of $[Fe^{III}(CN)_5(OH_2)]^{2-}$. Other experiments showed that the reaction of the latter species with Br_2 did not produce a red complex. The results are consistent with the following Scheme.



Typical spectrophotometric titration of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ (1.0×10^{-3} mol dm^{-3}) against Br_2 at $I = 1.0$ mol dm^{-3} (NaCl), pH 7.5, and 10 °C using a 4-cm optical cell at 490 (●) and 660 nm (○)



SCHEME (*i*) + e$^-$; (*ii*) hydrolysis; (*iii*) rapid hydrolysis

Attempts to precipitate salts of the red complex were unsuccessful due to its instability in the presence of many cations; for example, addition of $Ag[NO_3]$ and $BaCl_2$ to solutions of the complex gave precipitates which were not red. Evaporation to dryness of a solution of the complex which had been passed down a chromatographic column to separate the complex from the excess of Br_2 and the other reaction products gave a hygroscopic purple solid which did not give a red solution on redissolution in water. Analysis of this purple solid gave: C, 11.15; H, 0.45; Br, 20.55; Fe, 12.15; N, 12.6; S, 8.0%, which is consistent with the stoicheiometric ratio Fe : C : N : S : Br of 1.00 : 4.28 : 4.14 : 1.15 : 1.18. We note that one cyanide ligand per iron complex is lost on dehydrating the red complex.

We suggest that the red complex might be $[Fe^{III}(CN)_4(CNBr)(SO_4)]^{4-}$ where the $[CNBr]^-$ ligand is formed by the addition of a bromine atom to a cyanide ligand in a similar way[7] to the addition of a $[SO_3]^-$ radical ion to a cyanide ligand in the $[Fe(CN)_6]^{3-}$–$[SO_3]^{2-}$ reaction. A gravimetric determination[8] of sulphate as $Sr[SO_4]$ of a solution of the red complex showed that this contained 1.06 ± 0.04 mol of sulphate per mol of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ present initially. The formation of the proposed complex from $[Fe^{II}(CN)_5(SO_3)]^{5-}$ would require four equivalents of Br_2, and it would require two equivalents of ascorbic acid to give a species which hydrolysed to $[Fe^{II}(CN)_5(OH_2)]^{3-}$.

Evaporation of a solution of $[Fe^{III}(CN)_4(CNBr)(SO_4)]^{4-}$ might lead to a rearrangement of the CNBr ligand with the expulsion of one mol of cyanogen per two mol of iron(III) complex which would be lost in the evaporation process.

Kinetic Investigation.—The reactions of Br_2 and $[Ir^{IV}Cl_6]^{2-}$, which have reduction potentials[9] of 1.09 and 1.02 V respectively, with $[Fe^{II}(CN)_5(SO_3)]^{5-}$ rapidly ($t_{\frac{1}{2}} < 1$ s at 0 °C) gave $[Fe^{III}(CN)_5(SO_3)]^{4-}$, and the

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[7] R. S. Murray, *J.C.S. Dalton*, 1974, 2381.

[8] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, 1962, p. 464.

[9] 'Handbook of Chemistry and Physics,' 51st edn., The Chemical Rubber Co., 1970—1971, p. D-112.

subsequent oxidation of the latter species was followed spectrophotometrically at 660 nm. Plots of $\log(A_t - A_\infty)$ against time were linear for at least 85% completion of reaction and the observed first-order rate constants, $k_{obs.}$ {where $-d[Fe^{III}(CN)_5(SO_3)^{4-}]/dt = k_{obs.}[Fe(CN)_5(SO_3)^{4-}]$} are given in the Table. Values of $k_{obs.}$ were independent of the nature and the concentration of the oxidising agent under the same conditions of pH, temperature, and ionic strength. When Br_2 was the oxidant, the rate of loss of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ was found to be identical to the rate of formation of the red complex by making measurements at 490 nm. The value of $k_{obs.}$ at 11.9 °C, pH 6.8, and $I = 1.0$ mol dm^{-3} was 6.8 ± 0.2 s^{-1}, and was at least a factor of 10 greater than the reported first-order rate constants for the hydrolysis reactions[10] of $[Fe^{II}(CN)_5(SO_3)]^{5-}$ and $[Fe^{III}(CN)_5(SO_3)]^{4-}$. Thus our investigation of the oxidation reactions of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ were not complicated by the hydrolysis reaction of this complex or by catalysis[5] by $[Fe^{II}(CN)_5(SO_3)]^{5-}$.

Kinetic data for the oxidation of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ by Br_2 and $[Ir^{IV}Cl_6]^{2-}$ at 11.9 °C and $I = 1.0$ mol dm^{-3} [a]

pH	$10^2[Br_2]$ / mol dm^{-3}	$10^2[Ir^{IV}Cl_6^{2-}]$ / mol dm^{-3}	$10^3k_{obs.}$ / s^{-1}
3.8 [b]	2.38		8.7 [c]
	1.30		9.0 [c]
	0.24		8.3 [c]
6.8 [d]	0.47		6.6 [e]
	1.23		7.2 [e]
	0.5		6.8 [e]
	2.37		6.6 [c]
	2.37		6.8 [c]
	1.28		6.8 [c]
	0.66		7.1 [c]
	0.35		7.1 [c]
	0.24		6.6 [c]
3.8		3.63	10.2 [e]
		1.82	8.5 [e]
		0.68	8.3 [e]
		1.36	7.3 [e]
		0.30	7.7 [e]

[a] Maintained using NaCl. [b] Phthalate buffer. [c] Obtained from plots of $\ln(A_\infty - A_t)$ against time at 490 nm. [d] Phosphate buffer. [e] Obtained from plots of $\ln(A_t - A_\infty)$ against time at 650 nm.

Oxidation of $[Fe^{III}(CN)_5(SO_3)]^{4-}$ by both $[Ir^{IV}Cl_6]^{2-}$ and Br_2 in excess results in the oxidation of the sulphito-ligand to sulphate. Reactions (4)—(6) are consistent with the kinetic data providing $k_5[Br_2] \gg k_4 \ll k_6[Ir^{IV}Cl_6^{2-}]$ and assuming a first-order dependence on Br_2 and $[Ir^{IV}Cl_6]^{2-}$.

$$[Fe^{III}(CN)_5(SO_3)]^{4-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{Intermediate; rate determining} \quad (4)$$

$$\text{Intermediate} + 1.5\,Br_2 \xrightarrow{k_5} \text{red complex} \quad (5)$$

$$\text{Intermediate} + 2[IrCl_6]^{2-} \xrightarrow{k_6} [Fe^{III}(CN)_5(OH_2)]^{2-} + [SO_4]^{2-} \quad (6)$$

It is proposed that (4) is an intramolecular isomerism as in (7). It has been shown that

$$[Fe^{III}(CN)_5(SO_3)]^{4-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Fe(CN)_5(OSO_2)]^{4-} \quad (7)$$

pentacyanoferrate(II and III) centres are soft or class (b) centres[3] and thus the *S*-bonded isomer should be the more stable form. Also the position of $\lambda_{max.}$ of the ligand-field band in $[Fe^{II}(CN)_5(SO_3)]^{5-}$ is very similar to that for $[Fe^{II}(CN)_5(dmso)]^{3-}$ (dmso = dimethyl sulphoxide) at 352 nm, and the latter species is known[11] to be *S*-bonded. In connection with the postulated isomerism reaction, we note[12] that *O*-bonded organic sulphite esters are oxidised much more readily than the corresponding *S*-bonded isomer.

A mechanism for the oxidation of the *O*-bonded isomer $[Fe^{III}(CN)_5(OSO_2)]^{4-}$ by $[Ir^{IV}Cl_6]^{2-}$ is suggested in equations (8) and (9), followed by (10) or (11).

$$[Fe^{III}(CN)_5(OS^{IV}O_2)]^{4-} + [Ir^{IV}Cl_6]^{2-} \longrightarrow [Fe^{III}(CN)_5(OS^{V}O_2)]^{3-} + [Ir^{III}Cl_6]^{3-} \quad (8)$$

$$[Fe^{III}(CN)_5(OS^{V}O_2)]^{3-} + H_2O \longrightarrow [Fe^{III}(CN)_5(OH_2)]^{2-} + [S^{V}O_3]^{-\cdot} \quad (9)$$

$$[S^{V}O_3]^{-\cdot} + [Ir^{IV}Cl_6]^{2-} + H_2O \longrightarrow [SO_4]^{2-} + 2H^+ + [Ir^{III}Cl_6]^{3-} \quad (10)$$

$$2[S^{V}O_3]^{-\cdot} \longrightarrow [S_2O_6]^{2-} \quad (11)$$

Equation (11) becomes important at low concentrations of $[Ir^{IV}Cl_6]^{2-}$ when less than the stoicheiometric amount of $[Ir^{IV}Cl_6]^{2-}$ was consumed according to equation (3).

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[10] J. Legros, *J. Chim. phys.*, 1964, **61**, 911, 923.

[11] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2084.

[12] F. C. Whitmore in ' Organic Chemistry,' Chapman and Hall, 1937, p. 167.