Kinetics and Mechanism of the Anation and Complexation between Hydroxopentaaquochromium(III) Ions and the Hexacyanoferrate(II) Ion

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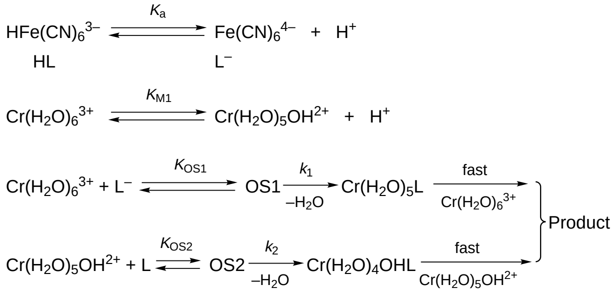
The kinetics of the anation of the chromium(III) species, $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$, by hexacyanoferrate(II) ions in the pH range 4.5–5.4 are reported.

The recognition of the formation and of the interconversion of hydrolytic chromium(III) oligomers, as well as the reactivity of the conjugate base pairs of the starting material, has resulted in tetravalent chromium attracting the attention of many workers.[2,3] Here we report our mechanistic studies on the anation of chromium(III) by hexacyanoferrate(II) in the pH range 4.5-5.4.

It was observed that the reaction followed a first-order rate law with respect to $[Cr^{III}]_T$ under pseudo-first-order conditions [an excess of $Fe(CN)_6^{4-}$]. Under the kinetic conditions, the stoichiometry conforms to:

$$2Cr(H_2O)_5OH^{2+} + Fe(CN)_6^{4-} \longrightarrow [Cr(H_2O)_4OH]_2Fe(CN)_6 + 2H_2O \qquad (1)$$

The present kinetic studies were carried out in the pH range 4.5–5.4. It is noted that, at constant $Fe(CN)_6^{4-}$ concentration, as the pH increased, k_{obs} increased (Table 1). The plot of log k_{obs} *vs.* log $[H^+]$ (pH = 5.0–5.4) shows a fractional order in $[H^+]$. It was observed that the reaction rate increases with increasing ionic-strength, indicating the easy removal[8,17,29] of coordinated water molecules and the formation of outer-sphere complexes. Under our experimental conditions (pH = 4.5–5.4), $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$ were the main reactive species. The hexacyanoferrate(II) ion also participated in the acid–base equilibria. Scheme 1 explains all the observations.



Scheme 1

Consistent with the proposed mechanism, the following rate equation was derived:

$$1/k_{obs} = A/C + B/C[Fe(CN)_6^{4-}]_T \qquad (11)$$

where $A = K_aK_{OS1}[H^+] + K_aK_{M1}K_{OS2}$, $B = [H^+]^2 + [H^+]K_a + K_{M1}[H^+] + K_{M1}K_a$ and $C = k_1K_{OS1}K_a[H^+] + k_2K_{OS2}K_aK_{M1}$. The double reciprocal plots {*i.e.* $1/k_{obs}$ *vs.* $1/[Fe(CN)_6^{4-}]_T$, Fig. 1} are linear with positive intercepts and therefore confirmed the proposed mechanism.

In the pH range 5.0–5.4, $k_1K_{OS1}K_a[H^+]$ and $K_aK_{OS1}[H^+]$ can be neglected in comparison with $k_2K_{OS2}K_aK_{M1}$ and $K_aK_{M1}K_{OS2}$, respectively, and $[H^+]K_a$ and $[H^+]^2k_a$ can also be neglected. Therefore, eqn. (11) can be written as eqn. (12). Double

Table 1 Rate constants at various pH, ionic strength and temperature for the anation of $Cr(H_2O)_5OH^{2+}$ with hexacyanoferrate(II) ions

pH	Ionic strength/ mol dm^{-3}	Temp. *T*/K	10^4 $[Cr(H_2O)_5OH^{2+}]_T$/ mol dm^{-3}	10^3 $[Fe(CN)_6^{4-}]_T$/ mol dm^{-3}	10^4 k_{obs}/ s^{-1}
5.0	0.04	313	2.7	2.67	3.0±0.4
				3.20	3.6±0.4
				3.73	4.0±0.5
				4.27	4.5±0.6
				4.80	5.0±0.2
				5.32	5.7±0.4
5.0	0.05	313	2.7	2.67	2.5±0.3
	0.10				3.0±0.4
	0.20				4.0±0.5
	0.30				5.0±0.5
	0.40				6.3±0.6
	0.50				7.5±0.4
4.5	0.10	313	2.7	2.67	1.5±0.3
5.0					3.0±0.5
5.2					5.0±0.2
5.4					7.2±0.5
5.0	0.04	313	2.7	2.67	2.0±0.6
			3.1		2.4±0.3
			4.3		2.7±0.3
			4.8		3.3±0.5
			5.3		3.5±0.2
5.0	0.10	303	2.7	2.67	1.2±0.2
		308			1.8±0.3
		318			4.4±0.4
		323			4.6±0.3

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*To receive any correspondence.

Table 2 Values of anation rate constant (k_2), outer-sphere complexation constant (K_{OS2}), activation and thermodynamic parameters for the anation of $Cr(H_2O)_5OH^{2+}$ by hexacyanoferrate(II); $[Cr(H_2O)_5OH^{2+}] = 2.6 \times 10^{-4}$ mol dm^{-3}, $[Fe(CN)_6^{4-}] = 2.6 \times 10^{-3}$ mol dm^{-3}, pH = 5.0, ionic strength = 0.1 mol dm^{-3}

T/K	$10^4\ k_2$/ s^{-1}	K_{OS2}/ dm^3 mol^{-1}	$10^4\ k_{2\,(cal)}$/ s^{-1}	$K_{OS2\,(cal)}$/ dm^3 mol^{-1}	k_T/h 10^{-12}
303.2	5.5	115.7	5.8	115.7	6.32
308.2	8.4	110.2	6.6	110.2	6.42
313.2	14.7	90.9	12.5	90.9	6.52
318.2	17.7	89.0	18.0	89.0	6.63
323.2	23.9	83.3	25.5	83.3	6.73
$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1}mol^{-1}	ΔH^0/ kJ mol^{-1}	ΔS^0/ J K mol^{-1}	ΔG^0/ kJ mol^{-1}	
57.60	−117.1	−14.2	−7.4	−12.0	

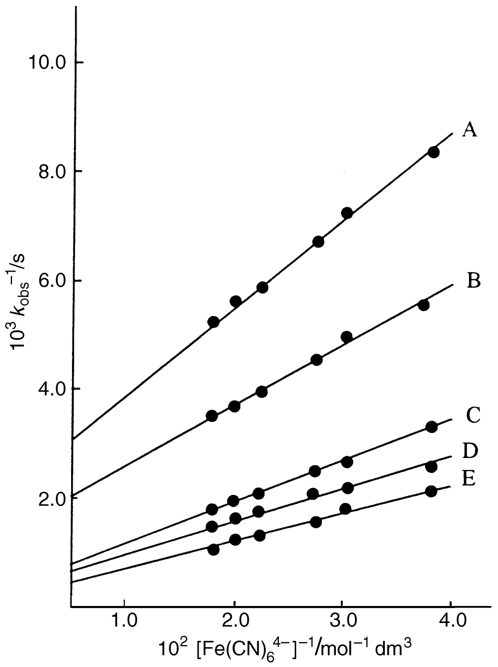

Fig. 1 The dependence of k_{obs}^{-1} *vs.* $[Fe(CN)_6^{4-}]^{-1}$ at various temperatures. (A) 30, (B) 35, (C) 40, (D) 45 and (E) 50 °C, pH = 5.0, $[Cr(H_2O)_5OH^{2+}] = 2.6 \times 10^{-4}$ mol dm^{-3} and ionic strength = 0.1 mol dm^{-3}

reciprocal plots between k_{obs}^{-1} and $[\text{hexacyanoferrate(II)}]_T^{-1}$ at constant pH (which are linear) confirmed the proposed mechanism. Plots according to eqn. (12) were used to evaluate k_2 and K_{OS2} at different temperatures, the values for which are given in Table 2. To confirm the validity of rate law (12), the rate constants were calculated (k_{cal}) in various kinetic runs by substituting the values of k_2 and K_{OS2} in eqn. (12) and comparing with the k_{obs} values. The close agreement between the k_{obs} and k_{cal} values provides supporting evidence for the proposed mechanism (Scheme 1).

$$1/k_{obs} = 1/k_2\{1 + ([H^+] + K_a)/K_{OS2}K_a[Fe(CN)_6^{4-}]\} \qquad (12)$$

Techniques used: Spectrophotometry

References: 31

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Equations: 12

Schemes: 1

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