Chromium(III)-catalysed Oxidation of Antimony(III) by Alkaline Hexacyanoferrate(III) and Analysis of Chromium(III) in Microamounts by a Kinetic Method

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The oxidation of antimony(III) by hexacyanoferrate(III) has been studied in alkaline media. A microamount of chromium(III) (10^{-6} mol dm^{-3}) is sufficient to catalyse the reaction. The active species of catalyst and oxidant in the reaction are understood to be $[Cr(OH)_4]^-$ and $[Fe(CN)_6]^{3-}$. The autocatalysis exhibited by one of the products, *i.e.* antimony(V), is attributed to complex formation between antimony(V) and $[Fe(CN)_6]^{3-}$. A composite mechanism and rate law are proposed. The reaction has been utilised for the analysis of chromium(III) in the range 5.2 ng cm^{-3}–1.14 μg cm^{-3}.

Although arsenic(III) and antimony(III) belong to the same Group in the Periodic Table and have striking similarities, arsenic(III) compounds are used as insecticides and weed-killers while those of antimony(III) are employed as medicaments.[1] Antimony(III) oxide is slightly soluble in water and dilute acid but rather more soluble in alkali.[2] The species in solution are not well characterized.

Chromium(VI) compounds irritate the skin and mucuous membranes, whereas chromium(III) appears to be an essential trace metal in mammalian metabolism and there is no evidence that its compounds have any toxic effects. Chromium(III) co-ordinates with proteins. A deficiency of chromium(III) leads to a decrease in the glycogen reserve, causing a disturbance in the utilisation of amino acids in protein synthesis and a syndrome resembling diabetes. To determine the chemical processes that affect biological systems[3] the aqueous species of chromium(III) at all pH conditions must be identified and the analysis of chromium(III) in microamounts is crucial.

The chemistry of chromium(III) in alkaline medium is not as well developed as in acid. Only recently has it become known that the relatively high solubility of chromium(III) in solutions of pH > 11.5 is due to species like $[Cr(OH)_4]^-$, and that, in such solutions, the presence of polymeric chromium(III) species is unlikely.[4] The reduction potentials[5] of $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$ and Cr^{VI}–Cr^{III} couples of $+0.45$ and -0.13 V respectively in alkaline medium indicate that $[Fe(CN)_6]^{3-}$ and Cr^{III} may react with facility and the species and mechanism have been studied in detail.[6] The reduction potential of Sb^{V}–Sb^{III} in alkaline medium being -0.58 V makes the chromium(III)-catalysed oxidation of antimony(III) by alkaline hexacyanoferrate(III) more feasible. Due to the various intermediate species of chromium(III) and antimony(III) [*i.e.* chromium(IV), chromium(V) and antimony(IV)] involved, this reaction has been undertaken to learn more about the alkaline redox chemistry of these species.

Furthermore, there is also the possibility of complex formation in the reaction. The uncatalysed reaction between antimony(III) and hexacyanoferrate(III) in alkaline medium has been studied previously.[7] A microamount of chromium(III) (10^{-6} mol dm^{-3}) is sufficient to catalyse the reaction in alkaline medium and a variety of mechanisms are possible. Herein, we report the results of a study of the chromium(III)-catalysed oxidation of antimony(III) by hexacyanoferrate(III) in alkaline medium.

Experimental

Materials.—Reagent-grade chemicals and doubly distilled water were used throughout. The second distillation of water was from permanganate in a glass still. Stock solutions of the oxidant, hexacyanoferrate(III), were prepared by dissolving potassium hexacyanoferrate(III) (BDH) in water and the concentrations ascertained by iodometric titrations. Hexacyanoferrate(II) was prepared by dissolving a known amount of potassium hexacyanoferrate(II) (BDH) in water. The aqueous chromium(III) solutions were obtained by dissolution of chromium(III) potassium sulfate (BDH, AnalaR), $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$. The concentration of chromium(III) was determined[8a] by oxidising it to chromium(VI) upon boiling with excess persulfate in the presence of one or two drops of 1×10^{-2} mol dm^{-3} silver nitrate followed by titration with standard iron(II) solution in acidic medium. The stock solution of antimony(III) was made by dissolving antimony(III) oxide (E. Merck, AR) in 3.0 mol dm^{-3} hydrochloric acid and standardised[8a] against potassium bromate using methyl red as indicator. Antimony(V) was prepared from $K_4Sb_2O_7$ (BDH). Sodium hydroxide and sodium perchlorate were used to provide the required alkalinity and to maintain the ionic strength respectively.

The chromium(III) solutions at pH > 12 were clear when freshly prepared and turbidimetry showed no insoluble material over a period of *ca.* 40 h; after this period, a low initial turbidity developed. In view of this, kinetic studies were restricted to fresh solutions of chromium(III) in alkali, *i.e.* chromium(III) was added to the reaction mixture containing alkali when the experiment was started. The appropriate amount of alkali just to neutralise the acid present in the antimony(III) solution was added to the reaction mixture. The concentration of liberated NaCl was also taken into account in calculating the ionic strength.

Kinetic Studies.—Runs were followed under conditions where antimony(III) was present in a nearly ten-fold excess over hexacyanoferrate(III) at a constant temperature of 25 ± 0.05 °C unless otherwise stated. The reaction was initiated by mixing the thermostatted hexacyanoferrate(III) and antimony(III) solutions which also contained the required amounts of chromium(III), sodium perchlorate and sodium hydroxide. The reaction was followed by measuring the absorbance of hexacyanoferrate(III) in the reaction solution in a 1 cm cell in a thermostatted compartment of a Hitachi 150-20 spectrophotometer at 420 nm where the other constituents of the reaction mixture do not absorb significantly. The application of Beer's law for hexacyanoferrate(III) at 420 nm, under the reaction conditions had earlier been verified giving ε 1060 ± 20 dm^3 mol^{-1} cm^{-1}. The choice of initial rates was made according to the autocatalytic nature of the reaction and the failure of the data to fit good first-order kinetics in [Fe(CN)$_6$$^{3-}$]. Initial rates were obtained from tangents at the initial stages of concentration *versus* time curves by the plane mirror method and were reproducible to within ±4%.

In view of the modest concentrations of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessels on the kinetics. Use of polythene/acrylic ware and quartz or polyacrylate cells gave the same results as with glass vessels and cells, indicating that the surfaces play no important role in the reaction rate.

The effect of dissolved oxygen on the rate of the reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In view of the ubiquitous contamination of carbonate in basic solutions, the effect of carbonate on the reaction was also studied. Added carbonate up to 1.0 × 10^{-3} mol dm^{-3} showed no effect on the reaction rate. However, fresh solutions were used while performing the experiments.

Results

Stoichiometry.—Different sets of concentrations of reactants in 0.15 mol dm^{-3} sodium hydroxide at a constant ionic strength of 0.40 mol dm^{-3} and with a constant amount of catalyst were kept for 10 h at 25 °C under a nitrogen atmosphere. The unreacted hexacyanoferrate(III) was estimated by acidifying the reaction mixture with sulfuric acid in the presence of zinc sulfate which prevents the back reaction of hexacyanoferrate(II) with antimony(V). Antimony(III) was determined by the method given in the Experimental section. The total oxidant was then found by iodometry and, after accounting for the antimony(V) formed, the remaining oxidant concentration could be derived. The results indicate that the consumption ratio [Fe(CN)$_6$$^{3-}$]:[Sb^{III}] is 2.0 ± 0.1 (Table 1) as shown in equation (1).

$$2[Fe(CN)_6]^{3-} + Sb^{III} \xrightarrow{Cr^{III}} 2[Fe(CN)_6]^{4-} + Sb^{V} \quad (1)$$

The concentration of the chromium(III) catalyst did not change during the reaction as observed by measuring the absorbance of the reaction mixture at 590 nm. The absence of chromium(VI) was confirmed by measuring the absorbance at 372 nm.

Reaction Order.—The order of the reaction was determined from log–log plots of initial rate *versus* concentration at a constant alkalinity of 0.15 mol dm^{-3} and ionic strength of 0.40 mol dm^{-3}. At a fixed concentration of chromium(III) of 5.0 × 10^{-6} mol dm^{-3}, the apparent order in [Fe(CN)$_6$$^{3-}$] in the range 1.0 × 10^{-4}–1.0 × 10^{-3} mol dm^{-3} was significantly less than unity and the order in [Sb^{III}] in the range 2.0 × 10^{-4}–2.0 × 10^{-3} mol dm^{-3} was unity (Table 2).

The order in [catalyst] was unity in the range 1.0 × 10^{-6}–1.0 × 10^{-5} mol dm^{-3} with all other reactant concentrations and conditions being constant (Table 2) and taking into account the uncatalysed path. With increasing concentration of alkali, the rate increased (Table 2).

Effect of Added Products and Cl$^-$ *Ions.*—Initially added [Fe(CN)$_6$]$^{4-}$ in the range 1.0 × 10^{-4}–2.0 × 10^{-3} mol dm^{-3}, other conditions and reactant concentrations being constant, did not affect the reaction significantly. However, it was found that when the concentration of antimony(V) was varied between 1.0 × 10^{-4} and 1.5 × 10^{-3} mol dm^{-3}, other conditions being constant, the measured initial rates led to an order of around 0.6 in [Sb^V]. This illustrates the autocatalytic effect of the product (Table 3) which is also evident from the absorbance *versus* time plots (Fig. 1).

Chloride ions might also affect the results [complex formation with antimony(III)]. However chloride ions added up to 2.0 × 10^{-3} mol dm^{-3} did not change the results significantly.

Effect of Ionic Strength and Solvent Polarity.—The ionic strength of the reaction solution was varied between 0.15 and 1.0 mol dm^{-3} with sodium perchlorate at constant oxidant, reductant, catalyst and OH$^-$ concentrations of 3.0 × 10^{-4},

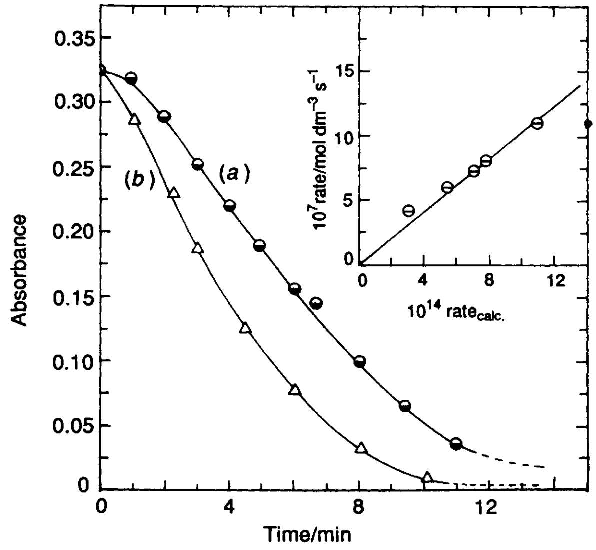

Fig. 1 Absorbance *vs.* time plots: [Sb^{III}] = 1.0 × 10^{-3}, [Fe(CN)$_6$$^{3-}$] = 3.0 × 10^{-4} and [OH$^-$] = 0.15 mol dm^{-3}, I = 0.40 mol dm^{-3}. (*a*) [Cr^{III}] = 7.5 × 10^{-6} mol dm^{-3} and (*b*) [Cr^{III}] = 1.0 × 10^{-5} mol dm^{-3}. Inset: plot of rate *vs.* rate calc. {= [Sb^{III}][Fe(CN)$_6$$^{3-}$]$^{0.7}$ [Cr^{III}][OH$^-$]$^{0.4}$ [Sb^V]$^{0.6}$}

Table 1 Stoichiometry* of Cr^{III}-catalysed oxidation of Sb^{III} by [Fe(CN)$_6$]$^{3-}$ in alkaline medium at 25 °C; [Cr^{III}] = 5.0 × 10^{-6} mol dm^{-3}, [OH$^-$] = 1.5 × 10^{-1} mol dm^{-3}, I = 0.40 mol dm^{-3}

Taken		Found			
10^4[Fe(CN)$_6$$^{3-}$]	10^4[Sb^{III}]	10^4[Fe(CN)$_6$$^{4-}$]	10^4[Sb^{III}]	10^4[Fe(CN)$_6$$^{3-}$]	10^4[Sb^V]
2.0	2.0	2.0	1.0	0.0	1.0
3.0	2.0	2.98	0.49	0.0	1.5
4.0	2.0	4.0	0.0	0.0	2.0
2.0	1.0	2.0	0.0	0.0	1.0
2.0	0.5	1.0	0.0	1.0	0.5
4.0	0.5	1.0	0.0	3.0	0.5

* All concentrations are in mol dm^{-3}. Error ±5%.

Table 2 Effect of $[Sb^{III}]$, $[Fe(CN)_6{}^{3-}]$, $[Cr^{III}]$ and $[OH^-]$ on Cr^{III}-catalysed oxidation of Sb^{III} by $[Fe(CN)_6]^{3-}$ in alkaline medium at 25 °C and $I = 0.40$ mol dm^{-3}

$10^3[Sb^{III}]$/ mol dm^{-3}	$10^4[Fe(CN)_6{}^{3-}]$/ mol dm^{-3}	$10^6[Cr^{III}]$/ mol dm^{-3}	$10^2[OH^-]$/ mol dm^{-3}	10^7 Initial rate/ mol dm^{-3} s^{-1}	
				Exptl.	Calc.
0.20	3.0	5.0	15	1.0	0.97
0.40	3.0	5.0	15	2.0	2.0
0.80	3.0	5.0	15	3.6	3.8
1.0	3.0	5.0	15	4.5	4.7
1.5	3.0	5.0	15	6.9	7.3
2.0	3.0	5.0	15	10	9.7
1.0	1.0	5.0	15	3.2	3.1
1.0	2.0	5.0	15	4.0	4.2
1.0	3.0	5.0	15	4.5	4.8
1.0	5.0	5.0	15	5.6	5.6
1.0	7.0	5.0	15	6.3	6.1
1.0	10	5.0	15	7.1	7.0
1.0	3.0	0.0	15	0.50	0.50
1.0	3.0	1.0	15	1.0	1.0
1.0	3.0	2.0	15	2.2	1.9
1.0	3.0	4.0	15	3.8	3.9
1.0	3.0	7.5	15	4.9	6.3
1.0	3.0	10	15	5.6	7.2
1.0	3.0	5.0	3.0	2.2	2.2
1.0	3.0	5.0	6.0	3.5	3.3
1.0	3.0	5.0	10.5	4.0	4.2
1.0	3.0	5.0	19.5	5.1	5.2
1.0	3.0	5.0	31.0	5.6	5.8

Error ±4%.

Table 3 Effect of products, $[Sb^V]$ and $[Fe(CN)_6{}^{4-}]$ on Cr^{III}-catalysed oxidation of Sb^{III} by $[Fe(CN)_6]^{3-}$ in alkaline medium at 25 °C; $[Sb^{III}] = 1.0 \times 10^{-3}$, $[Fe(CN)_6{}^{3-}] = 3.0 \times 10^{-4}$, $[Cr^{III}] = 5.0 \times 10^{-6}$ and $[OH^-] = 1.5 \times 10^{-1}$ mol dm^{-3}, $I = 0.40$ mol dm^{-3}

$10^4[Sb^V]^a$/ mol dm^{-3}	10^7 Rate/ mol dm^{-3} s^{-1}	10^4 $[Fe(CN)_6{}^{4-}]^b$/ mol dm^{-3}	10^7 Rate/ mol dm^{-3} s^{-1}
0.0	4.5	0.0	4.5
1.0	4.6	1.0	4.6
2.5	6.0	5.0	4.5
4.0	7.4	7.0	4.5
5.0	8.1	9.0	4.5
9.0	11	15	4.6
15	12	20	4.6

Error ±4%. [a] $[Fe(CN)_6]^{4-}$ was absent. [b] Sb^V was absent.

1.0×10^{-3}, 5.0×10^{-6} and 0.15 mol dm^{-3} respectively. The initial rates increased with increase in ionic strength and the plot of log (rate) *versus* $I^{\frac{1}{2}}$ was linear with a positive slope (0.7 ± 0.1) (Fig. 2).

The relative permittivity (ε_r) effect was studied by varying the *tert*-butyl alcohol content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivity of the media failed. However, they were computed from the values of the pure liquids as in earlier work.[8b] There was no reaction of the solvent with the oxidant under the experimental conditions used. Initial rates increased with decrease in relative permittivity of the medium. The plot of log (rate) *versus* $1/\varepsilon_r$ was linear (Fig. 2).

Effect of Temperature.—A decrease in rate was observed with increase in temperature. The rate constants (k) of the slow step of Scheme 1 were obtained from the intercepts of plots of $([Sb^{III}][Cr^{III}])$/rate *versus* $1/[Fe(CN)_6{}^{3-}]$ at four different temperatures and used to calculate the activation parameters. The values of k (dm^3 mol^{-1} s^{-1}) were 1.60×10^2, 1.11×10^2, 0.83×10^2 and 0.60×10^2 at 25, 35, 40 and 45 °C respectively and $\Delta H^\ddagger$ *and* $\Delta S^\ddagger$ for the slow step were calculated to be −33.0 (±2) kJ mol^{-1} and −330.0 (±20) J K^{-1} mol^{-1} respectively.

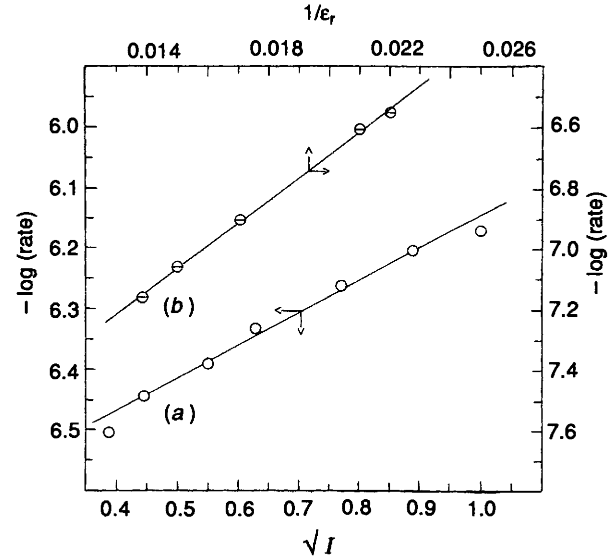

Fig. 2 Effect of ionic strength (*a*) and relative permittivity (*b*) on Cr^{III}-catalysed oxidation of Sb^{III} by $[Fe(CN)_6]^{3-}$ in alkaline medium

Discussion

The relatively high solubility of chromium(III) in alkaline medium at pH > 11.5 is due to the predominance of the species $[Cr(OH)_4]^-$ at 22 °C in aged solutions.[4] Also, slow formation of polynuclear species occurs as well as a decrease in solubility with time. It could therefore be expected that the insolubility in such solutions might be due to the formation of polynuclear chromium(III) species in greater and greater proportions with time. In the present case, the solubility of chromium(III)

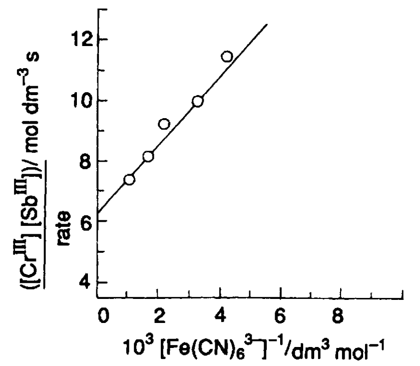

Fig. 3 Verification of rate law (2) (conditions as in Table 2)

$$Cr(OH)_3 + OH^- \overset{K_1}{\rightleftharpoons} [Cr(OH)_4]^-$$

$$[Fe(CN)_6]^{3-} + [Cr(OH)_4]^- \overset{K_2}{\rightleftharpoons} \text{Complex A}$$

$$A + Sb^{III} \xrightarrow[\text{slow}]{k} Sb^{IV} + [Fe(CN)_6]^{4-} + [Cr(OH)_4]^-$$

$$Sb^{IV} + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} Sb^{V} + [Fe(CN)_6]^{4-}$$

Scheme 1

increases rapidly with pH. As monitored by a Nephelometer, while the solutions are clear above pH 12.0, the turbidity increases with acidity and precipitation occurs below pH 12.0. Only reactions under conditions of pH > 12 have been studied in this work for these reasons. The solubility of chromium(III) above pH 12 has been ascribed to the formation of $[Cr(OH)_4]^-$ and the spectrum under such conditions is similar to that of Cr^{3+} (aq) except that some hyperchromicity is found in the former ($\varepsilon_{590} = 25 \pm 1$ *versus* 17 dm^3 mol^{-1} cm^{-1}).

Interestingly, $[Cr(OH)_6]^{3-}$, widely believed[9] to be responsible for the amphoterism of chromium(III), is not one of the species present in alkaline solutions.[4] As for the catalyst, chromium(III), the species $[Cr(OH)]^{2+}$, $[Cr(OH)_2]^+$, $Cr(OH)_3$ and $[Cr(OH)_4]^-$ in addition to polymers are known to exist in aqueous solution.[4] In acid media $[Cr(OH)]^{2+}$ and $[Cr(OH)_2]^+$ exist and at pH 7–10 $Cr(OH)_3$ is known to exist in colloidal form. In alkaline medium at pH > 12, chromium(III) exhibits greater solubility by its amphoterism due to the predominance[4] of $[Cr(OH)_4]^-$. It is also noteworthy that polymeric chromium(III) species in such solutions, as in the present case, at ordinary temperatures and when the chromium(III) solution is freshly made, are almost completely absent.[4] The order of less than unity in OH^- concentration may also be understood in terms of the predominant chromium(III) species $[Cr(OH)_4]^-$, which is due to the pre-equilibrium involving $Cr(OH)_3$ and OH^-. In accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the possible mechanism shown in Scheme 1 is proposed. The order of unity in $[Sb^{III}]$ and fractional order in $[Fe(CN)_6^{3-}]$ is well accommodated in Scheme 1, which incorporates all the experimental results except the autocatalysis by antimony(V). Since the order in $[Sb^{III}]$ is unity, the presence of the monomeric species of antimony(III) in the present reaction conditions is most likely which contrasts with the opinion of Meites and Schlossel.[7a]

Although experimental evidence for the formation of a Sb^{IV} complex as an intermediate was not observed, such a species was observed in earlier studies.[7a] Attempts to obtain spectral evidence were in vain, no appreciable change resulting in the spectra of the oxidant and catalyst in presence of one another. A feeble interaction is probably involved. However, evidence for the complex formation is obtained kinetically. Such complex formation between the catalyst and oxidant has been observed in other studies.[7b] The complex might be formed through CN bridging. Indeed complex formation between iron and Cr^{III} by cyanide linkages[10a] and other similar complexes[10b] have been observed.

From Scheme 1, the rate law (2) is obtained. Strictly, the

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{kK_1K_2[Sb^{III}]_T[Fe(CN)_6^{3-}]_T[Cr^{III}]_T[OH^-]_T}{1 + K_1[OH^-] + K_1K_2[Fe(CN)_6^{3-}][OH^-]} \qquad (2)$$

factors $(1 + K_1[Cr^{III}])$ and $(1 + K_2[Cr^{III}])$ should also be included in the denominator on the right hand side of the equation but, in view of low concentrations of chromium(III) used, they approximate to unity.

The mechanism of Scheme 1 and rate law (2) may be verified by rearranging it in the form of (3). The plot of $([Sb^{III}][Cr^{III}])$/rate against $1/[Fe(CN)_6^{3-}]$ is linear (Fig. 3), the slope

$$\frac{[Sb^{III}][Cr^{III}]}{\text{Rate}} = \frac{1}{[Fe(CN)_6^{3-}]}\left[\frac{1}{kK_1K_2[OH^-]} + \frac{1}{kK_2}\right] + \frac{1}{k} \qquad (3)$$

and intercept of which lead to values of K_2 and k at 25 °C of $2.62 \times 10^4 \pm 1.0 \times 10^2$ dm^3 mol^{-1} and $1.60 \times 10^2 \pm 8$ dm^3 mol^{-1} s^{-1} respectively. The value of K_1 is taken as 1.62 dm^3 mol^{-1} from earlier work.[6] From these values, rates for several experimental conditions may be calculated from equation (2) and compared with the experimentally found data. Such a comparison is made in Table 1 and shows good agreement between the calculated and experimental rates.

The effect of increasing ionic strength on the rate qualitatively explains the reaction between the two negatively charged species, $[Cr(OH)_4]^-$ and $[Fe(CN)_6]^{3-}$. However, increasing the content of *tert*-butyl alcohol in the reaction medium leads to an increase in the rate of the reaction, contrary to the expected slower reaction between like ions in media of lower relative permittivity. Perhaps the effect is countered substantially by the formation of active reaction species to a greater extent in low relative permittivity media leading to net increase in rate.

The negative temperature dependence of rate and negative value of $\Delta H^\ddagger$ obtained indicate that the reaction embodies a prior equilibrium (Scheme 1). Such situations have been reported in the literature.[11] The complex involved in the mechanism of Scheme 1 is expected to lead to a sizeable negative entropy of activation and this is found to be the case.

The autocatalysis by one of the products, antimony(V), is interesting. The apparent order of significantly less than unity in antimony(V) concentration, when antimony(V) is initially present, may be attributed to complex formation between antimony(V) and $[Fe(CN)_6]^{3-}$. The complex, **B**, is then subsequently involved in the interaction with antimony(III). These steps, shown in Scheme 2, will form part of Scheme 1.

$$Sb^{V} + [Fe(CN)_6]^{3-} \overset{K_3}{\rightleftharpoons} \text{Complex } \mathbf{B}$$

$$\mathbf{B} + Sb^{III} \xrightarrow{k_3} Sb^{IV} + Sb^{V} + [Fe(CN)_6]^{4-}$$

$$Sb^{IV} + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} Sb^{V} + [Fe(CN)_6]^{4-}$$

Scheme 2

Thus, when antimony(V) is initially present, a composite scheme involving all the steps of Schemes 1 and 2 operates and the rate law (4a) and then (4b) and (4c) may be derived. Rearranging gives equation (5).

$$\text{Rate} = \frac{kK_1K_2[\text{Sb}^{\text{III}}][\text{Fe(CN)}_6{}^{3-}][\text{Cr}^{\text{III}}][\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1K_2[\text{Fe(CN)}_6{}^{3-}][\text{OH}^-]} + \frac{k_3K_3[\text{Fe(CN)}_6{}^{3-}][\text{Sb}^{\text{V}}][\text{Sb}^{\text{III}}]}{(1 + K_3[\text{Sb}^{\text{V}}])(1 + K_3[\text{Fe(CN)}_6{}^{3-}])} \quad (4a)$$

$$\text{Rate}_{\text{gross}} = \text{Rate}_{\text{cat}} + \text{Rate}_{\text{autocat}} \quad (4b)$$

$$\text{Rate}_{\text{gross}} - \text{Rate}_{\text{cat}} = \text{Rate}_{\text{autocat}} = \frac{k_3K_3[\text{Fe(CN)}_6{}^{3-}][\text{Sb}^{\text{III}}][\text{Sb}^{\text{V}}]}{(1 + K_3[\text{Sb}^{\text{V}}])(1 + K_3[\text{Fe(CN)}_6{}^{3-}])} \quad (4c)$$

$$\frac{[\text{Fe(CN)}_6{}^{3-}][\text{Sb}^{\text{III}}]}{\text{Rate}_{\text{gross}} - \text{Rate}_{\text{cat}}} = \frac{1}{k_3[\text{Sb}^{\text{V}}]}\left\{\frac{1}{K_3} + [\text{Fe(CN)}_6{}^{3-}]\right\} + \frac{1}{k_3}(1 + K_3[\text{Fe(CN)}_6{}^{3-}] \quad (5)$$

At constant concentrations of oxidant and antimony(III), a plot of the left hand side of equation (5) *vs.* $1/[\text{Sb}^{\text{V}}]$ should be linear and this was observed (Fig. 4). Indeed, it is to be noted that the plot shows an intercept which is in agreement with a complex formation as in Scheme 2. From the slope and intercept the values of K_3 and k_3 are obtained as $4.5 \times 10^2 \pm 6$ dm^3 mol^{-1} and 7.0 ± 0.2 dm^3 mol^{-1} s^{-1} respectively. Using these values, experimental rates can be regenerated.

Analysis of Chromium(III) *in Microamounts by a Kinetic Method*.—Methods of analysis of chromium(III) usually involve its oxidation to chromium(VI) followed by a titrimetric or spectrophotometric procedure.[12] The complexometric method for chromium(III) involves prolonged boiling with ethylenediaminetetraacetate and back-titration of the latter.[13] A recent micro method[14] to determine chromium(III) utilises conversion to its complex in the presence of triethanolamine and spectrophotometric detection. Microamounts of chromium(VI) have been determined by kinetic methods.[15] However no direct method has been found feasible for chromium(III). Chromium(III) catalyses several redox reactions[16] and this has been used in its analysis by a kinetic procedure.[17] However this method enables chromium(III) analysis in the range 1.0×10^{-4}–8×10^{-4} mol dm^{-3}. Since chromium(III) catalyses the Sb^{III}–$[\text{Fe(CN)}_6]^{3-}$ reaction in alkaline media in 10^{-6} mol dm^{-3}, this reaction can be used for the analysis of chromium(III) in the range 1.0×10^{-7}–8.0×10^{-6} mol dm^{-3}.

The chromium(III)-catalysed oxidation of antimony(III) by alkaline hexacyanoferrate(III) under the conditions studied leads to antimony(V) and hexacyanoferrate(II) *via* the formation of a catalyst–oxidant complex as shown in Scheme 1.

At constant alkali concentration and ionic strength, the initial rate is a linear function of the concentration of the catalyst as shown in Table 4. In view of this, a kinetic method of measuring the chromium(III) concentration becomes available. For this purpose, a calibration curve of initial rate *vs.* concentration of chromium(III) can be constructed from data such as those of Table 4, as shown in Fig. 5, under a known set of conditions of concentration of oxidant, substrate, alkali, temperature *etc.* The reaction can be repeated under similar conditions in the presence of unknown amounts of chromium(III) and the rate leads to the concentration of chromium(III) from the calibration curve. Alternatively, after a specific time interval, *e.g.* 3 min, one of the concentrations, *e.g.* that of hexacyanoferrate(III) can be measured both in presence and absence of a known amount of catalyst. Such data again lead to a calibration curve and consequently the unknown concentration of chromium(III) can be obtained.

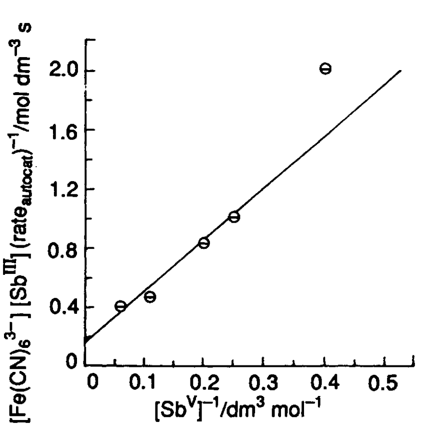

Fig. 4 Verification of rate law (5) (conditions as in Table 3)

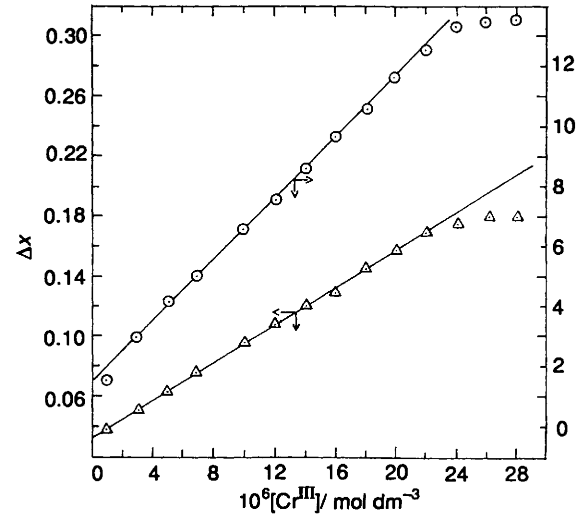

Fig. 5 Plots of initial rate *vs.* $[\text{Cr}^{\text{III}}]$(○) and ΔX *vs.* $[\text{Cr}^{\text{III}}]$ (△) for Cr^{III} analysis by a kinetic method (conditions as in Table 4)

Table 4 Effect of $[\text{Cr}^{\text{III}}]$ on Cr^{III}-catalysed oxidation of Sb^{III} by $[\text{Fe(CN)}_6]^{3-}$ in alkaline medium at 25 °C; $[\text{Sb}^{\text{III}}] = 1.0 \times 10^{-3}$, $[\text{Fe(CN)}_6{}^{3-}] = 3.0 \times 10^{-4}$ and $[\text{OH}^-] = 0.15$ mol dm^{-3}, $I = 0.40$ mol dm^{-3}

10^6 $[\text{Cr}^{\text{III}}]$/mol dm^{-3}	10^7 Rate/mol dm^{-3} s^{-1}	ΔX (3 min)
1.0	1.30	0.042
3.0	3.00	0.050
5.0	4.31	0.064
7.0	5.00	0.076
10	6.60	0.094
12	7.60	0.108
14	8.51	0.120
16	9.60	0.130
18	10.5	0.144
20	11.6	0.158
22	12.5	0.170
24	13.2	0.174
26	13.5	0.180
28	13.6	0.181

Error ±4%.

For routine measurements, the latter procedure is recommended. However, as shown in Fig. 5 for concentrations of chromium(III) higher than 2.2×10^{-5} mol dm^{-3} under the reaction conditions of Table 4, deviations from linearity occurred and the method is no longer satisfactory.

Table 5 Chromium(III) analysis (kinetic method); conditions as in Table 4

$[Cr^{III}]/\mu g\ cm^{-3}$		
Taken	Found*	Standard deviation
0.005	0.0049	±0.02
0.014	0.015	±0.03
0.026	0.025	±0.02
0.050	0.049	±0.03
0.156	0.158	±0.03
0.260	0.258	±0.02
0.312	0.313	±0.03
0.364	0.365	±0.04
0.405	0.404	±0.03
0.520	0.522	±0.03

* Average of 5 sets.

Method recommended for analysis. A known set of concentrations of hexacyanoferrate(III), antimony(III), alkali and chromium(III) (*e.g.* 3.0×10^{-4}, 1.0×10^{-3}, 0.15 and 5.0×10^{-6} mol dm^{-3} respectively) was thermostatted and mixed. The absorbance of hexacyanoferrate(III) at 3 min was taken at 420 nm. With the same concentrations of reactants and alkali, chromium(III) was varied, the reading at 3 min being taken in each case. With the difference in absorbance of hexacyanoferrate(III) between the catalysed and uncatalysed reactions as ΔX (Table 4), a calibration curve of ΔX *vs.* $[Cr^{III}]$ (Fig. 5) was used to determine the unknown concentrations of chromium(III). The results are shown in Table 5.

Interference by a few metals up to a concentration of 2.0×10^{-4} mol dm^{-3} was tested. Apart from the reductants which reduce hexacyanoferrate(III) and the oxidants which oxidise antimony(III), it was found that Zn^{2+}, Te^{4+}, Se^{4+}, Mg^{2+}, Pb^{2+} have no effect, whereas Cu^{2+}, Mn^{2+}, Li^{+}, Co^{2+}, Os^{8+}, Ni^{2+} interfere. The method enables the analysis of chromium(III) in the range 5.2 ng cm^{-3}–1.1 μg cm^{-3}. The method finds its applications in the analysis of chromium(III) in microamounts in its complex form (*e.g.*, chromium(III) acetylacetonate), ores and minerals (*e.g.*, chromium garnets, chromium micas *etc.*) and such other similar forms. Analysis in this range has become increasingly important in recent years since chromium(III) is an essential element in mammalian metabolism.

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