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Kinetics and Mechanisms of the Reaction between Chromium(VI) and Hexacyanoferrate(II) in Aqueous Solution

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The kinetics of oxidation of $Fe(CN)_6^{4-}$ *by* $Cr(VI)$ *in mildly acidic aqueous solution follow the rate law* $-d[HCrO_4^-]/dt = [Fe(CN)_6^{4-}][HCrO_4^-][H^+](k_o+k'[M^+])$ *where* $k_o = 2.0_5\times10^6$ l^2 mol^{-2} s^{-1} *and* k' *has values of* 6.5×10^6 l^3 mol^{-3} s^{-1} *and* 3.0×10^6 l^3 mol^{-3} s^{-1} *for* $M^+ = K^+$ *and* Na^+ *respectively, all at 303.1 K.* $Fe(CN)_6^{3-}$ *has a small retarding effect upon the rate. The kinetically important steps are considered to proceed by outer-sphere mechanisms.*

Introduction

The kinetics and mechanisms of the reduction of Cr(VI) by various substrates have been of interest for many years[1].

The reaction of Cr(VI) with 1-equivalent reductants has often been interpreted[2] in terms of a general mechanism:

$$\mathrm{Cr(VI)+Red} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr(V)+Ox} \qquad 1$$

$$\mathrm{Cr(V)+Red} \xrightarrow{k_2} \mathrm{Cr(IV)+Ox} \qquad 2$$

$$\mathrm{Cr(IV)+Red} \xrightarrow{k_3} \mathrm{Cr(III)+Ox} \qquad 3$$

By assuming that [Cr(V)] reaches a steady-state value the general rate-law of the reduction is

$$-d[\mathrm{Cr(VI)}]/dt = k_1k_2[\mathrm{Cr(VI)}][\mathrm{Red}]^2/(k_{-1}[\mathrm{Ox}]+k_2[\mathrm{Red}])$$

and the observed kinetics of reduction by NpO_2^+ [2a], Fe^{2+} [2b], VO^{2+} [3], and $Fe(phen)_3^{2+}$ [4], have been variously interpreted in terms of this mechanism. However, other mechanisms are known, *e.g.* that found in reduction by $S_2O_3^{2-}$ [5], in which an initial Cr(VI)–S_2O_3 complex is formed by elimination of water, followed by reaction of this complex with further reductant.

Following an earlier brief examination by Stefanovskii[6], kinetics of the oxidation of $Fe(CN)_6^{4-}$ by Cr(VI) were observed near-simultaneously by Birk[7] and by the present authors[8], but the experimental conditions and the results of these two latter studies differ in some respects.

Experimental

Analytical grade, or recrystallised reagents were used. Stock solutions of $K_2Cr_2O_7$ made up by weight, were checked spectrophotometrically at 370 nm after dilution with 0.1 mol l^{-1} NaOH. Freshly prepared solutions of sodium or potassium hexacyanoferrate(II) (in de-oxygenated distilled water made slightly alkaline with NaOH or KOH) were always used.

Preliminary studies showed that the reaction is rapid but that, in the region of pH≈4, the reaction can be followed by fast-mixing/quenching methods. Excess of copper(II) was used as a quencher to precipitate the hexacyanoferrates. Separate experiments showed that the simultaneous addition of $Fe(CN)_6^{4-}$ and $Cr_2O_7^{2-}$ to excess of an acidic solution of Cu(II) leads to a mixture with an absorbance at 370 nm (mainly due to Cr(VI)) which is identical to that obtained in control experiments without $Fe(CN)_6^{4-}$. The quencher is therefore effective.

A simple flow apparatus contained in an air thermostat was used[8]. Reagent solutions (alkali-stabilised $Fe(CN)_6^{4-}$ and buffered $Cr_2O_7^{2-}$) were supplied from graduated 100 cm³ burettes through a three-way capillary mixing tap to the reaction tube which delivered its effluent a few mm above the surface of the quenching solution. The reagent solutions were driven by nitrogen at a constant pressure of about 1.5 atm. Each experiment involved opening the T-tap for a timed period. From the burette readings and the known volume of the mixing tap plus each reactor used, the compositions of the reaction mixtures and the reaction times were calculated.

The efficiency of mixing at the tap was checked using equimolar solutions of HCl and NaOH (coloured with phenolphthalein). The efficiency was better than 95% in 1 ms (*cf.* ref. 9). The rates of flow through the

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reactor were always high enough to ensure non-laminar, turbulent motion.

Reaction products and quencher were centrifuged to remove hexacyanoferrates, quantitatively rendered alkaline with NaOH, re-centrifuged to remove Cu(II), and analysed for residual CrO_4^{2-} by means of the absorbance at 370 nm.

The reported 6:1 stoichiometry of the $Fe(CN)_6^{4-}/Cr_2O_7^{2-}$ reaction was confirmed using conditions similar to those used kinetically. Excess $Fe(CN)_6^{4-}$ was treated with Cr(VI) at pH 4 for 20 min, *i.e.* for about 1000 half-lives of the reaction. The final excess was determined titrimetrically either with Cr(VI) or iodometrically. Using approximately 1×10^{-2} mol l^{-1} $Fe(CN)_6^{4-}$ and 1×10^{-3} mol l^{-1} $Cr_2O_7^{2-}$ the average stoichiometries found by the two methods were respectively 6.07 : 1 and 5.95 : 1 (see later).

The $Fe(CN)_6^{4-}$/Cr(VI) reaction involves a large consumption of H^+. All experimental mixtures therefore contained acetate buffers. The effectiveness of the buffers used was checked by first allowing the effluent from control experiments to react to completion in absence of the quencher and then comparing the pH of these solutions with those of admixtures of slightly alkaline water with the buffered Cr(VI). The buffer employed either sodium or potassium acetate as appropriate.

To avoid confusion, concentrations of Cr(VI) are henceforth invariably referred to the mononuclear species $HCrO_4^-$. Over the range of initial reactant concentrations $[Fe(CN)_6^{4-}] = 1\text{–}4 \times 10^{-2}$ mol l^{-1}, $[HCrO_4^-] = 4\text{–}24 \times 10^{-4}$ mol l^{-1}, $[H^+] = 2\text{–}9 \times 10^{-5}$ mol l^{-1} and over a range of fractions of completion, the reaction is closely first order in $Fe(CN)_6^{4-}$ and in Cr(VI). At the upper end of the pH range the reaction is also first order in $[H^+]$ but this order appears to fall near pH 4. Some representative results (see ref. 8 for tables) obtained at 303.1 K, are given in Table I. In this table, *k* is the third order constant defined by

$$-d[HCrO_4^-]/dt = k[H^+][HCrO_4^-][Fe(CN)_6^{4-}]$$

assuming that $[HCrO_4^-]$ = total [Cr(VI)]. The concentration of H^+ is taken as $\log^{-1}$ pH. No correction is made for ionic strength because $I > 0.2$ mol l^{-1} and hence corrections are subjective, depending on the assumed variation of activity coefficient with ionic strength.

Apart from H^+, only one cation (usually K^+) was present in any experiment. Initially difficulty was found in obtaining repeatability of rate constants from runs using different relative volumes of the two reagent solutions. However, this was overcome when the concentration of K^+ (or Na^+) was made the same in each of the feed solutions.

Each experiment (*cf.* Table I) gives one result. Results from groups of runs at constant T, pH and [cation] may also be plotted as time against the integrated function.

$$\frac{2.3}{([Fe(CN)_6^{4-}]_o - 3[HCrO_4^-]_o)} \log \frac{[HCrO_4^-]_o[Fe(CN)_6^{4-}]}{[HCrO_4^-][Fe(CN)_6^{4-}]_o}$$

These graphs give straight lines passing through the origins up to varying degrees of exhaustion of the minor component. With the ratio $[Fe(CN)_6^{4-}]_o/HCrO_4^-]_o$ at 4, virtual linearity is observed for 40% of reaction whilst at 50 the graph is linear to over 90% completion. Thereafter in every case rate constants appear to fall.

The mean rate constant, *k*, from some 40 experiments is $3.4_5 \times 10^6$ l^2 mol^{-2} s^{-1} at 303.1 K with $[K^+] = 0.2$ mol l^{-1} and I = 0.25 mol l^{-1}. The mean deviation is 0.2×10^6 l^2 mol^{-2} s^{-1}.

The rate is greatly influenced by the nature and concentration of the cation present. As our discussion will show, these results cannot in the main be general ionic strength effects. Fig. 1 illustrates some results obtained at 303.1 K in the presence of different concentrations of K^+ or of Na^+. This indicates that for each cation $k = k_o + k'[M^+]$; that the rate constant, k_o, of a process devoid of cationic effects is $2.0_5 \times 10^6$ l^2 mol^{-2} s^{-1} from each experimental set, and that

TABLE I. k_3 Values. Temp. 303.1 K, $[K^+] = 0.2$ mol l^{-1}, I = 0.25 mol l^{-1}.

$10^2[Fe(CN)_6^{4-}]_o$ mol l^{-1}	$10^4[HCrO_4^-]_o$ mol l^{-1}	$10^5[H^+]$ mol l^{-1}	Time s	10^{-6} k_3 l^2 mol^{-2} s^{-1}
3.14	7.44	2.28	0.18	3.5
2.54	9.82	2.26	0.32	3.6_5
2.58	3.88	2.29	0.51	3.6
2.36	21.12	5.10	0.22	3.5_5
2.52	19.88	3.20	0.35	3.4
0.838	17.66	2.44	0.42	3.5
1.379	17.94	2.25	0.28	3.5
1.075	24.00	2.24	0.56	3.5
2.52	19.88	8.9	0.37	3.1

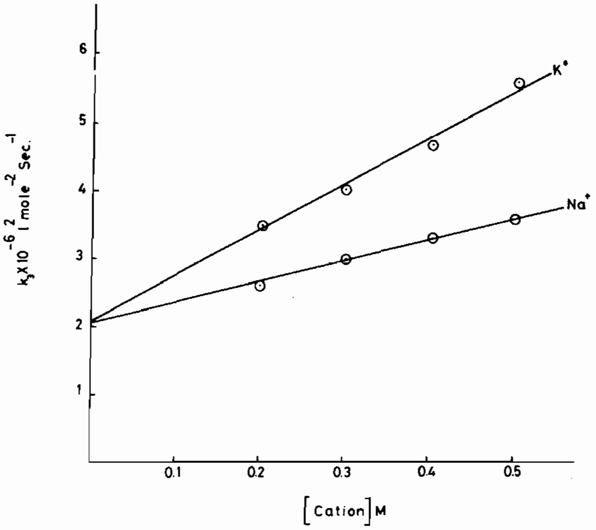

Figure 1. Variation of rate constant with $[M^+]$ at 303.1K.

$k'(K^+)$ and $k'(Na^+)$ are 6.5×10^6 and 3.0×10^6 l^3 mol^{-3} s^{-1} respectively, all at 303.1K. Extra $[M^+]$ is always added as nitrate.

The $Fe(CN)_6^{4-}$/Cr(VI) reaction was reported by Stefanovskii to be retarded by $Fe(CN)_6^{3-}$, and if true this fact could account for our observed diminution in rate constant as reaction proceeds, and for the variable extent of "well-ordered" behaviour with changes in reactant ratio. However, Birk (using somewhat different conditions) found that this anion had no effect upon the kinetics. Table II reports some results of experiments carried out at 303.1 K with deliberate initial additions of $Fe(CN)_6^{3-}$ and these results support the claim made by Stefanovskii. This table is merely a crude indication that the rate is lowered by the presence of $Fe(CN)_6^{3-}$. The actual observations are analysed later.

TABLE II. *k* Values.

$[K^+]$ mol l^{-1}	$10^3[Fe(CN)_6^{3-}]_o$ mol l^{-1}	No. of Runs	10^{-6} Mean *k* l^2 mol^2 s^{-1}
0.2	0.0	40	3.4_5
0.2	3.0	5	2.9
0.2	6.0	5	2.0
0.4	0.0	3	4.6
0.4	6.0	8	3.6

TABLE III. Temperature Dependence of *k*.

T, K	298.5	303.1	308.1	313.1
10^{-6} *k*, l^2 mol^{-2} s^{-1}	2.5_4	3.4_5	3.8_5	4.2_6

A brief investigation of the temperature dependence of the rate constant, *k*, obtained in the presence of 0.2 mol l^{-1} K^+ led to the results shown in Table III. The apparent activation energy is 26 kJ mol^{-1}.

Discussion

The species so far called $Fe(CN)_6^{4-}$ needs closer definition. The first and second thermodynamic proton addition constants of hexacyanoferrate(II) ion are approximately 2×10^4 l mol^{-1} and 250 l mol^{-1} at 298 K[10]. Under our working conditions the corresponding concentration constants would be about 1.5×10^3 l mol^{-1} and 40 l mol^{-1} [11]. Hence under our conditions only monoprotonation is really developed and even this to a small extent. If however, a monoprotonated hexacyanoferrate(II) species is important as a reactant then this is consistent with the observed order of slightly less than one in H^+, because this species will increase in concentration as H^+ rises, linearly at high pH, but less so at lower pH values.

However, it is also necessary to note that cation concentrations are high. In general[10b] ion association constants (I = 0) between alkali metal ions and tetra-, tri- and bi-valent anions are approximately 200, 25 and 10 l mol^{-1} respectively. At I = 0.25 the corresponding figures would be about 16, 4 and 3 l mol^{-1}.

Considering both ion association and protonation, a nominal value of $[Fe(CN)_6^{4-}] = 3 \times 10^{-2}$ mol l^{-1} at pH 4 and $[K^+] = 0.2$ mol l^{-1} therefore implies approximately the following constitution at equilibrium, which will be established and rapidly restored under reaction conditions.

$[Fe(CN)_6^{4-}] = 4 \times 10^{-3}$ mol l^{-1},
$[K\,Fe(CN)_6^{3-}] = 1.4 \times 10^{-2}$ mol l^{-1}
$[K_2Fe(CN)_6^{2-}]$ and more highly cation associated species $= 1.1 \times 10^{-2}$ mol l^{-1}
$[HFe(CN)_6^{3-}] = 5 \times 10^{-4}$ mol l^{-1},
$[KHFe(CN)_6^{2-}] = 4 \times 10^{-4}$ mol l^{-1}

The last two species are particularly significant. Distinct from the others both these species increase in concentration almost linearly with $[H^+]$ and the concentration of the last one also increases roughly proportional to $[K^+]$. Since K^+ is not likely to be much associated with Cr(VI), there are good grounds for favouring $HFe(CN)_6^{3-}$ as being a significant contributor to the activated state for the unassisted reaction; and $KHFe(CN)_6^{2-}$ may be important for the cation catalysed path.

Cr(VI) is buffered before reaction starts so that the equilibrium

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \quad K(I = 0.25) \approx 0.015 \text{ mol } l^{-1}$$

is established, the acetate buffer accounting for virtually all the ionic strength. Near pH 4 the concentrations of these species are pH independent and together they virtually account for all the [Cr(VI)]. The value of the concentration equilibrium constant shows that more than 95% of the Cr(VI) is present as $HCrO_4^-$ under all our conditions. This means that any slow relaxation of the equilibrium has negligible effect upon the kinetics of the redox process if $HCrO_4^-$ is the effective oxidant. Since $[Cr(VI)] \approx [HCrO_4^-]$, the observed first order behaviour in Cr(VI) is consistent with $HCrO_4^-$ being the oxidant. At equilibrium $[Cr_2O_7^{2-}]$ is proportional to $[HCrO_4^-]^2$, and hence approximately to $[\text{total } Cr(VI)]^2$; thus if $Cr_2O_7^{2-}$ were the effective species the observed order in Cr(VI) would be near 2.

Since the effective Cr(VI) species is monovalent, its association with alkali metal cations will be low.

After the above pre-equilibria have been established the first electron transfer steps consist of parallel steps.

$$HFe(CN)_6^{3-} + HCrO_4^- \rightarrow HFe(CN)_6^{2-} + Cr(V) \qquad 4$$

$$KHFe(CN)_6^{2-} + HCrO_4^- \rightarrow KHFe(CN)_6^- + Cr(V) \qquad 5$$

Noting the effective composition of the hexacyanoferrate(II) discussed earlier, $KFe(CN)_6^{3-}$ is seen to be a dominant species, and hence for a major component of the reaction we have

$$KFe(CN)_6^{3-} + H^+ + HCrO_4^- \rightleftharpoons [\text{Transition State}^{3-}]$$

as the main overall equilibrium which could be affected by ionic strength and hence cause variations in rate. Assuming that charge is the dominant property determining an activity coefficient (f) and that[10]

$$\log f = 0.5\, z^2\{I^{1/2}/(1 + I^{1/2}) - 0.25\, I\}$$

on applying this to a reaction whose rate is proportional to $[\text{Transition State}^{3-}]$ we find $\log k = \text{constant} - \{I^{1/2}/(1+I^{1/2}) - 0.25\, I\}$. Over our experimental range of I, 0.25 to 0.65, the maximum discrepancy in rate constant due to ionic strength effects is thus calculated to be 5%. Taking this result together with the marked differences between rates in the presence of Na^+ and those with K^+ present it is clear that our reaction shows marked specific ion effects, and we are unable to say anything about the general effect of ionic strength.

Taking note of the retarding effect of accumulating, or of added hexacyanoferrate(III), we can dismiss the idea that the reaction may go to an analytically detectable position of equilibrium from consideration of the redox couples at the experimental pH. Therefore $Fe(CN)_6^{3-}$ must be involved in some reversible mechanistic step in which it can react only with an intermediate oxidation state of Cr. Evidence has been advanced by Westheimer that Cr(V) may not be a very powerful oxidant. The Cr(IV)/Cr(III) couple on the other hand shows that Cr(IV) is a very strong oxidising agent. Hence it is steps 4 and 5 which are probably reversible whilst subsequent electron transfer steps leading to Cr(IV) or Cr(III) are virtually irreversible. This subsequent "irreversibility" implies that, despite the reversibility of early steps, the reaction will approach complete exhaustion of one reactant.

The effect of accumulating $Fe(CN)_6^{3-}$ is not great so that the reversibility will have negligible effects during the early stages and steps 4 and 5 must be rate determining under these conditions, consistent with the kinetics.

In general with a variety of reductants the reversibilities of steps corresponding to 4 are more likely to be significant the poorer the reducing agent. This conclusion is borne out *e.g.* by the differing kinetic forms obtained on oxidising NpO_2^+ and VO^{2+} with Cr(VI)[2,3].

To facilitate discussion of an analysis of the retardation due to $Fe(CN)_6^{3-}$, some detailed results are given in Table IV for a series of runs at 303.1 K with $[H^+] = 1.91 \times 10^{-5}$ mol l^{-1}, $[K^+] = 0.5$ mol l^{-1} and with a roughly constant reactant composition.

From these results we deduce a value of 3.5×10^{-3} mol l^{-1} s^{-1} for $-d[HCrO_4^-]/dt$ at time 0 starting from an average composition of 19.4×10^{-4} mol l^{-1} $HCrO_4^-$, 2.56×10^{-2} mol l^{-1} $Fe(CN)_6^{4-}$ and 6.2×10^{-3} mol l^{-1} $Fe(CN)_3^{3-}$. In the absence of $Fe(CN)_6^{3-}$ the rate equation leads to a value of 5.03×10^{-3} mol l^{-1} s^{-1}.

The general rate expression for our reaction, at constant pH, starting via steps 1 and 2 could be expressed as

$$-d[HCrO_4^-]/dt = k_1[HCrO_4^-][Fe(CN)_6^{4-}]^2/ \{(k_{-1}/k_2)[Fe(CN)_6^{3-}] + [Fe(CN)_6^{4-}]\}$$

and substitution of the above figures in this expression leads to a value of 0.18 for k_{-1}/k_2.

A different set of runs at $[K^+] = 0.2$ mol l^{-1} gives a value of 0.25 for this ratio. The retardation is definite and $k_{-1}/k_2 \approx 0.2$.

Moreover, it is easily seen that this result is consistent with the main group of experiments carried out without deliberate additions of hexacyanoferrate(III). Use of the figure, 0.2, shows that in our experiments at $[Fe(CN)_6^{4-}]_o/[HCrO_4^-]_o = 7$ the apparent rate constant at half exhaustion of Cr(VI) is 5% lower than it would be in the absence of accumulated $Fe(CN)_6^{3-}$. Similarly with an initial reactant ratio of 70, the apparent fall in rate constant is about 0.5%.

Our general conclusion is that the hexacyanoferrate (II)/chromium(VI) reaction is another example of the operation of the general steps 1–3.

Conclusions about the nature of the Cr(III) product involve another difference between our results and those of Birk. Birk produced evidence that some of the product is a binuclear complex of Cr(III) with Fe(III) which is unreactive towards I^-. The binuclear complex could arise via an inner-sphere reduction of Cr(IV) or from an outer-sphere reduction of a Cr (IV)–Fe(III) complex formed in turn by inner-sphere reduction of Cr(V). However, in our measurements

TABLE IV. Retardation Due to $Fe(CN)_6^{3-}$.

Time s	$10_4[HCrO_4^-]_o$ mol l^{-1}	$10^4[HCrO_4^-]_t$ mol l^{-1}	$10^2[Fe(CN)_6^{4-}]_o$ mol l^{-1}	$10^3[Fe(CN)_6^{3-}]_o$ mol l^{-1}
0.19	18.05	12.56	2.74	6.59
0.25	20.00	13.76	2.50	6.00
0.28	19.47	11.72	2.57	6.16
0.35	19.26	10.30	2.59	6.22
0.51	18.82	8.55	2.65	6.35
0.55	19.64	7.80	2.54	6.11
0.74	19.43	6.34	2.57	6.17

of stoichiometry we found near-theoretical theoretical values on titrating the $Fe(CN)_6^{3-}$ product iodometrically. Birk concluded that one third of the Fe(III) product is present as a stable complex with an intense absorption at 340 nm ($\varepsilon > 3500$ l mol^{-1} cm^{-1}). We have repeated runs in both the lithium perchlorate type of medium used by Birk and in acetate media, and on examining the reacting solution as reaction approached completion, have failed to detect any peak or inflexion in the absorption curve between the composite peaks (mainly due to the hexacyanoferrates) near 320 and 420 nm.

The cation catalysis suggests that some important step helping to determine the overall rate (*e.g.* step 5) has an outer-sphere mechanism[12]. Support for this contention comes from the fact that $Fe(CN)_6^{4-}$ is relatively inert to substitution even where present in protonated and ion-associated forms. Furthermore we have observed that the visible and u.v. absorption spectra of mixtures of $Fe(CN)_6^{3-}$ and Cr(VI) are the sum of the spectra of the separate solutions, indicating that in this closely analogous case there is no noticeable interaction.

The essential role of the kinetically active proton is presumably also that of bridging two unsubstituted centres in step 4; an oxygen atom of $HCrO_4^-$ being a favourable point for hydrogen attachment.

Although we report somewhat different conclusions from those of Birk it may be significant that his work involved higher acidities and lower concentrations of Cr(VI) than ours. An exact comparison of rates is not possible, because this requires knowledge of the catalytic effect of Li^+ and of the temperature variation of two rate constants etc. However, it is easily seen that at say $[H^+] = 10^{-4}$ mol l^{-1} and 298 K the two rate equations lead to similar rates; that appropriate to our conditions being about twice that calculated for Birk's conditions.

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