Kinetics of the Reaction between Chlorite and Hexacyanoferrate(II) in Aqueous Solution; Evidence for an Interfacial Redox Reaction

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The kinetics of oxidation of $[Fe(CN)_6]^{4-}$ by chlorite have been studied spectrophotometrically at 25.0 °C in buffered aqueous solutions of pH 4.8—6.7. With hexacyanoferrate(II) in considerable excess, the rate equation is $-d[ClO_2^-]/dt = 0.25d[Fe^{III}]/dt = E[ClO_2^-][Fe^{II}]/(D + [Fe^{III}])$. The value of D is affected by $[H^+]$, buffer concentration, and the material of the surface of the optical cell in which reaction takes place; E is affected by $[H^+]$ only. These observations are interpreted in terms of a reaction mechanism in which the first stage, a reversible electron transfer, can occur both in homogeneous solution and at the interface between the optical cell and the solution.

MECHANISMS of various redox reactions involving chlorine oxo-anions have previously been investigated, notably by Gordon and co-workers.[1-3] Several reactions involving chlorite anion, ClO_2^-, have been studied.[2-4] The reducing agent hexacyanoferrate(II) features in many mechanistic investigations, but in only a few with oxohalate ions, notably with bromate [5] and iodate.[6] However, no detailed study has been published about the redox reaction between chlorite and hexacyanoferrate(II), although it is known that the reaction is slow.[4] Here, we report observations on this system. Initially we investigated the system chlorate, ClO_3^-, plus hexacyanoferrate(II) and in agreement with others [6] we found that reaction is very slow or non-existent in acid solutions at 25 °C.

EXPERIMENTAL

With the exceptions noted below, reagents were of AnalaR quality and were used without purification. Sulphamic acid was of B.D.H. OAS grade. Allyl alcohol (May and Baker) was allowed to stand for several days over iron powder and was then distilled under nitrogen. The peroxide-free product and its aqueous solutions were kept under argon. Sodium chlorite '98% pure' (Research Organic/Inorganic Corp.) was used without purification. Sodium chlorite '80% pure' (Pierce Inorganics B.V.) was purified by recrystallisation from thrice distilled water; the temperature of the solutions did not exceed 40 °C. Chlorite in these specimens was determined iodometrically in 0.2 mol dm^{-3} sulphuric acid; other chlorine-containing salts were shown to be present collectively to less than 2% by weight.[3] Both specimens contained *ca.* 15% of water of hydration. In otherwise identical kinetic experiments, samples from these two sources gave the same results. Aqueous hypochlorous acid (*ca.* 0.2 mol dm^{-3}) was obtained *via* a solution of chlorine monoxide in carbon tetrachloride prepared by procedure 'A', as described by Cady.[7] The aqueous solution was standardised iodometrically.

Except in preliminary experiments, water for kinetic experiments and stock solutions was thrice distilled prior to use, the final time from potassium permanganate in an all-glass still. This water was then passed through a column of Zerolit DM-F mixed bed resin and finally through a well washed column of Amberlite IRC-50(H) analytical grade cation-exchange resin. It was stored in Polythene containers, as also were stock solutions of reagents. Stock solutions of trisodium hydrogenpyrophosphate and of disodium dihydrogenpyrophosphate contained equivalent concentrations of sodium sulphamate; they were made by dissolving appropriate amounts of tetrasodium pyrophosphate decahydrate and sulphamic acid. All stock solutions were degassed and kept under argon before use. Those of sodium chlorite, potassium hexacyanoferrate(II), and potassium hexacyanoferrate(III) were prepared daily.

Experiments to determine the stoicheiometry of reaction and most of the kinetic experiments were done with hexacyanoferrate(II) present in excess. Reaction mixtures were made up in the optical cell, previously flushed with argon, the chlorite solution being added last. Transfer of stock solutions was by syringe, minimising contact with air, following a routine described previously.[8] Readings of optical density at 420 nm were obtained with the cell in a thermostatically controlled holder in a Unicam SP 500 spectrophotometer, 1.5 min after mixing. Optical cells were normally of silica or polystyrene, as indicated in the Tables. A few experiments were in a glass cell which had been treated internally with dichlorodimethylsilane and subsequently well washed with purified water. Experiments in Table 2 were in cells of path length 4.0 cm, otherwise all experiments were in cells of path length 1.0 cm. A standard volume of 3.0 cm^3 of reaction mixture was used for all experiments in 1.0-cm cells.

From the spectrophotometric measurements the corresponding values of hexacyanoferrate(III) concentration at various times were obtained by using the molar absorption coefficients of hexacyanoferrate(III) and hexacyanoferrate(II), 1 020 and 1 dm^3 mol^{-1} cm^{-1} respectively, at 420 nm. The corresponding values of the hexacyanoferrate(II) and chlorite concentrations were then obtained by using the initial concentrations of the reactants and the value of the stoicheiometry, $\Delta[Fe^{II}]/\Delta[ClO_2^-] = 4.00$. Measurements of the pH of reaction solutions were made by meter after spectrophotometric measurements had been completed. The glass electrode was standardised against 0.050 mol dm^{-3} potassium hydrogenphthalate (pH 4.00).

RESULTS AND DISCUSSION

The Reaction in Solution.—All kinetic experiments were at 25.0 °C. Preliminary results were obtained with 0.50 mmol dm^{-3} $[Fe(CN)_6]^{4-}$ and 10.0 mmol dm^{-3} ClO_2^- in $H_2PO_4^-$–HPO_4^{2-} buffers of pH 5.81 and 6.11 at ionic strength 1.00 mol dm^{-3} (Na[NO_3]). Plots of $-\log(A_\infty - A_t)$ against t were gently curved, the gradient decreasing with time. Here A_t is the optical density at time t and A_∞ is the optical density corresponding to complete oxidation of the complex to hexacyanoferrate(III). The ' first-order ' rate constant obtained from the average gradient over the first half of the reaction was used for comparison between different experiments. This rate constant was increased several times if reaction occurred in the presence of air or was continuously illuminated by daylight. Consequently all further experiments were done in absence of air and with minimum exposure of the reaction mixture and hexacyanoferrate solutions to daylight and the light beam of the spectrophotometer. The rate constant varied with the treatment of the water used in making up the solutions. Lowest rates were obtained with thrice distilled water followed by the ion-exchange treatment described in the Experimental section. This treatment was adopted as standard for all further experiments; almost identical results were subsequently obtained with tap water which had been passed through Elgastat Spectrum ion-exchange cartridges types SC1 and SC2 in series.

The following reagents, in the concentrations shown, decreased the rate constant to about half its normal value: 1 mmol dm^{-3} dihydrogenethylenediaminetetra-acetate (H_2edta^{2-}), 0.5 mmol dm^{-3} hexacyanoferrate(III), 0.2 mol dm^{-3} phenol, and 0.1 mmol dm^{-3} pyridine. Further experiments with pyridine showed a limiting decrease in the rate constant to 0.127 of its normal value, the limit being obtained with *ca.* 1 mmol dm^{-3} pyridine or greater. No change in rate constant was observed with 0.04 mol dm^{-3} allyl alcohol or with 1 mol dm^{-3} propan-2-ol. We assumed the retardation by hexacyanoferrate(III) to be the mass-action effect of this species in a reversible step contributing to the overall reaction. The sensitivity of the reaction to the treatment of the solvent water and the effect of edta were tentatively ascribed to catalysis by traces of heavy metal ions. However, in several experiments the optical density continued to increase beyond the value corresponding to complete oxidation of hexacyanoferrate(II). This was caused by the hexacyanoferrate(III)-catalysed decomposition of chlorite to chlorine dioxide, recognised by its characteristic spectrum,[9] as one of the products. Also, although the reduction of hypochlorous acid (0.10 mmol dm^{-3}) by hexacyanoferrate(II) (0.40 mmol dm^{-3}) was complete in 1.5 min at pH 6.1 and 25.0 °C, the yield of hexacyanoferrate(III) at 1.5 min when the reaction was conducted in the presence of an excess of chlorite (3.0 mmol dm^{-3}) was only 60% of that expected. This evidence of the complexity of the system when chlorite is present in excess led to the further study of the reaction with hexacyanoferrate(II) present in excess.

Most of the further experiments were done with *ca.* 10 mmol dm^{-3} $[\mathrm{Fe(CN)_6}]^{4-}$ and *ca.* 0.1 mmol dm^{-3} $\mathrm{ClO_2}^-$. Solutions of 10 mmol dm^{-3} $[\mathrm{Fe(CN)_6}]^{4-}$, with no chlorite present, made up in the absence of air showed a slow formation of hexacyanoferrate(III). We do not fully understand this oxidation although it occurred more rapidly in the presence of air. The rate of ' spontaneous ' formation of iron(III) in hexacyanoferrate(II) solutions was found under similar conditions to those employed in the study of the reaction with chlorite. Except at the highest pH studied, *i.e.* 6.11, the rate of spontaneous formation of iron(III) was very small compared with that due to oxidation by chlorite. At pH 6.11 and 50% reduction of 0.10 mmol dm^{-3} $\mathrm{ClO_2}^-$ the rate of oxidation of hexacyanoferrate(II) was *ca.* 12 times the rate of spontaneous formation of iron(III). Experiments to determine the stoicheiometry of the reaction also showed that the extent of the spontaneous reaction was negligible. With *ca.* 10 mmol dm^{-3} $[\mathrm{Fe(CN)_6}]^{4-}$ and *ca.* 0.1 mmol dm^{-3} $\mathrm{ClO_2}^-$, the stoicheiometry $\Delta[\mathrm{Fe(CN)_6}^{4-}]/\Delta[\mathrm{ClO_2}^-]$ was 4.0 ± 0.1 over the range of pH used in the kinetic experiments. In the presence of up to 10 mmol dm^{-3} pyridine or 0.2 mol dm^{-3} phenol the decrease in the rate of reaction was less than 10% at pH 6.11, in contrast to the large decreases reported above for experiments with chlorite in excess. We conclude that under the latter conditions one or more chlorine-containing intermediates attack chlorite, leading to a complicated sequence of reactions, and that pyridine competes for these intermediates. With hexacyanoferrate(II) in excess and lower concentrations of chlorite, such intermediates are efficiently removed by reaction with hexacyanoferrate(II), even in the presence of pyridine. An alternative interpretation was considered: that aquapentacyanoferrate(II), highly reactive as a reductant of chlorite, is present as an impurity in hexacyanoferrate(II) and is removed by pyridine to form the relatively unreactive pentacyanopyridineferrate(II). This alternative was discounted because pyridine would be expected to cause a major retardation even if iron(II) is present in excess over chlorite. Dihydrogenethylenediaminetetra-acetate (1 mmol dm^{-3}) had a negligible effect on the rate of reaction, in contrast to its effect in the preliminary experiments.

Sets of experiments in which the initial concentrations of chlorite, hexacyanoferrate(II) (present in substantial excess over chlorite), and hexacyanoferrate(III) were varied at a fixed pH were done to obtain the rate equation. Equation (1) was the simplest found to hold, as

$$-\mathrm{d}[\mathrm{ClO_2}^-]/\mathrm{d}t = 0.25\mathrm{d}[\mathrm{Fe^{III}}]/\mathrm{d}t = E[\mathrm{ClO_2}^-][\mathrm{Fe^{II}}]/(D + [\mathrm{Fe^{III}}]) \quad (1)$$

shown by the use of its integrated form, equation (2)

$$(a + c + D)\ln[\mathrm{Fe^{II}}] - (b + c + D)\ln 4[\mathrm{ClO_2}^-] = E(a - b)t + \text{constant} \quad (2)$$

where $a = [\mathrm{Fe^{II}}]_0$, $b = 4[\mathrm{ClO_2}^-]_0$, $c = [\mathrm{Fe^{III}}]_0$, the subscripts zero indicating initial concentrations, and D and E are constants. We considered other equations similar to (1), but with alterations such as the replacement of $[\mathrm{Fe^{II}}]$ by $[\mathrm{Fe^{II}}]^2$ or the addition of a term in $[\mathrm{Fe^{II}}]$ to the denominator of the expression on the right-hand side. None of these, tested in its integrated form, gave fits to the experimental data as satisfactory as did equation (2).

The form of equation (2) is such that it was convenient to choose an appropriate value of D and then to evaluate the left-hand side for each reading in a given experiment. A plot of corresponding values of the left-hand side and t enabled E to be obtained from the gradient of the resulting straight line. Inappropriate values of D led to curved plots; it was possible to vary D by *ca.* ±25% from the best value before curvature was evident. The corresponding variation in E is *ca.* ±10%.

TABLE 1

Values of the rate constant E at different initial reactant concentrations [a]

$10^4[Fe^{II}]$/mol dm^{-3}	$10^5[Fe^{III}]$/mol dm^{-3}	E/s^{-1}
(*a*) At $[ClO_2^-] = 1.25 \times 10^{-5}$ mol dm^{-3}		
1.0	0	8.0
2.0	0	7.9
5.0	0	7.6
10	0	7.9
20	0	7.8
30	0	8.0
50	0	8.4
100	0	8.2
150	0	8.0
200	0	8.2
(*b*) At $[ClO_2^-] = 2.5 \times 10^{-5}$ mol dm^{-3}		
100	0	8.2
100	1.0	8.1
100	2.5	8.5
100	5.0	7.8
(*c*) At $[ClO_2^-] = 5.0 \times 10^{-5}$ mol dm^{-3}		
3.0	0	8.1
6.0	0	7.4
10	0	8.2
100	0	7.7
100	10	7.5
100	20	7.5
100	40	8.0
(*d*) At $[ClO_2^-] = 10 \times 10^{-5}$ mol dm^{-3}		
20	0	7.6
20	2.5	7.5
20	5.0	7.8
50	0	7.9
100	0	7.5
100	0	8.4
100	0	7.7 [b]
100	2.5	8.3
100	5.0	7.6
150	0	8.4
200	0	8.0
300	0	8.3
400	0	7.8
400	0	8.3
400	2.5	8.1
400	5.0	7.6
400	10	8.4

[a] At pH 4.98; $[H_2PO_4^-] = 0.10$ mol dm^{-3}, $[HPO_4^{2-}] = 4.0 \times 10^{-3}$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3} (*ca.* 0.8 mol dm^{-3} $Na[NO_3]$), and $D = 1.4 \times 10^{-5}$ mol dm^{-3}. Silica optical cell. [b] Ionic strength made 1.0 mol dm^{-3} with NaCl in place of $Na[NO_3]$.

The uncertainties in individual D and E values are estimated as approximately half of these extreme variations. It was subsequently established that, for a group of experiments at fixed pH and buffer concentration, the value of D was approximately constant. Experiments such as those in Table 1 have therefore been presented by using their mean value of D for the evaluation of each experiment. Most of these experiments were followed to *ca.* 80% completion of reaction and linearity was achieved to *ca.* 70%. Marginal improvements in linearity could be obtained for individual experiments by changes in D of ±15% from the mean value. The value of E is satisfactorily constant, the relative standard deviation being ±4.0%. It can be seen from equation (1) that the value of D is not trivial, especially for experiments at low $[ClO_2^-]_0$. When $[ClO_2^-]_0 = 1.25 \times 10^{-5}$ mol dm^{-3} the value of D exceeds that of $[Fe^{III}]$ for the first quarter of the reaction and is 28% of the final value of $[Fe^{III}]$.

TABLE 2

Effects on D and E of cell surface and buffer concentration (I)*

Cell	$10^4[HPO_4^{2-}]$/mol dm^{-3}	10^5D/mol dm^{-3}	10^4E/s^{-1}
Silica	5.0	16	3.4
Glass	5.0	8	3.5
Glass	30	14	3.5
Glass	100	22	3.4

* At pH 5.38; $[H_2PO_4^-]/[HPO_4^{2-}] = 10$, $[ClO_2^-] = 2.5 \times 10^{-5}$ mol dm^{-3}, $[Fe^{II}] = 0.020$ mol dm^{-3}, $[Fe^{III}] < 4 \times 10^{-5}$ mol dm^{-3}; cell path length = 4.0 cm; $D_0 = 70 \times 10^{-5}$ mol dm^{-3}; ionic strength = 1.0 mol dm^{-3}.

The rate of reaction was affected by pH and by the concentration of buffer at a fixed pH. The latter observation was at first thought to imply alteration of the catalytic activity of traces of metal ions by their partial conversion into complexes with the buffer anions. Further experiments showed that trace metal catalysis had been virtually eliminated under the experimental conditions finally adopted, notably by the use of solvent water prepared as described above. It was then found that the rate of reaction was affected by the material of which the optical cell was made. This effect and the effect of buffer concentration at a fixed pH is evident as a variation in the constant D for the results summarised in Tables 2 and 3; there was no significant change in E. At a fixed pH the value of D tended to an upper limit as the concentration of buffer was increased. The limit for D was reached with lower buffer concentrations in polystyrene optical cells compared with silica. Consequently, values of E and D_0 (the limiting value of D) summarised in Table 4 were mainly obtained from experiments in polystyrene cells. It can be seen that D_0 is independent of the buffer system and of the surface of the optical cells employed, although it was not possible to use sufficiently high buffer concentrations to obtain D_0 from experiments in untreated glass cells. We estimate a relative error of *ca.* ±5% in E and of *ca.* $\pm(10 + 1.0 \times 10^{-3}/D_0)\%$ in D_0, the term in $1/D_0$ arising through uncertainty in the initial concentration of $[Fe(CN)_6]^{3-}$, this ion being introduced with $[Fe(CN)_6]^{4-}$ in a proportion not exceeding 0.2% of the latter. Taking into account these errors, we find by a weighted least-squares treatment that $E/s^{-1} = (91.8 \pm 3.3)[H^+]$ and D_0/mol dm^{-3} $= (162 \pm 14)[H^+]$ where $[H^+]$ is expressed in mol dm^{-3}, these results holding for the pH range 4.82—6.66.

A mechanism in accordance with equations (1) and (2)

TABLE 3

Effects on D and E of cell surface and buffer concentration (II) [a]

Cell	pH	$10^3[HPO_4^{2-}]$ / mol dm^{-3}	$10^3[H_2PO_4^-]$ / mol dm^{-3}	10^5D / mol dm^{-3}	10^4E / s^{-1}
Silica (i)	5.38	4.0	40	3.0	3.6
Silica (ii)	5.37	4.0	40	3.0	3.5
Polystyrene	5.38	4.0	40	8.0	3.5
Treated glass [b]	5.39	4.0	40	7.5	3.4
Polystyrene	5.39	10	100	18	3.3
Treated glass [b]	5.38	10	100	17	3.3
Polystyrene	5.44	12.6 [c]	38 [d]	65	3.1
Treated glass [b]	5.43	12.6 [c]	38 [d]	65	3.0
Polystyrene	6.13	70	140	20 [e]	0.71
Polystyrene	6.14	70	140	3.0	0.65 [f]
Polystyrene	6.13	10	20	3.0	0.65 [f]

[a] At $[ClO_2^-] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[Fe^{II}] = 0.010$ mol dm^{-3}, $[Fe^{III}] < 2 \times 10^{-5}$ mol dm^{-3}, and ionic strength = 1.0 mol dm^{-3}. Silica (i) and (ii) are different cells. [b] Glass cell treated with dichlorodimethylsilane. [c] Buffer base = $HP_2O_7^{3-}$. [d] Buffer acid = $H_2P_2O_7^{2-}$. [e] Value equal to D_0. [f] Bright platinum surface (3 cm^2) in contact with reaction mixture.

TABLE 4

Dependence of D_0 and E upon pH [a]

pH	Buffer base	10^3[Base] / mol dm^{-3}	10^3[Acid] / mol dm^{-3}	10^5D_0 / mol dm^{-3}	10^4E / s^{-1}
4.82	$HP_2O_7^{3-}$	3.2—6.3	38—76	200	12.0
5.12	$HP_2O_7^{3-}$	3.2—13	19—76	105	6.8
5.43 [b]	$HP_2O_7^{3-}$	13	38	65	3.0
5.44	$HP_2O_7^{3-}$	13—25	38—76	65	3.1
5.76	HPO_4^{2-}	35—75	140—300	34	1.70
5.81	$HP_2O_7^{3-}$	25—38	25—38	34	1.67
5.81	$HP_2O_7^{3-}$	38	38	34 [c]	1.69 [c]
6.13	HPO_4^{2-}	40—150	80—300	20	0.72
6.16	$HP_2O_7^{3-}$	38	13	20	0.71
6.22 [d]	$HP_2O_7^{3-}$	76	25	20	0.76
6.44	HPO_4^{2-}	40—160	40—160	8.0	0.32
6.66	$HP_2O_7^{3-}$	76	13	4.0	0.22

[a] At $[ClO_2^-] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[Fe^{II}] = 0.010$ mol dm^{-3}, $[Fe^{III}] < 2 \times 10^{-5}$ mol dm^{-3}, and ionic strength = 1.0 mol dm^{-3} (Na[NO$_3$]). [b] Glass cell treated with dichlorodimethylsilane. [c] Ionic strength made 1.0 mol dm^{-3} with NaCl in place of Na[NO$_3$]. [d] Silica cell, other experiments in polystyrene cells.

in which D_0 and E vary linearly with the hydrogen-ion concentration is shown in equations (3)—(6). The

$$[Fe(CN)_6]^{4-} + ClO_2^- \xrightarrow{k_1} [Fe(CN)_6]^{3-} + {}^{\bullet}ClO_2^{2-} \quad (3)$$

$$[Fe(CN)_6]^{3-} + {}^{\bullet}ClO_2^{2-} \xrightarrow{k_{-1}} [Fe(CN)_6]^{4-} + ClO_2^- \quad (4)$$

$$H^+ + {}^{\bullet}ClO_2^{2-} \xrightleftharpoons{K_2} {}^{\bullet}ClO_2H^- \quad (5)$$

$$^{\bullet}ClO_2H^- \xrightarrow{k_3} {}^{\bullet}ClO + OH^- \quad (6)$$

further reduction of $^{\bullet}$ClO to hypochlorous acid and finally to chloride ion follows by steps with sufficiently large rate constants that they do not appear in the rate equation. This mechanism involves steps occurring only in solution; we presume that the observation of limiting values of D which are independent of the nature of the surface of the optical cells justifies this restriction for the reaction under these conditions. By making the stationary-state approximation $d([{}^{\bullet}ClO_2^{2-}] + [{}^{\bullet}ClO_2H^-])/dt = 0$, this scheme yields the kinetic equation (7). This equation accords with equation (1)

$$\frac{-d[ClO_2^-]}{dt} = \frac{0.25d[Fe^{III}]}{dt} = \frac{k_1(k_{-1})^{-1}K_2k_3[H^+][ClO_2^-][Fe^{II}]}{(k_{-1})^{-1}K_2k_3[H^+] + [Fe^{III}]} \quad (7)$$

with $D = D_0 = (k_{-1})^{-1}K_2k_3[H^+]$ and $E = k_1(k_{-1})^{-1}K_2k_3[H^+]$. The absence of evidence for the participation of protonated species in the forward redox stage (3) is surprising; $^{\bullet}ClO_2^{2-}$ is an unexpected intermediate. However, under our conditions the proportion of each reactant present in a protonated form is less than 1%.[10] Also, at the ionic strength (1.0 mol dm^{-3}) employed in our experiments it is likely that there is substantial ion pairing between sodium ions and the species involved in reactions (3) and (4). The lack of appropriately oriented water molecules round the uncharged species HClO$_2$ may be a further barrier to its ready acceptance of an electron.

The Interfacial Reaction.—When the buffer concentration is sufficiently small, the value of D becomes smaller than D_0 at the same pH and depends on the nature of the surface of the optical cell. A smaller value of D corresponds to a more rapid overall reaction and we attribute this to the occurrence of a reaction at the interface between the optical cell and the solution concurrently with the reaction in the bulk solution. Results are summarised in Tables 5 and 6 for experiments conducted in polystyrene and silica optical cells respectively. Comparison of values of D at pH *ca.* 5.4 shows that pyrophosphate buffer is more effective than phosphate buffer in decreasing the extent of the interfacial reaction, whether at a polystyrene or silica surface. We have attempted a quantitative interpretation of the effect of buffer concentration on the extent of the interfacial reaction by supposing that one step in the solution reaction can also occur at the cell surface and that an increase in the adsorption of a buffer constituent at this surface will decrease the surface concentration of an adsorbed reactant or reactants. This approach predicted that a linear relationship might hold between $1/D$ and $1/[\text{buffer}]$ or $1/[\text{buffer}]^2$. A useful form of the relationship is equation (8) in which F is constant for a fixed pH, a particular buffer system, and a given surface

$$(D_0/D) - 1 = F/[\text{buffer}] \qquad (8)$$

of the optical cell. Equation (8) and the corresponding equation with the right-hand side replaced by $F'/[\text{buffer}]^2$ have been applied to the results in Tables 5 and 6. These data are in much better accord with an inverse dependence upon the first power of the buffer concentration. Values of F are given in Table 7; the errors quoted were obtained from least-squares plots of the left-hand side of equation (8) against the reciprocal of the buffer base concentration. We note that for the dihydrogenphosphate–hydrogenphosphate buffer system the charge on the acid form is -1 and that replacement of the nitrate ions, normally used to maintain ionic strength at 1.0 mol dm^{-3}, by chloride ions caused little change in D and E. On the other hand the addition of sulphate ions caused an increase in D, *i.e.* a slower rate of reaction. The base form of the buffer, having the higher charge, is thus likely to be the active entity in adsorption, hence our use of the buffer base concentration in equation (8).

TABLE 5

Dependence of D and E upon pH and buffer concentration, polystyrene optical cell [a]

$10^3[\text{Buffer base}]$/mol dm^{-3}	$10^5 D$/mol dm^{-3}	$10^4 E$/s^{-1}
(*a*) At pH 4.82, $[H_2P_2O_7^{2-}]/[HP_2O_7^{3-}] = 12$		
0.15	170	12.2
high	200 (D_0)	
(*b*) At pH 4.98, $[H_2PO_4^-]/[HPO_4^{2-}] = 25$		
2.0	1.5	8.2
4.0	3.0	7.8
8.0	6.0	8.2
12.0	9.0	8.4
high	160 (D_0)	
(*c*) At pH 5.38, $[H_2PO_4^-]/[HPO_4^{2-}] = 10$		
2.0	4.0	3.5
4.0	8.0	3.5
4.0	14 [b]	3.4 [b]
10.0	18	3.3
30.0	45	3.3
high	65 (D_0)	
(*d*) At pH 5.42, $[H_2P_2O_7^{2-}]/[HP_2O_7^{3-}] = 3$		
0.50	55	3.1
high	65 (D_0)	
(*e*) At pH 5.76, $[H_2PO_4^-]/[HPO_4^{2-}] = 4$		
2.5	8.0	1.75
2.5	22 [c]	1.73 [c]
5.0	14	1.65
10.0	20	1.69
20.0	30	1.65
high	34 (D_0)	
(*f*) At pH 6.11, $[H_2PO_4^-]/[HPO_4^{2-}] = 2$		
2.0	3.5	0.66
5.0	8.0	0.65
10.0	12	0.64
20.0	16	0.62
high	20 (D_0)	

[a] All at $[ClO_2^-] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[Fe^{II}] = 0.010$ mol dm^{-3}, $[Fe^{III}] < 2 \times 10^{-5}$ mol dm^{-3}, and ionic strength = 1.0 mol dm^{-3} ($Na[NO_3]$). [b] $[Co(CN)_6^{3-}] = 0.020$ mol dm^{-3}. [c] $[SO_4^{2-}] = 0.10$ mol dm^{-3}.

TABLE 6

Dependence of D and E upon pH and buffer concentration, silica optical cell *

$10^3[\text{Buffer base}]$/mol dm^{-3}	$10^5 D$/mol dm^{-3}	$10^4 E$/s^{-1}
(*a*) At pH 5.38, $[H_2PO_4^-]/[HPO_4^{2-}] = 10$		
4.0	3.0	3.5
4.0	3.0	3.6
high	65 (D_0)	
(*b*) At pH 5.39, $[H_2P_2O_7^{2-}]/[HP_2O_7^{3-}] = 3$		
3.3	10	3.1
5.0	15	3.2
8.3	20	3.1
12.5	60	3.1
high	65 (D_0)	
(*c*) At pH 5.81, $[H_2P_2O_7^{2-}]/[HP_2O_7^{3-}] = 1$		
8.3	10	1.46
8.3	11	1.46
12.5	15	1.63
25.0	22	1.49
25.0	28	1.53
high	34 (D_0)	
(*d*) At pH 6.23, $[H_2P_2O_7^{2-}]/[HP_2O_7^{3-}] = 0.3$		
15.0	11	0.81
25.0	13	0.68
37.5	15	0.73
37.5	16	0.73
high	20 (D_0)	

* All at $[ClO_2^-] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[Fe^{II}] = 0.010$ mol dm^{-3}, $[Fe^{III}] < 2 \times 10^{-5}$ mol dm^{-3}, and ionic strength = 1.0 mol dm^{-3} ($Na[NO_3]$).

TABLE 7

Dependence of F upon pH*

(*a*) In $H_2PO_4^-/HPO_4^{2-}$ buffer and polystyrene optical cell

pH	4.98	5.38	5.76	6.11
$10^3 F$/mol dm^{-3}	210 ± 2	29.9 ± 0.8	7.82 ± 0.37	9.05 ± 0.50

(*b*) In $H_2P_2O_7^{2-}/HP_2O_7^{3-}$ buffer and silica optical cell

pH	5.39	5.81	6.23
$10^3 F$/mol dm^{-3}	17.2 ± 2.0	17.5 ± 1.6	12.3 ± 0.6

* Data obtained from results in Tables 5 and 6.

Three major experimental findings have been taken into account in suggesting a mechanism for the interfacial reaction. (*i*) The form of the rate equation (1) is the same for the homogeneous path ($D = D_0$) and for the reaction in which the heterogeneous path is dominant ($D \ll D_0$). (*ii*) The constant E is virtually unaffected over a range of buffer concentrations within which D is considerably altered. (*iii*) There is a linear relationship between $1/D$ and $1/[\text{buffer base}]$. The addition of two steps (3′) and (4′) to the steps (3)—(6) of the homogeneous reaction mechanism is sufficient to permit a quantitative description which includes the interfacial contribution and is in accord with the above findings, for experiments at a given pH. In these additional steps,

$$\{\mathrm{Fe(CN)_6}^{4-}\} + \mathrm{ClO_2}^- \xrightarrow{k_1'} \{\mathrm{Fe(CN)_6}^{3-}\} + {}^{\bullet}\mathrm{ClO_2}^{2-} \quad (3')$$

$$\{\mathrm{Fe(CN)_6}^{3-}\} + {}^{\bullet}\mathrm{ClO_2}^{2-} \xrightarrow{k_{-1}'} \{\mathrm{Fe(CN)_6}^{4-}\} + \mathrm{ClO_2}^- \quad (4')$$

only $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Fe(CN)_6}]^{3-}$ are present as adsorbed species and as such are denoted by braces, *e.g.* $\{\mathrm{Fe(CN)_6}^{4-}\}$. Thus, the additional steps postulated to account for the interfacial component of the reaction are both electron transfers between an adsorbed species and a species in solution. In deriving the rate equation we again make the stationary-state approximation, $\mathrm{d}([{}^{\bullet}\mathrm{ClO_2}^{2-}] + [{}^{\bullet}\mathrm{ClO_2H}^-])/\mathrm{d}t = 0$, and we obtain (9) where

$$\frac{-\mathrm{d}[\mathrm{ClO_2}^-]}{\mathrm{d}t} = \frac{0.25\mathrm{d}[\mathrm{Fe^{III}}]}{\mathrm{d}t} = \frac{(k_1[\mathrm{Fe^{II}}] + k_1'T_{\mathrm{Fe^{II}}})K_2k_3[\mathrm{H^+}][\mathrm{ClO_2}^-]}{K_2k_3[\mathrm{H^+}] + k_{-1}[\mathrm{Fe^{III}}] + k_{-1}'T_{\mathrm{Fe^{III}}}} \quad (9)$$

$T_{\mathrm{Fe^{II}}}$ and $T_{\mathrm{Fe^{III}}}$ represent the fractions of the wet surface of the optical cell on which are adsorbed the species $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Fe(CN)_6}]^{3-}$ respectively.

By the application of an adsorption isotherm of Langmuir form to a system in which three species X, Y, and Z are present in solution and can adsorb at a surface in contact with the solution we obtain the usual equations for adsorption such as equation (10), with corresponding equations for T_{Y} and T_{Z}. Here T_{X} is the fraction of the

$$T_{\mathrm{X}} = P_{\mathrm{X}}[\mathrm{X}]/(1 + P_{\mathrm{X}}[\mathrm{X}] + P_{\mathrm{Y}}[\mathrm{Y}] + P_{\mathrm{Z}}[\mathrm{Z}]) \quad (10)$$

wet surface on which X is adsorbed and P_{X} is an adsorption coefficient with the dimensions of reciprocal concentration ($\mathrm{dm^3\,mol^{-1}}$) and which is dependent on the nature of X, the nature of the solvent, the nature and dimensions of the wetted surface, and the temperature. Similar definitions hold for T_{Y}, T_{Z}, and P_{Y}, P_{Z}. If conditions are such that $P_{\mathrm{Z}}[\mathrm{Z}]$ greatly exceeds $(1 + P_{\mathrm{X}}[\mathrm{X}] + P_{\mathrm{Y}}[\mathrm{Y}])$, *i.e.* if T_{Z} is near to unity, equation (10) assumes the simpler form (11), with a corresponding equation for

$$T_{\mathrm{X}} = P_{\mathrm{X}}[\mathrm{X}]/P_{\mathrm{Z}}[\mathrm{Z}] \quad (11)$$

T_{Y}. For our experiments in phosphate buffers, X, Y, and Z correspond to $[\mathrm{Fe(CN)_6}]^{4-}$, $[\mathrm{Fe(CN)_6}]^{3-}$, and $\mathrm{HPO_4}^{2-}$, and we assume that adsorption of singly charged anions is negligible. The interfacial reaction is suppressed at sufficiently high values of buffer concentration (Table 4), but proceeds at buffer concentrations which are lower, but of similar order of magnitude (Tables 4—6). This observation is consistent with a high value of T for the buffer base, enabling equations of the form of (11) rather than (10) to be used, *i.e.* equations (12) and (13). By substituting (12) and (13) into (9) we

$$T_{\mathrm{Fe^{II}}} = P_{\mathrm{Fe^{II}}}[\mathrm{Fe^{II}}]/P_{\mathrm{HP}}[\mathrm{HPO_4}^{2-}] \quad (12)$$

$$T_{\mathrm{Fe^{III}}} = P_{\mathrm{Fe^{III}}}[\mathrm{Fe^{III}}]/P_{\mathrm{HP}}[\mathrm{HPO_4}^{2-}] \quad (13)$$

eliminate $T_{\mathrm{Fe^{II}}}$ and $T_{\mathrm{Fe^{III}}}$ and obtain (14), noting that the proportions of the hexacyanoferrates in the adsorbed form are likely to be very small. If we introduce the

$$\frac{-\mathrm{d}[\mathrm{ClO_2}^-]}{\mathrm{d}t} = \frac{(k_1 + k_1'P_{\mathrm{Fe^{II}}}/P_{\mathrm{HP}}[\mathrm{HPO_4}^{2-}])K_2k_3[\mathrm{H^+}][\mathrm{ClO_2}^-][\mathrm{Fe^{II}}]}{K_2k_3[\mathrm{H^+}] + (k_{-1} + k_{-1}'P_{\mathrm{Fe^{III}}}/P_{\mathrm{HP}}[\mathrm{HPO_4}^{2-}])[\mathrm{Fe^{III}}]} \quad (14)$$

equilibrium quotients, $k_1/k_{-1} = [\mathrm{Fe^{III}}][{}^{\bullet}\mathrm{ClO_2}^{2-}]/[\mathrm{Fe^{II}}][\mathrm{ClO_2}^-]$ and $k_1'/k_{-1}' = T_{\mathrm{Fe^{III}}}[{}^{\bullet}\mathrm{ClO_2}^{2-}]/T_{\mathrm{Fe^{II}}}[\mathrm{ClO_2}^-]$, then by using (12) and (13) we obtain (15). This relationship

$$k_1'/k_{-1}' = k_1P_{\mathrm{Fe^{III}}}/k_{-1}P_{\mathrm{Fe^{II}}} \quad (15)$$

enables (14) to be simplified to give (16), an equation of

$$\frac{-\mathrm{d}[\mathrm{ClO_2}^-]}{\mathrm{d}t} = \frac{k_1(k_{-1})^{-1}K_2k_3[\mathrm{H^+}][\mathrm{ClO_2}^-][\mathrm{Fe^{II}}]}{(k_{-1})^{-1}K_2k_3[\mathrm{H^+}]/(1 + k_{-1}'P_{\mathrm{Fe^{III}}}/k_{-1}P_{\mathrm{HP}}[\mathrm{HPO_4}^{2-}]) + [\mathrm{Fe^{III}}]} \quad (16)$$

the same form as the empirical equation (1) and, with $E = k_1(k_{-1})^{-1}K_2k_3[\mathrm{H^+}]$, exactly the same as proposed for the homogeneous reaction alone. The value of D is given by equation (17) and it is evident that, at sufficiently high

$$D = (k_{-1})^{-1}K_2k_3[\mathrm{H^+}]/(1 + k_{-1}'P_{\mathrm{Fe^{III}}}/k_{-1}P_{\mathrm{HP}}[\mathrm{HPO_4}^{2-}]) \quad (17)$$

values of $[\mathrm{HPO_4}^{2-}]$, D will tend to an upper limit D_0. Moreover, the relationship found experimentally, equation (8), is equivalent to (17) with $F = k_{-1}'P_{\mathrm{Fe^{III}}}/k_{-1}P_{\mathrm{HP}}$.

An equivalent treatment for the pyrophosphate buffer system involves the assumption that the principal buffer species adsorbed is $\mathrm{HP_2O_7}^{3-}$, on account of its higher charge. Nevertheless, $\mathrm{H_2P_2O_7}^{2-}$ may also adsorb to a significant degree and its extent will change with pH because the ratio of buffer acid to base changes. It can be shown that the consequence is likely to be a small increase in the value of P_{HP} (the apparent adsorption coefficient for $\mathrm{HP_2O_7}^{3-}$) with decrease in pH. This would lead to a decrease in F with decrease in pH. In fact, our results (Table 7) give no evidence that adsorption of $\mathrm{H_2P_2O_7}^{2-}$ is important. Over the range studied, pH 5.39—6.23, F is independent of pH for the combination of pyrophosphate buffer with a silica optical cell. In a similar range of pH with the phosphate buffer system there is a small change in F, but a large change occurs in the range pH 4.98—5.38. Thus the proposed mechanism is consistent with the experimental findings at values of pH exceeding *ca.* 5.4. Below this value some modification of the mechanism seems necessary, but our experiments are insufficient to indicate its nature.

Various other combinations of adsorbed species were considered and we deduced relationships corresponding to equations (14) and (16). With one exception, none leads to both the independence of E and the dependence of $1/D$ upon 1/[buffer base] which our experiments show. The exception involves $\mathrm{ClO_2}^-$ and ${}^{\bullet}\mathrm{ClO_2}^{2-}$ as the sole adsorbed species, and the assumption that the subsequent reactions leading to ${}^{\bullet}\mathrm{ClO}$ occur in the bulk solution only. We do not favour this alternative because of this extra assumption and because ClO_2^- has a single charge whereas experiments suggest that adsorption by multiply charged anions is predominant. The condition that both reactants, ClO_2^- and $[Fe(CN)_6]^{4-}$, adsorb and react with one another in this state can be discounted because it leads to a dependence of $1/D$ upon $1/[\text{buffer base}]^2$.

Although interfacial catalysis has been demonstrated in the reaction between chlorite and hexacyanoferrate(II), we are unable to offer a full explanation of the phenomenon. Various examples of the interfacial catalysis of a solution reaction have previously been investigated and interpreted.[11] However, the step subject to catalysis in our system appears to be a reversible electron transfer and we know of no instance of the catalysis of such a type of reaction at an inert surface which is a non-conductor of electricity. We have evidence that the hexacyanoferrate-(II) and -(III) ions are adsorbed at the cell surface, whether of silica or polystyrene. On the solution side of the potential-determining layer of these and the buffer anions a Stern layer [12] containing predominantly cations will form. Anions such as chlorite in the bulk solution in the region of the interface may therefore be able to approach relatively closely to the adsorbed hexacyanoferrate ions because of the net positive charge of the intervening layer. It is well established that electron transfer between species of like charge can be assisted by ions of opposite charge. Hence the possibility arises of the promotion of such assistance under favourable conditions, if one of the two ions adsorbs at an inert surface. Verification of this suggestion would require a detailed investigation of the nature of the adsorbed electrolyte species under the conditions of our experiments. In particular, it would be necessary to vary the nature and concentrations of the cations present, sodium being the predominant cation in all the experiments reported in this paper.

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