Kinetics of the Reaction between Hypochlorous Acid and Hexacyanoferrate(II) Ion in Aqueous Solution

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The kinetics of the reaction of hypochlorous acid with potassium hexacyanoferrate(II) has been investigated spectrophotometrically at 25.1 °C in buffered aqueous solutions at pH 7.74 and 9.45. With HOCl in excess, the rate is given by equation (i). However, with hexacyanoferrate(II) in

$$-\frac{d}{dt}[\mathrm{Fe^{II}}] = k_{\mathrm{obs.}}[\mathrm{Fe^{II}}] \qquad \text{(i)}$$

$$-\frac{d}{dt}([\mathrm{Fe^{II}}]_0 + [\mathrm{Fe^{III}}]_0 - [\mathrm{Fe^{III}}]_t) = \frac{k^0([\mathrm{Fe^{II}}]_0 + [\mathrm{Fe^{III}}]_0 - [\mathrm{Fe^{III}}]_t)^2[\mathrm{HOCl}]}{k^*([\mathrm{Fe^{II}}]_0 + [\mathrm{Fe^{III}}]_0) + (k_b - k^*)([\mathrm{Fe^{II}}]_0 + [\mathrm{Fe^{III}}]_0 - [\mathrm{Fe^{III}}]_t)} \qquad \text{(ii)}$$

excess, the rate is given by equation (ii). The results obtained are interpreted in terms of a reaction mechanism in which the first stage, $\mathrm{Fe^{II}} + \mathrm{HOCl} \longrightarrow \mathrm{Cl^{\bullet}} + \mathrm{OH^-} + \mathrm{Fe^{III}}$, can occur either by an irreversible or reversible process.

The kinetics and mechanism of redox reactions involving hypochlorous acid have been investigated by various workers.[1-5] The reaction between hypochlorous acid and the reducing agent potassium hexacyanoferrate(II) has been found to be slow at pH 6.1 and 25 °C.[5] Also, the reduction of hypochlorous acid to give chloride ion occurs at a relatively fast rate compared to the reduction of chlorite with hexacyanoferrate(II). Therefore I wished to continue the study of this reaction system in order to obtain more information concerning its kinetics and mechanism, and the results are presented here.

Experimental

All solutions were prepared and used with exclusion of air.[6] A Shimadzu UV-240 recording spectrophotometer was employed to monitor the reaction. Light of wavelength 420 nm was used for all kinetic studies. The reaction solution was removed from the light beam between measurements. Computations were made using a Hewlett Packard HP85 microcomputer and NEC PC8801 microcomputer system.[7,8]

The pH of all solutions was measured by using an Orion Research digital pH/mV meter type 661 at the end of the reaction. The glass electrode was standardised against 0.050 mol dm^{-3} potassium hydrogenphthalate: the pH of this solution was assumed to be 4.00. Carbonate–bicarbonate buffers were used for all experiments.

Hypochlorous acid was prepared immediately before use by shaking a known quantity of $\mathrm{OCl_2}$ in carbon tetrachloride solution with a known volume of water; the $\mathrm{OCl_2}$–$\mathrm{CCl_4}$ solution was prepared by the method of Cady[9] and was analysed by the analytical methods of Cady[9] and Chen.[10] Experiments to determine the stoicheiometry of reaction were carried out in the optical cell which was previously flushed with nitrogen; the hypochlorous acid solution was added last. In order to minimise contact with air, transfer of stock solutions (which were degassed and kept under nitrogen) was carried out by syringe. All other chemicals used for this work were pure grade and were used without further purification.

All kinetic studies were carried out in doubly distilled water which had been passed through a Houseman Ionizer model 3C portable deionizer (a mixed-bed cartridge deionizer) giving a rate constant uneffected by the presence of dihydrogenethylenediamine-*NNN'N'*-tetra-acetate ($\mathrm{H_2edta^{2-}}$), as shown in Table 1. Presumably the $\mathrm{H_2edta^{2-}}$ added was scavenging metal ions such as copper(II) which could interfere with the reactions.

Results and Discussion

The Reactions.—Results obtained show that for the reaction of HOCl with $\mathrm{K_4[Fe(CN)_6]}$ plots of $\log(A_\infty - A_t)$ against time are linear up to 98% of reaction with hypochlorous acid present in large excess: *e.g.* 1.96×10^{-2} mol dm^{-3} HOCl and 2.71×10^{-3} mol dm^{-3} $\mathrm{K_4[Fe(CN)_6]}$ at pH 9.45 and at 25.1 °C. Otherwise (*i.e.* $[\mathrm{Fe^{II}}]_0 \geqslant [\mathrm{HOCl}]_0$) the plots are gently curved, the slope 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 reaction between 2.71×10^{-3} mol dm^{-3} hexacyanoferrate(II) and 1.08×10^{-3} mol dm^{-3} hypochlorous acid was studied at several pH values. It was found that the reaction was too rapid at pH < 5.0 and too slow at pH > 11.0 to monitor by using convenient spectrophotometry. Some of the results obtained at pH 7.74 are given in Table 2 for comparison. It can be seen that the reaction rate of hexacyanoferrate(II) with hypochlorous acid is acid dependent; the p*K* of HOCl is *ca.* 7.5 which would explain the change in k_a from *ca.* 1.3 at pH 9.45 to *ca.* 13 at pH 7.74 if HOCl rather than $\mathrm{ClO^-}$ is the reactive species. It was decided to investigate the reaction at pH 9.45 in detail. A series of experiments was performed in which the initial concentrations of hypochlorous acid, hexacyanoferrate(II), and hexacyanoferrate(III) were thus changed at pH 9.45 to establish the required stoicheiometry and the rate equation described below.

Stoicheiometry.—Experiments designed to determine the stoicheiometry of the reaction showed that the spontaneous formation of hexacyanoferrate(III) in the absence of hypochlorous acid[5] was negligible under the conditions and times of the reactions; also it was found that the analysis for unreacted HOCl is unaffected by the hexacyanoferrate(III) formed, with

0.25 × 10^{-3} mol dm^{-3} $[Fe(CN)_6]^{4-}$ and 1.08 × 10^{-3} mol dm^{-3} HOCl, and with 1.35 × 10^{-3} mol dm^{-3} $[Fe(CN)_6]^{4-}$ and 1.08 × 10^{-3} mol dm^{-3} HOCl, the stoicheiometry $\Delta[Fe(CN)_6{}^{4-}]/\Delta[HOCl]$ was found to be 1.97 ± 0.15 at pH 9.45 ± 0.08 and 25.1 °C. However, with 1.49 × 10^{-3} mol dm^{-3} $[Fe(CN)_6]^{4-}$ and 5.40 × 10^{-3} mol dm^{-3} HOCl, the stoicheiometry was measured as 1.84 ± 0.14.

Reaction in Excess of Hypochlorous Acid.—In addition to a linear plot of $\log(A_\infty - A_t)$ against time, experiments also showed that when the reaction occurs in the presence of a large excess of HOCl, similar k_a values (4.67 ± 0.11 × 10^{-2} dm^3 mol^{-1} s^{-1}) were obtained for runs without the addition of $[Fe(CN)_6]^{3-}$ or with the addition of different amounts of this compound. Results obtained are listed in Table 1; they show a linear relationship between $k_{obs.}$ and [HOCl]. The experimental results obtained in the presence of a large excess of HOCl can be represented by equation (1), where $k_{obs.} = 2k_a[HOCl]$. $[Fe^{II}]_t$

$$-\frac{d}{dt}[Fe^{II}]_t = k_{obs.}[Fe^{II}]_t \qquad (1)$$

and $[Fe^{III}]_t$ are the concentrations of hexacyanoferrate(II) and hexacyanoferrate(III) respectively at time t. The mechanism of the reaction in accordance with equation (1) is given by equation (2).

$$\begin{aligned} &Fe^{II} + HOCl \xrightarrow{k_a} Cl^{\bullet} + OH^- + Fe^{III} \\ &Fe^{II} + Cl^{\bullet} \xrightarrow{k_b} Cl^- + Fe^{III} \qquad (2) \end{aligned}$$

Reaction of Hexacyanoferrate(II) *with Hypochlorous Acid of Similar Concentrations.*—When the reaction was performed without a large excess of HOCl (pseudo-first-order), curved kinetic plots were obtained. Several reactions mechanisms were designed and used to explain the experimental results; equation (3) was found to give the best representation. In accordance

$$\begin{aligned} &Fe^{II} + HOCl \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Cl^{\bullet} + OH^- + Fe^{III} \\ &Fe^{II} + Cl^{\bullet} \xrightarrow{k_b} Cl^- + Fe^{III} \qquad (3) \end{aligned}$$

with this mechanism, the rate of reaction can be written as in equation (4), where $k^0 = 2k_ak_b$ and $k^* = k_{-a}[OH^-]$. In the reaction medium, $[Fe^{II}]_t = [Fe^{II}]_0 + [Fe^{III}]_0 - [Fe^{III}]_t$. Therefore from equation (4) the rate law (5) is found. The integrated form of equation (5) is given by equation (6).

$$\frac{d[Fe^{II}]_t}{dt} = \frac{-k^0[Fe^{II}]_t{}^2[HOCl]}{k_b[Fe^{II}]_t + k^*[Fe^{III}]_t} \qquad (4)$$

$$-\frac{d}{dt}([Fe^{II}]_0 + [Fe^{III}]_0 - [Fe^{III}]_t) = \frac{k^0([Fe^{II}]_0 + [Fe^{III}]_0 - [Fe^{III}]_t)^2[HOCl]}{k^*([Fe^{II}]_0 + [Fe^{III}]_0) + (k_b - k^*)([Fe^{II}]_0 + [Fe^{III}]_0 - [Fe^{III}]_t)} \qquad (5)$$

$$\ln([Fe^{II}]_0 + [Fe^{III}]_0 - [Fe^{III}]_t) - \frac{k^*([Fe^{II}]_0 + [Fe^{III}]_0)}{(k_b - k^*)}\cdot\frac{1}{[Fe^{II}]_0 + [Fe^{III}]_0 - [Fe^{III}]_t} = \left(\frac{k^0}{k_b - k^*}\right)[HOCl]_t + \text{constant} \qquad (6)$$

Table 1. Reaction of $[Fe(CN)_6]^{4-}$ with a large excess of HOCl: 25.1 °C, pH 9.45 ± 0.08, I = 1.00 mol dm^{-3} ($NaNO_3$); $[Fe^{II}]_0$ = 2.71 × 10^{-4}, $[Na_2CO_3]$ = 0.15, $[NaHCO_3]$ = 0.15 mol dm^{-3}

$10^2[HOCl]_0$/ mol dm^{-3}	$10^4[Fe^{III}]_0$/ mol dm^{-3}	$10^3k_{obs.}$/ dm^3 mol^{-1} s^{-1}
0.108	0.135	0.205
0.108	0.271	0.209
1.26	0	1.20
1.58	0	1.48
1.82	0	1.64
1.96	0	1.84
2.05	0	1.91
2.20	0	2.07
1.82	2.72	1.69
1.82	5.12	1.56
1.58[a]	0	1.50
1.58[b]	0	1.48
1.58[c]	0	1.48
1.58[d]	0	1.51
2.05[a]	0	1.91
2.05[b]	0	1.93
2.05[e]	0	1.91

[a] $[H_2edta^{2-}]$ added, 4.0 mmol dm^{-3}. [b] $[H_2edta^{2-}]$ added, 2.0 mmol dm^{-3}. [c] $[H_2edta^{2-}]$ added, 0.8 mmol dm^{-3}. [d] $[H_2edta^{2-}]$ added, 0.1 mmol dm^{-3}. [e] $[H_2edta^{2-}]$ added, 0.6 mmol dm^{-3}.

From equation (5), it is not surprising that a plot of $\ln(A_\infty - A_t)$ against time (t) is curved. The computer programs REACTA and REACTG were employed to determine the rate constants using equation (5). The results are given in Table 2. From Table 2, it can be seen that under the adopted experimental conditions, retardation effects (k_{-a}/k_b) for the reaction between hypochlorous acid and hexacyanoferrate(II) increase with decrease in the initial concentration of $[Fe(CN)_6]^{4-}$ and there is a negligible effect of the concentration of $[Fe(CN)_6]^{3-}$ on the values of k_{-a}/k_b. However I have seen that there is no interfering dependence on $[Fe(CN)_6]^{3-}$ in the reaction of $[Fe(CN)_6]^{4-}$ with a large excess of hypochlorous acid but it does occur in the reaction of $[Fe(CN)_6]^{4-}$ with a similar concentration of hypochlorous acid. The magnitude of k_b is important only to the extent that it is sufficiently larger than k_a (*ca.* 100 times or more) for $Cl^{\bullet}$ to be small compared with [HOCl] and $[Fe(CN)_6{}^{4-}]$, so that $d[Cl^{\bullet}]/dt = 0$, which is used in deriving the kinetic equation (4).

It can be seen from the results that only the ratio k_{-a}/k_b can be obtained experimentally. However it is quite clear that k_b (and hence $k_{-a}[OH^-]$) is very much larger than k_a. The latter relates to the reaction of a stable molecule HOCl with $[Fe(CN)_6]^{4-}$ whereas k_b refers to the reaction of a reactive intermediate, $Cl^{\bullet}$ with $[Fe(CN)_6]^{4-}$. It is impossible to obtain the absolute rate constants k_b in any way from experiments of this kind; fortunately, it is not necessary to do so. Reaction (7) must have a very negative change in free energy. The E^0 value for $Cl^{\bullet} + e \longrightarrow Cl^-$ would be expected to be *ca.* 1 V larger than that for $\frac{1}{2}Cl_2 + e \rightleftharpoons Cl^-$ which has $E^0 = -1.36$ V and involves the half-bond strength of Cl–Cl;[11,12] also, $[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$ has E^0 = 0.37—0.40 V,[11,12] so a rapid reaction is expected, especially as no covalent bonds are broken. Hence comparison with reaction (2) suggests that the free radical reaction will be much faster. The reverse reaction, k_{-a}, is not observable when HOCl is in a large excess because the $Cl^{\bullet}$ atoms are scavenged by direct reaction with HOCl: *e.g.* $Cl^{\bullet} + HOCl \longrightarrow Cl^- + H^+ + ClO^{\bullet}$. However, with sufficient HOCl present this reaction would predominate

$$Cl^{\bullet} + [Fe(CN)_6]^{4-} \longrightarrow Cl^- + [Fe(CN)_6]^{3-} \qquad (7)$$

Table 2. Kinetic retardation effect observed for the reaction of HOCl with $[Fe(CN)_6]^{4-}$: 25.1 °C, pH 9.45 ± 0.08; I = 1.00 mol dm^{-3} ($NaNO_3$); $[HOCl]_0$ = 1.08 × 10^{-3}, $[Na_2CO_3]$ = 0.15, $[NaHCO_3]$ = 0.15 mol dm^{-3}

$10^3[Fe^{II}]_0$/ mol dm^{-3}	$10^3[Fe^{III}]_0$/ mol dm^{-3}	k_{-a}/k_b	k_a/dm^3 mol^{-1} s^{-1}
0.271	0	0 (linear)	0.23
0.377	0	0 (linear)	0.49
1.08	0	48.2	1.03
1.35	0	47.5	1.08
2.03	0	47.6	1.16
2.22	0	47.3	1.21
2.51	0	47.5	1.25
2.51[a]	0	47.1	1.29
2.71	0	46.1	1.35
3.38	0	46.2	1.44
2.71	0.51	46.5	1.32
2.71	1.08	47.3	1.33
2.71	0.27	47.0	1.35
2.71	0.13	46.2	1.32
2.71[b]	0	46.7	1.35
2.71[c]	0	46.8	1.32
0.271[d]	0	44.6	6.9
1.35[d]	0	41.3	11.4
2.03[d]	0	35.8	12.6
2.71[d]	0	32.1	13.5
2.71[d]	0.50	31.5	13.7
2.71[d]	1.02	32.0	13.8
2.71[d]	0	32.5	13.6

[a] I = 1.00 mol dm^{-3} (NaCl). [b] $[NaCO_3]$ = 0.10, $[NaHCO_3]$ = 0.10 mol dm^{-3}. [c] $[Na_2CO_3]$ = 0.05, $[NaHCO_3]$ = 0.05 mol dm^{-3}. [d] pH 7.74 ± 0.11; $[Na_2CO_3]$ = 0.005, $[NaHCO_3]$ = 0.10 mol dm^{-3}.

over the back reaction, especially as there is never much Fe^{II} present in the experiments of Table 1.

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