

Kinetics of Oxidation of Hexacyanoferrate(II) with Chloramine in Aqueous Medium

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Summary: The kinetics of the oxidation hexacyanoferrate(II) with chloramine has been investigated spectrophotometrically at 25.0 °C in buffered aqueous solution at pH 8.5-9.50. Reaction does not show significant dependence on $[\text{Fe}(\text{CN})_6^{3-}]$ in the reaction of $[\text{Fe}(\text{CN})_6^{4-}]$ with a large excess of chloramine solution, but it does show in the reaction of $[\text{Fe}(\text{CN})_6^{4-}]$ with a similar concentration of chloramine. With chloramine in excess, the rate as given by $-\text{d}/\text{dt} [\text{Fe}^{\text{II}}] = k_{\text{obs}}[\text{Fe}^{\text{II}}]$. The result obtained is interpreted in terms of a reaction mechanism in which the first stage, $\text{Fe}^{\text{II}} + \text{NH}_2\text{Cl} \longrightarrow \text{Fe}^{\text{III}} + \text{Cl}^-$, can occur by an irreversible or reversible process.

Introduction

Chloramine (NH_2Cl) has been known useful in a number of synthetic reactions [1-4]. It was first proposed by Rasching [5] as an intermediate in the synthesis of hydrazine from chlorine and ammonia. The mechanism of this reaction has been well characterized [6-7]. Chloramine can be prepared as a pure compound and is useful in a number of synthetic reactions [1-4].

Chlorine which is widely used as disinfectant in potable and waste water, reacts with water to give hypochlorous and hypochloric acid. When ammonia and organic amines are present they react with chlorine or hypochlorous acid to form chloramine [8] (monochloramine, dichloramine and trichloramine) and these species can cause significant environmental problems [9]. The chlorination process is referred to an break-point chlorination and produces [10] N_2 and Cl^- . In addition to N_2 , NO_2^- , NO_3^- , as much as 15% of the nitrogenous products may be formed [11].

Mechanisms have been proposed for break-point chlorination but with limited success because the detailed kinetics of the reaction is not known. Wei [12] suggested that the mechanism involves NOH , whereas others [13-14] indicated that hydroxylamine is a precursor of this species. Although few studies about the existence of chloramine in solution have been recently established [15], there is no direct evidence for the presence of NOH , and no detailed study have been published about the redox reaction between the chloramine and hexacyanoferrate (II) ion. Another similar study, between hypochlorous acid and the reducing agent, hexacyanoferrate(II) has been

found to be slow at pH 6.1 and 25.0 °C [16]. Also the reduction of chloramine to give chloride ion occurs at a relatively fast rate compared to the reduction of hypochlorite by hexacyanoferrate(II). Therefore, we wished to probe and obtained more information concerning the kinetics and mechanism of the reduction.

Experimental

Spectrophotometric methods were used for the kinetic measurements of the reaction solutions. Shimadzu UV-visible 120-02 spectrometer, attached with a recorder, was used to monitor the reaction. Measurements were made at 420 nm, the maxima shown by hexacyanoferrate(III) ion. Gas tight syringes were used for making up reaction solutions as well as for injecting the required volumes of solution in to the reaction optical cell. Gas tight syringes (Hamilton Syringes Series 1000) of various sizes with detachable needles (Hamilton Stainless Steel with Kel-7-Hub, type Kf-720, and K-722) were used for making up solutions.

The pH of solutions was measured by using Radiometer PHM 26 pH meter, provided with glass (G202B) and calomel (BE 1) electrodes. The pH meter was standardized against potassium hydrogen phthalate (0.050M) to which a pH value of 4.0 was assigned. Carbonate- bicarbonate buffers were used for maintaining the pH of solutions.

Preparation of halogen, chloramine, and hexacyanoferrate(II) solutions

Halogen solutions were prepared by dissolving gaseous chlorine in distilled water. This halogen

stock solution, $5 \times 10^{-2} \text{M}$, was prepared, standardized by iodometry [17] and stored in dark. The solution of initial halogen, Cl_2 , was prepared by diluting the former to $5 \times 10^{-4} \text{M}$. The chloramine solution were obtained at fixed temperature in buffered medium, by mixing together solutions of initial halogen and ammonium sulphate with $1 \times 10^{-4} < \text{NH}_4^+ < 5 \times 10^{-2} \text{M}$.

All potassium hexacyanoferrate(II) solutions were prepared fresh every day. Potassium ions were replaced by adding known concentrations of sodium perchlorate (also used for adjusting the ionic strength). The solution was then filtered through sintered crucible, washed with distilled water, and found free from potassium perchlorate, and then the volume was made up to the mark.

A fresh solution of hexacyanoferrate(II) was made (every day) for each set of experiments and was protected from light. Stock solutions were diluted with distilled water.

The buffer used in the experiments were bicarbonate/carbonate and stock solution of buffer (0.50M) Na_2CO_3 , and NaHCO_3 (0.05M) were prepared by weight ($\text{pK}_a = 9.59$ at ionic strength 1.0M NaClO_4).

Experiments to determine the stoichiometry of reaction were carried out in the optical cell which was previously flushed with nitrogen, the hexacyanoferrate(II) solution was added in the optical cell in the last to avoid the possibility of air oxidation. The possibility of formation of hexacyanoferrate(III) by air oxidation was minimized by transferring stock solutions by syringes which minimize the contact with air, following a routine described previously [17]. Readings of optical density at 420 nm were obtained in the optical cell placed in the thermostatically controlled cell compartment of spectrophotometer.

Stoichiometric measurements

The stoichiometry of the reaction was determined by spectrophotometric methods. Solutions were injected by syringes into a septum-capped 1.0 or 2.0 cm optical cell which was previously nitrogen-purged. Spectral scans were taken of the same solutions at different intervals of time to determine when the reaction was complete. Concentration

changes were determined by monitoring the hexacyanoferrate(III) absorbance at 420 nm.

Kinetic measurements

The kinetics of reduction of chloramine with hexacyanoferrate(II) were determined by Shimadzu 120-02 UV-visible spectrophotometer.

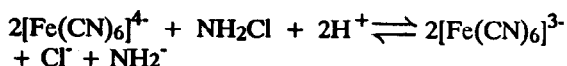
Pseudo first-order conditions were maintained by the use of at least a 10-fold excess of one of the reactants [11] in the reaction mixture. Rate constants were determined from a least square programme. Plot of $\log(A_\infty - A_t)$ vs time, where A_∞ represents the absorbance at infinite time, and A_t is the absorbance at time, t , were linear to 75% of the total reactions. Reaction was studied over a period of 4 half lives of the reaction. All the reaction solutions were studied at $25.0 \pm 0.10^\circ\text{C}$.

Results and Discussion

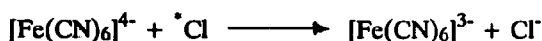
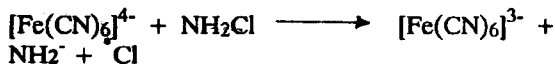
The results obtained show that for the reaction of NH_2Cl with $\text{K}_4\text{Fe}(\text{CN})_6$, plots of $\log(A - A_t)$ against time are linear up to 75% of the reaction with hexacyanoferrate(II) ion present in large excess; e.g. $0.010 \text{ mol dm}^{-3} [\text{Fe}(\text{CN})_6]^{4-}$, and $[\text{NH}_2\text{Cl}]$ at $0.0002 \text{ mol dm}^{-3}$ at pH 8.5-9.5 and 25.0°C . The reaction between hexacyanoferrate(II) and chloramine was studied at limited pH values, since the nature and quantity of chloramine formed is affected by pH. Monochloramine, NH_2Cl , and NCl_3 , are present in the acidic conditions (below pH 6). It was found that the reaction was too rapid at pH 5, and too slow at pH 11 to monitor by using convenient UV-visible spectrophotometers.

A series of experiments was performed in which the initial concentration of chloramine, hexacyanoferrate(II), and hexacyanoferrate(III), were thus changed at pH 9.25 to establish the required stoichiometry. The stoichiometry of the reaction under the condition of the experiment with $2.20 \times 10^{-3} \text{M} [\text{Fe}(\text{CN})_6]^{4-}$, and $3.1 \times 10^{-4} \text{M}$, $[\text{NH}_2\text{Cl}]$ and $\Delta[\text{Fe}(\text{CN})_6]^{4-} / \Delta[\text{NH}_2\text{Cl}]$ was found to be 1.98 ± 0.10 at pH 9.25 and 25.0°C .

The stoichiometry may be described by the equation,



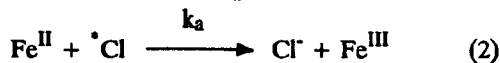
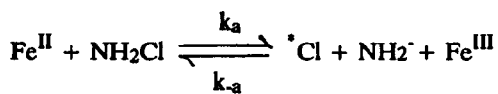
and one might expect the reaction to involve the principal stages:



Reaction in excess of chloramine in concentration

Under the condition where the concentration of chloramine was in large excess (pseudo first-order) over hexacyanoferrate(II) the plots of $\log(A - A_t)$ vs time, were linear to 80% of the total reaction. The rate value, k_{obs} , of $2.89 - 0.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were obtained under the conditions of the experiment. Results obtained are listed in Table 1. The results obtained can be expressed by equation (1), where $k_{\text{obs}} = 2k_a [\text{NH}_2\text{Cl}]$. $[\text{Fe}^{II}]_t$ and $[\text{Fe}^{III}]_t$ 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).

$$-d/dt[\text{Fe}^{II}]_t = k_{\text{obs}} [\text{Fe}^{II}]_t \quad (1)$$



Reaction in excess of hexacyanoferrate(II) concentration

Reaction was performed under the condition where the concentration of hexacyanoferrate(II) was in large excess over the concentration of chloramine and the plots of $\log(A - A_t)$ vs time, t , were linear to about 50% of the reaction and curved kinetic plots were observed for the later part of the reaction. Several reaction mechanisms were designed and used to explain the experimental results, equation (2). In accordance with this mechanism, the rate of reaction can be described as in equation (4), where $k^{\circ} = 2K_a k_b$, and $k^{\cdot} = K_a[\text{NH}_2^{\cdot}]$. In the reaction medium, $[\text{Fe}^{II}]_t = [\text{Fe}^{II}]_o + [\text{Fe}^{III}]_o - [\text{Fe}^{III}]_t$. Therefore, from equation (3) the rate law, is found. The integrated form of the rate law equation is given by equation (4).

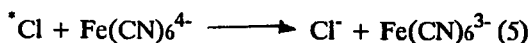
$$d[\text{Fe}^{II}]_t/dt = \frac{-k^{\circ}[\text{Fe}^{II}]_t^2 + [\text{NH}_2\text{Cl}]}{k_b[\text{Fe}^{II}]_t + k^{\cdot}[\text{Fe}^{III}]_t} \quad (3)$$

$$\ln([\text{Fe}^{II}]_o + [\text{Fe}^{III}]_o - [\text{Fe}^{III}]_t) - \frac{K^{\circ}[\text{Fe}^{II}]_o + [\text{Fe}^{III}]_o}{(k_b - k^{\cdot})} \frac{1}{[\text{Fe}^{II}]_o + [\text{Fe}^{III}]_o - [\text{Fe}^{III}]_t} = \left(\frac{k^{\circ}}{k_b - k^{\cdot}} \right) [\text{NH}_2\text{Cl}]_t + \text{constant} \quad (4)$$

Table 1: Reaction of $\text{Fe}[\text{CN}_6]^{4-}$ with a large excess of NH_2Cl , 25.0°C , $\text{pH } 9.25 \pm 0.05$, $I = 1.00 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{Fe}^{II}] = 2.1 \times 10^{-3} \text{ mol/dm}^3$, $\text{Na}_2\text{CO}_3 = 0.10$, $\text{NaHCO}_3 = 0.12 \text{ mol dm}^{-3}$

$10^2 [\text{NH}_2\text{Cl}]_o / \text{mol} \cdot \text{dm}^{-3}$	$10^4 [\text{Fe}^{III}]_o / \text{mol} \cdot \text{dm}^{-3}$	$10^3 k_{\text{obs}} / \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
0.11	0.13	0.21
0.11	0.26	0.22
1.30	0	0.21
1.56	0	0.49
1.82	0	62
1.93	0	82
2.05		90
2.20	0	0.06
1.84	2.70	1.70
1.84	5.40	1.52

It is evident from the rate law equation that a plot of $\ln(A - A_t)$ vs time (t) is curved. Results are given in Table 2, it can be seen that under the conditions of experiment retardation effect (k_{-a}/k_b) for the reaction between the chloramine and hexacyanoferrate(II) increases with decrease in the initial concentration of $[\text{Fe}(\text{CN})_6]^{4-}$, and then is negligible effect of concentration of $[\text{Fe}(\text{CN})_6]^{3-}$ on the values of k_{-a}/k_b and from the results it is evident that only the ratio k_{-a}/k_b can only be obtained experimentally. However, it is clear that k_b (and hence $k_{-a} [\text{NH}_2^{\cdot}]$ is very large than k_a . The latter relates to the reaction of a stable molecule NH_2Cl with $[\text{Fe}(\text{CN})_6]^{4-}$ where as k_b refers to the reaction of a reactive intermediate, Cl^{\cdot} with $[\text{Fe}(\text{CN})_6]^{4-}$. Reaction (5) must have a very negative change in free energy.



The E° value for ${}^{\bullet}\text{Cl} + e \longrightarrow \text{Cl}^-$ would be expected to be ca. 1 V larger than that for $1/2 \text{Cl}_2 + e \rightleftharpoons \text{Cl}$ which has $E^{\circ} = -1.36\text{V}$ and involves that half-bond strength of Cl-Cl [18-19], also, $[\text{Fe}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$ has $E^{\circ} = 0.37-0.40\text{V}$ [18-19] so a rapid reaction is expected, especially as no covalent bonds are broken. Hence comparison with reaction (2) suggests that a free radical reaction will be much faster.

Table 2: Kinetic retardation effect observed for the reaction of NH_2Cl with $[\text{Fe}(\text{CN})_6]^{4-}$ = 25.0 °C, pH 9.25 ± 0.05; $I = 1.00$ (NaClO_4) mol dm^{-3} , $[\text{NH}_2\text{Cl}]_0 = 2.0 \times 10^{-3}$, $\text{Na}_2\text{CO}_3 = 0.10$, $\text{NaHCO}_3 = 0.12$ mol dm^{-3}

$10^3[\text{Fe}^{II}]_0$ mol dm^{-3}	$10^3[\text{Fe}^{III}]_0$ mol dm^{-3}	k_a/k_b	$k_a/\text{dm}^3 \text{md}^{-1} \text{S}^{-1}$
0.27	0	0	0.22
0.36	0	0	048
1.10	0	47.5	1.02
1.35	0	47.02	1.05
2.00 ^a	0	46.90	1.12
2.20	0	46.90	1.22
2.70	0.51	46.10	1.30
2.70	1.05	46.05	1.32
2.70	0.25	46.05	1.30
2.70 ^b	0	46.05	1.30
2.70 ^c	0	45.09	6.81
1.35 ^c	0	41.00	10.92
2.04 ^c	0	40.00	12.50
2.71 ^c	0.50	38.00	13.50
2.70 ^c	1.02	38.00	13.20

^a $I = 1.00$ mol dm^{-3} (NaCl)^b, $\text{Na}_2\text{CO}_3 = 0.100$ $\text{NaHCO}_3 = 0.12$ mol dm^{-3} , ^cpH = 7.80 ± 0.15; $\text{Na}_2\text{CO}_3 = 0.005$, $\text{NaHCO}_3 = 0.10$ mol. dm^{-3}

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