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Kinetics and Mechanism of Oxidation of Hexacyanoferrate(II) by Periodate in Acidic Solutions. Evidence for Copper Catalysis

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The kinetics of oxidation of $Fe(CN)_6^{4-}$ *by periodate in acetate buffers follow the rate law (i):*

$$d[Fe(CN)_6^{3-}]/dt = k_{obs}[Fe(CN)_6^{4-}] \qquad (i)$$

in large excess of periodate concentrations, where $k_{obs} = 0.20 + 2.60 \times 10^{-3}/[\text{Periodate}]$. *Copper(II) but not Fe(II) ions catalyse the reaction. The inhibiting effect of periodate is believed to be due to the formation of a Cu(III)–periodate complex which is less reactive than a periodate free Cu(III) species. The rate of the reaction is greatly lowered by EDTA and in its presence the kinetics obey the rate law (ii):*

$$d[Fe(CN)_6^{3-}]/2dt = (a + b[Na^+] + k_3[H^+])[Fe(CN)_6^{4-}][\text{Periodate}] \qquad (ii)$$

where $a = 0.22$ M^{-1} *sec*$^{-1}$, $b = 0.66$ M^{-2} *sec*$^{-1}$ *and* $k_3 = 5.5 \times 10^4$ M^{-2} *sec*$^{-1}$ *at 25 °C. Mechanisms consistent with kinetics in absence and in presence of EDTA have been proposed.*

Introduction

The oxidation of hexacyanoferrate(II) by periodate has previously been investigated in weakly alkaline and neutral phosphate buffer solutions, and the kinetics were observed to be simple [1]. This study was carried out with the intention of extending the pH range down to about pH ≃4, in an attempt to get a better understanding of the hydrogen dependence of the reaction rate.

As will be seen later in this study, the kinetics of the hexacyanoferrate(II)–periodate reaction in acetate buffers are not as simple as observed previously. It was surprising that the rate of the reaction was not only independent of periodate, but also inhibited by its increasing concentrations. This observation has drawn our attention to the possibility of catalysis by trace amounts of metal ions originating in the reagents and in the solvent. In particular, attention has been drawn before to catalysis by copper ions present in less than 1 ppm [2, 3].

Experimental

Reagents

Sodium periodate, copper nitrate, disodium ethylenediaminetetra-acetate and glacial acetic acid were all reagent grade (BDH AnalaR). Potassium hexacyanoferrate(II) was recrystallised from distilled water and dried. Sodium acetate and ferrous ammonium sulphate were used as supplied (BDH G.P.R.). Sodium periodate stock solutions were prepared by weighing and were covered with Al foil and kept in the dark [4]. A copper nitrate stock solution, from which all dilute solutions were made up, was standardised iodometrically [5]. Buffer solutions were made up from sodium acetate and acetic acid solutions of known concentrations. Sodium perchlorate was used to keep the ionic strength constant in the different buffers used. Double distilled water was used. Hexacyanoferrate(II) and iron(II) solutions were used immediately after they were prepared.

Procedure for Kinetic Experiments

A Durrum–Gibson stopped-flow spectrophotometer was used to follow the rate of the reaction. The formation of the product $Fe(CN)_6^{3-}$ was monitored at 420 nm where all other species have negligible absorbance. The hexacyanoferrate(II) and periodate solutions, in the required buffers, were allowed 15–20 min in the drive syringes for thermostating before the reaction was initiated. The traces were photographed using a Polaroid camera. The pH of the reaction solution was measured using a Radiometer digital pH-meter model PHM62.

The metal ions Cu(II) and Fe(II) at the required concentration were added to periodate solutions when catalysis by these ions was investigated. EDTA solutions were added to both reactants.

The reaction was carried out under pseudo first-order conditions with the periodate concentration always in large excess over that of hexacyanoferrate (II). Under these conditions, complications by the product IO_3^- were avoided, since the oxidation of hexacyanoferrate(II) by iodate is much slower than its oxidation by periodate [6].

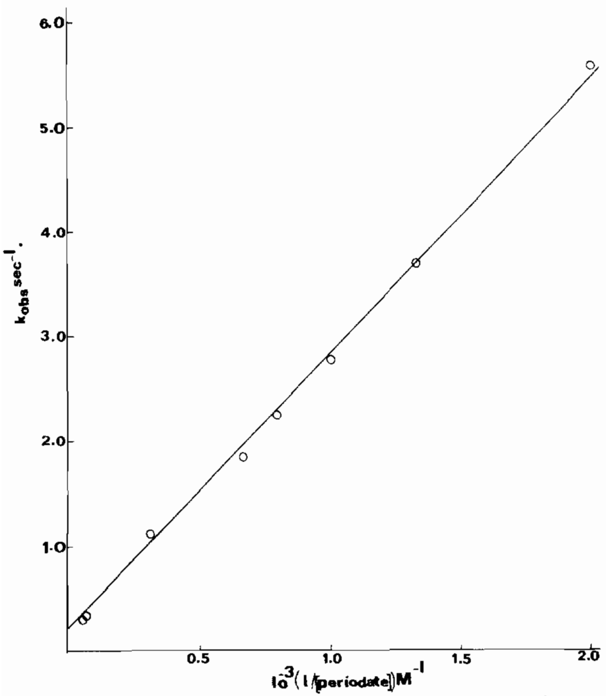

Fig. 1. Plot of k_{obs} against 1/[Periodate]. [$Fe(CN)_6^{4-}$] = 10^{-4} *M*, pH = 4.14, temp. 25 °C, I = 0.05 *M*.

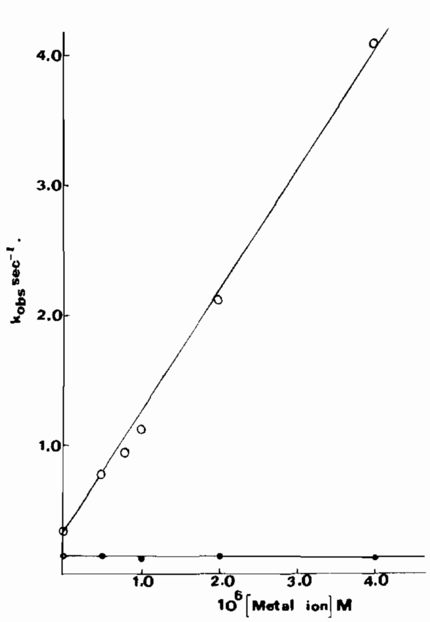

Fig. 2. Variation of k_{obs} with: (○) [Cu(II)] and (●) [Fe(II)]; [$Fe(CN)_6^{4-}$] = 10^{-4} *M*, [Periodate] = 9.0 × 10^{-3} *M*, pH = 4.07, I = 0.05 *M*, temp. = 25 °C. The non-correspondence of Cu(II) and Fe(II) intercepts is because different acetate stocks were used.

Results

Kinetics Without Addition of EDTA

The kinetics of the hexacyanoferrate(II)–periodate reaction were investigated at pH 4.14, temperature 25 °C and ionic strength 0.05 *M*. The $Fe(CN)_6^{4-}$ was maintained at 10^{-4} *M* and periodate concentration was varied over the range 0.0005–0.0175 *M*. Plots of $\log(A_\infty - A_t)$ *vs.* time, where A_∞ and A_t represent absorbances at infinity and time t respectively, were linear up to at least 80% of reaction. The value of the pseudo first-order rate constant, k_{obs}, was obtained from (gradient X 2.303). It was surprising that the magnitude of k_{obs} decreased with increasing concentration of periodate, the oxidant. The results are summarised in Fig. 1 where a plot of k_{obs} against 1/[Periodate] is linear with a positive gradient and in agreement with eqn. 1:

$$k_{obs} = 0.20 + \frac{2.60 \times 10^{-3}}{[\text{Periodate}]} \qquad (1)$$

The values 0.20 sec^{-1} and 2.60 X 10^{-3} *M* sec were obtained from the intercept and the gradient of Fig. 1 respectively.

It was also observed that the value of k_{obs} is not reproducible when the sources of the reagents, particularly the acetate buffer, were changed. These observations have led us to believe that trace amounts of metal ions are probably taking part in the oxidation process. Wilson and co-workers [2] demonstrated that oxidation of cysteine by hexacyanoferrate(II) is catalysed by Cu(II). The two metal ions likely to catalyse the hexacyanoferrate(II)–periodate reaction are Cu(II) and Fe(II). The effect of these two ions was therefore investigated.

At constant periodate and hexacyanoferrate(II) concentration, pH 4.07, I 0.05 *M* and temperature 25 °C, the effect of added Cu(II) on the reaction rate was investigated over the range 5.0–40.0 X 10^{-7} *M*. The results shown in Fig. 2 clearly indicate that the rate of the reaction is catalysed by Cu(II) ions, and that the dependence of k_{obs} on added [Cu(II)] is in agreement with eqn. 2:

$$k_{obs} = k_0 + k_c[\text{Cu(II)}] \qquad (2)$$

where k_0 and kc correspond to the intercept and gradient of Fig. 2 and have values of 0.32 sec^{-1} and 9.45 X 10^5 M^{-1} sec^{-1} respectively at the reported conditions. It is to be noted that the magnitudes of k_0 and k_c are composite values and are functions of periodate as shown by eqn. 1. It is also to be observed that the intercept of Fig. 2 coincides with the value of k_{obs} when added [Cu(II)] = 0. Fig. 2 also shows that k_{obs} is not markedly influenced by increasing Fe(II) in the range 0.5–4.0 X 10^{-6} *M*. This warrants the conclusion that Fe(III) is not a catalyst, as Fe(II) is rapidly oxidised by periodate to Fe(III) [7]. It is, however, worth mentioning that under these conditions ([$Fe(CN)_6^{4-}$] ≫ [Cu(II)] and [Fe(II)])$Fe(CN)_6^{4-}$ would not be precipitated as $Fe_2Fe(CN)_6$ or as $Cu_2Fe(CN)_6$ which are known to be insoluble in aqueous solutions.

TABLE I. Effect of EDTA on Reaction Rate.[a]

10^6[EDTA]	k_{obs}, sec^{-1}
0.00	2.79
0.025	1.46
0.050	1.44
1.00	1.24
2.00	0.014
6.00	0.013
10.00	0.014
100.00	0.014

[a] $[Fe(CN)_6^{4-}] = 10^{-4}$ *M*, [Periodate] = 10^{-3} *M*, temp. = 25 °C, I = 0.05 *M*, pH = 4.14 (acetate buffer).

Ethylenediaminetetra-acetate ion (EDTA) has often been used to retard metal-catalysed paths in some reactions. The effect of this species on the reaction rate is shown in Table I. It is evident that k_{obs} decreases gradually with increasing concentration of EDTA, but becomes independent of it at [EDTA] $\geqslant 2.0 \times 10^{-6}$ *M*. It is interesting to note that this is nearly the same concentration of EDTA required to inhibit the metal-ion catalytic path in the cysteine oxidation by hexacyanoferrate(III) [3]. It should also be noted that the complete masking of the metal ion(s) retards k_{obs} by about two hundred-fold.

Kinetics in Presence of EDTA

The kinetics of hexacyanoferrate(II)–periodate reaction were investigated in presence of [EDTA] = 10^{-4} *M* to ensure complete removal of metal ion impurities from the reaction site (see Table I). The results in Table II display simple kinetics with first-order dependence on each reactant, confirming our previous results. The rate law is described by eqn. 3:

$$\frac{d[Fe(CN)_6^{4-}]}{2dt} = k_2[Fe(CN)_6^{4-}][\text{Periodate}] \qquad (3)$$

where $k_2 = k_{obs}/2[\text{Periodate}]$, the integer 2 being used because $-d[Fe(CN)_6^{4-}]/dt = -2d[\text{Periodate}]/dt$. Table II also displays the dependence of k_2 on $[H^+]$, where k_2 is shown to increase with decreasing pH.

The dependence of k_2 on $[H^+]$ was investigated over the pH range 4.3–5.5 at various ionic strengths (0.05–0.50 *M*). Fig. 3 shows that k_2 varies with $[H^+]$ according to eqn. 4:

$$k_2 = k_2' + k_3[H^+] \qquad (4)$$

where k_2' and k_3 correspond to the intercept and gradient of Fig. 3. Similar relations were obtained for the dependence of k_2 on $[H^+]$ at all ionic strengths used. Table III contains the values of k_2' and k_3 at the various ionic strengths used. The results show that k_2' increases with increasing ionic strength whereas k_3 shows no significant dependence. The values of k_2' obtained at different ionic strengths when plotted against the $[Na^+]$ (see Table III) fit eqn. 5:

$$k_2' = a + b[Na^+] \qquad (5)$$

where a = 0.22 M^{-1} sec^{-1} and b = 0.66 M^{-2} sec^{-1}. From eqns. 3–5, the kinetics of oxidation of hexacyanoferrate(II) by periodate in presence of EDTA are described by the rate law 6:

TABLE II. Kinetic Data in Presence of EDTA.[a]

10^3[Periodate] *M*	pH = 4.14		pH = 4.47		pH = 4.81	
	10^2k_{obs} sec^{-1}	k_2[d] $M^{-1}sec^{-1}$	10^2k_{obs} sec^{-1}	k_2[d] $M^{-1}sec^{-1}$	10^2k_{obs} sec^{-1}	k_2[d] $M^{-1}sec^{-1}$
2.0	2.52	6.30	1.04	2.60		
2.5	2.76	5.52				
4.0	4.42	5.53				
6.0	6.24	5.20	2.68	2.23	1.40	1.17
8.0	8.28	5.20				
9.0	9.74	5.40				
10.0	10.44	5.20	4.58	2.29	2.70	1.35
11.0	11.50	5.25	4.58	2.29	2.70	1.35
11.0	11.50	5.25				
14.0			6.20	2.21	3.27	1.17
15.0	15.77	5.25				
18.0			7.59	2.11		
20.0[b]	19.70	4.98			4.45	1.11
20.0[c]	19.40	4.85				

[a] $[Fe(CN)_6^{4-}] = 10^{-4}$ *M*, temp. 25 °C, I = 0.05 *M*, [EDTA] = 10^{-4} *M*. [b] $[Fe(CN)_6^{4-}] = 7 \times 10^{-5}$ *M*. [c] $[Fe(CN)_6^{4-}] = 5 \times 10^{-5}$ *M*. Acetate buffers used throughout. [d] $k_2 = k_{obs}/2[\text{Periodate}]$.

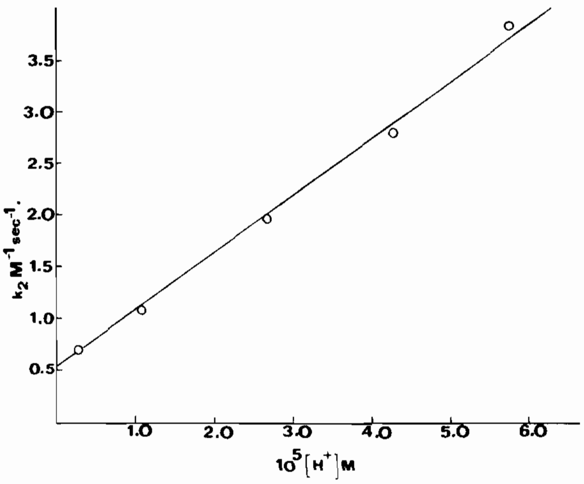

Fig. 3. Dependence of k_2 on $[H^+]$. $[Fe(CN)_6^{4-}] = 10^{-4}$ *M*, [Periodate] = 9.0×10^{-3} *M*, I = 0.50 *M*, temp. 25 °C, [EDTA] = 10^{-4} *M*.

TABLE III. Effect of Ionic Strength on k_2 and k_3.

Ionic Strength *M*	k_2^0 M^{-1}sec^{-1}	10^{-4} k_3 M^{-2}sec^{-1}
0.05	0.25	6.00
0.10	0.30	5.55
0.30	0.40	5.00
0.50	0.55	5.50

$[Fe(CN)_6^{4-}] = 10^{-4}$ *M*, [Periodate] = 9.0×10^{-3} *M*, temp. 25 °C.

$$\frac{d[Fe(CN)_6^{4-}]}{2dt} =$$

$$(a + b[Na^+] + k_3[H^+])[Fe(CN)_6^{4-}]\,[\text{Periodate}] \quad (6)$$

The average value of k_3 being 5.5×10^4 M^{-2} sec^{-1} at 25 °C.

Discussion

In this study catalysis by Cu(II) ions in periodate oxidations is reported for the first time. Catalysis by Cu(II) ions in a number of reactions is well established and is seen to result either from the reduction of Cu(II) to Cu(I) or *via* the involvement of Cu(III) [2, 9]. Wilson and co-workers have proposed that both Cu(II) and Cu(III) act as oxidising agents in the copper-catalysed oxidation of cysteine and related thiols by hexacyanoferrate(III) [2]. Tervalent copper has also been proposed to be formed as an intermediate in the copper-catalysed oxidation of both oxalate and diethylamine by peroxydisulphate [10, 11].

The existence of copper in the tervalent state has been reported in fluoro [12], periodato [13] and tellurato [14] complexes. Diperiodatocuprate(III) is well known and is stable in alkaline solutions to be used as an oxidising agent [15]. Oxidation of Cu(II) to Cu(III) is seen to be facilitated by a co-ordinating ligand which decreases the oxidation potential of Cu(III) to allow its formation by relatively mild oxidants [8]. Thus complexation of Cu(II) by oxalate [10] and thiols [2] precedes its oxidation to Cu(III). Periodate is a relatively strong oxidising agent, certainly stronger than hexacyanoferrate(III) and not much weaker than peroxydisulphate, to warrant oxidation of Cu(II) to Cu(III) in acetate media which are known to co-ordinate to Cu(II).

The mechanism which we propose for the oxidation of hexacyanoferrate(II) by periodate in absence of EDTA is shown in eqns. 7–11, where L^- stands for periodate ($H_4IO_6^-$ and/or IO_4^-) and $L^\bullet$ for the free radical (I(VI)):

$$Cu(II) + L^- \xrightarrow{\text{fast}} Cu(III) + L^\bullet \quad (7)$$

$$Cu(II) + L^\bullet \xrightarrow{\text{fast}} Cu(III) + IO_3^- \quad (8)$$

$$Cu(III) + L^- \rightleftharpoons Cu(III)L) \qquad K_2 \quad (9)$$

$$Fe(CN)_6^{4-} + Cu(III) \xrightarrow{k_{10}} Fe(CN)_6^{3-} + Cu(II) \quad (10)$$

$$Fe(CN)_6^{4-} + Cu(III)L) \xrightarrow{k_{11}} Fe(CN)_6^{3-} + Cu(II) + L^- \quad (11)$$

The rate law compatible with the above mechanism is given by eqn. 12:

$$d[Fe(CN)_6^{3-}]/dt =$$

$$\frac{(k_{11}K_2[L^-] + k_{10})}{(1 + K_2[L^-])}[Cu(III)]_T\,[Fe(CN)_6^{4-}]_T \quad (12)$$

$[Cu(III)]_T$ and $[Fe(CN)_6^{4-}]_T$ and $[L^-]$ are taken to be equal to the total concentrations of these species. Cu(II), Cu(III) and Cu(III)L may contain acetate ligands.

Since the kinetics showed first-order dependence on hexacyanoferrate(II) concentration, then

$$k_{obs} = \frac{(k_{11}K_2[L^-] + k_{10})}{(1 + K_2[L^-])}[Cu(III)]_T \quad (13)$$

Eqn. 13 would take the form of eqn. 1 if $K_2[L^-] \gg 1$, whereby eqn. 14 is obtained:

$$k_{obs} = k_{11}[Cu(III)]_T + \frac{k_{10}[Cu(III)]_T}{K_2[L^-]} \quad (14)$$

By comparing eqns. 1 and 14, we can see that $k_{11}[Cu(III)]_T = 0.20$ sec^{-1} and $k_{10}[Cu(III)]_T/K_2 = 2.60 \times 10^{-3}$ *M*sec^{-1}.

The rate constant obtained for the copper-catalysed path, k_c, may be approximately taken to represent $k_{10}/K_2[L^-]$, and substituting for $[L^-] = 9.0 \times 10^{-3}$ *M* and $k_c = 9.45 \times 10^5$ M^{-1} sec^{-1}, k_{10}/K_2 is obtained as 8.5×10^3 sec^{-1}. From this value,

$[Cu(III)]_T$ is calculated as 4.0×10^{-7} *M*, where this represents the copper concentration present as an impurity for conditions shown in Fig. 1. This seems to be a reasonable value for the copper impurity and agrees fairly well with the [EDTA] required to inhibit catalysis (see Table I). By using the copper impurity as 4.0×10^{-7} *M*, k_{11} is calculated as 5.0×10^5 M^{-1} sec^{-1} at 25 °C. The magnitude of K_2 is not known but can be estimated. The fact that $K_2[L^-] \gg 1$ holds even at $[L^-] = 5.0 \times 10^{-4}$ *M* indicates that $K_2 > 10^4$ M^{-1}, and therefore $k_{10} > 8.5 \times 10^7 M^{-1}$ sec^{-1} at 25 °C. This value is comparable to the second-order rate constants reported for the oxidation of NO_2^- and Br^- by aqueous Cu(III) [16]. Tervalent copper is believed to be an efficient oxidant only for reductants which are ligands complexed within its inner co-ordination sphere [16]. Hexacyanoferrate(II) is suitable for such a mechanism since it can co-ordinate to Cu(III) *via* its cyano-nitrogens. The reduction of the rate with increasing periodate concentration is in keeping with an inner-sphere mechanism since the latter ion forms a stable complex with Cu(III). An inverse first-order in periodate was observed in the reduction of diperiodatocuprate(III) by some alcohols [15], where the loss of a periodate ligand is a pre-requisite for oxidation.

A mechanism in presence of EDTA that fits the rate law is shown by eqn. 15–20:

$$Fe(CN)_6^{4-} + H^+ \rightleftharpoons HFe(CN)_6^{3-} \quad K_3 \qquad (15)$$

$$L^- + H^+ \rightleftharpoons LH \quad K_4 \qquad (16)$$

$$Fe(CN)_6^{4-} + L^- \xrightarrow{k_{17}} \qquad (17)$$

$$HFe(CN)_6^{3-} + L^- \xrightarrow{k_{18}} \qquad (18)$$

$$Fe(CN)_6^{4-} + HL \xrightarrow{k_{19}} \qquad (19)$$

$$HFe(CN)_6^{3-} + HL \xrightarrow{k_{20}} \qquad (20)$$

and the rate law is given by eqn. 21:

$$\frac{d[Fe(CN)_6^{3-}]}{2dt} = \frac{(k_{17} + (k_{18}K_3 + k_{19}K_3)[H^+] + k_{20}K_2K_4[H^+]^2)}{(1 + K_3[H^+])(1 + K_4[H^+])} \times [Fe(CN)_6^{4-}]_T[L^-]_T \qquad (21)$$

The dependence of k_2 on $[H^+]$ would be represented by eqn. 22:

$$k_2 = \frac{k_{17} + (k_{18}K_3 + k_{19}K_4)[H^+] + k_{20}K_3K_4[H^+]^2}{(1 + K_3[H^+])(1 + K_4[H^+])} \qquad (22)$$

The thermodynamic formation constants K_3 and K_4 are reported [17, 18] to be as 4×10^4 and 2×10^2 M^{-1} respectively at 25 °C. The magnitude of K_3 in the ionic strength range investigated (0.05–0.50 *M*) falls in the range $(2.0–0.5 \times 10^3)$ M^{-1}. These values indicate that $K_3[H^+]$ and $K_4[H^+]$ in the denominator are negligible compared to unity in the $[H^+]$ range investigated. The term in $[H^+]^2$ could also be dropped since only first dependence in $[H^+]$ was observed, and we obtain

$$k_2 = k_{17} + (k_{18}K_3 + k_{19}K_4)[H^+] \qquad (23)$$

which is identical to the experimental dependence of k_2 on $[H^+]$. The insensitivity of the proton assisted rate constant (k_3 in Table III) to ionic strength strongly suggests that reaction 19 is much faster than reaction 18, and HL is an uncharged periodate species (most probably H_5IO_6). The dependence of k_2 on $[Na^+]$ indicates that two paths are operative, where $Fe(CN)_6^{4-}$ and $NaFe(CN)_6^{3-}$ are reactive species.

The observation that a path independent of $[H^+]$ operates in the pH range 4.3–5.5 is in agreement with our previous suggestion [1] that the equilibrium

$$H_3IO_6^{2-} + H^+ \rightleftharpoons H_4IO_6 \qquad (23)$$

is the cause of the first-order dependence on $[H^+]$ observed in neutral and weakly alkaline media. A consideration of the formation constant of eqn. 23 reveals that the equilibrium lies virtually completely to the right in this pH range [18].

From eqn. 5 k_2' is calculated as 0.637 M^{-1} sec^{-1} for $[Na^+]$ = 0.633 *M* (I = 0.633 *M*; NaH_2PO_4/NaOH buffer was used in our previous study). Using this value for k_2' and 4.4×10^6 M^{-2} sec^{-1} for the acid dependent path observed in neutral and weakly alkaline media, the equilibrium constant for eqn. 23 is calculated as 3.5×10^6 M^{-1} which fairly agrees with literature values [18].

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