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Oxidation of Hexaaquoiron(II) by Periodate in Aqueous Acidic Solution

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The oxidation of Fe(II) by periodate in aqueous acidic solutions obeys the rate law (i)

$$Rate = \{k_0 + k_1/[H^+]\}\,[Fe(II)]^2 + \frac{k_2''[Fe(II)]\,[L^-]_T}{[H^+]} + k_3[Fe(II)]^2[L^-]_T \qquad (i)$$

where $[L^6]_T$ represents the total periodate concentration. The magnitudes of k_0, k_1', k_2'' and k_3 are 0.235 sec^{-1}, 120 sec^{-1}, 7.5 ± 1.5 sec^{-1}, and (7.3 ± 0.5) × $10^4 M^{-2}$ sec^{-1} respectively at 25 °C and I = 1.0 M. The terms in equation (i), that are first order in $[L^-]_T$, correspond to the oxidation process with possibly one-electron (term showing first order in [Fe(II)] and two electron-transfer (term showing second order in [Fe(II)]. At low $[H^+]$ (0.10 M), the pathway first order in [Fe(II)] predominates, whereas at high $[H^+]$ (0.80 M), the term second order in [Fe(II)] prevails. An explanation of the term independent of $[L^-]_T$ is not quite obvious.

Introduction

It was reported by Symons [1] that the oxidation of Fe(II) by periodate proceeds *via* one electron-transfer steps. The polymerisation of added acrylonitrile was taken as an evidence for the formation of free radicals (I(VI)) that would result from one electron-transfer. This reaction is studied with the aim of comparing the rates of oxidation of Fe(II) and V(IV) in order to assign an inner- or an outer-sphere mechanism for the latter metal ion based on Rosseinsky's approach [2]. The results on the V(IV)–periodate reaction has been reported [3].

Periodate is a two-electron oxidant (I(VII) → I(V)) and, therefore, a concurrent two electron-transfer is not ruled out. The two electrons could be abstracted either from one Fe(II), with the formation of unstable Fe(IV), as reported with some two-equivalent oxidants [4], or from two Fe(II). The latter alternative would manifest itself by showing a second order dependence on the reductant concentration.

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Experimental

A stock solution of perchloric acid was prepared by dilution from concentrated (BDH Analar) $HClO_4$ and standardised. Sodium perchlorate solution was standardized by feeding on a cation-exchange column (Amberlite IR 120(H)) and titrating against a standard sodium hydroxide solution. Iron(II) perchlorate solutions were prepared by dissolving fine iron powder (Reidel-DeHäen AG) in ~1*M* perchloric acid and gently heating to increase the dissolution rate. The solution was filtered and standardized against a standard permanganate solution [5]. Fresh solutions of iron(II) were always prepared, deaerated by flushing with purified nitrogen gas and kept at low temperature. The concentration of the total acid was determined by sodium hydroxide titration after passing through the cation-exchange column. The free acid concentration was obtained by subtracting twice the iron(II) concentration from that of the total. A stock solution of periodate was prepared by weight from $NaIO_4$ (BDH Analar). All periodate solutions were wrapped with Al foil to avoid photochemical decomposition [1]. Deionised doubly-distilled water was used in preparing all solutions.

Pseudo first order conditions were maintained in all kinetic runs with periodate concentrations being in large excess over that of iron(II). In this way any possible complications arising from the Fe(II)–iodate reaction, which has a complex rate law [6], were minimized. The ionic strength was maintained at 1.0 *M* by addition of $NaClO_4$. The $[H^+]$ was varied over the range 0.10–0.40 *M*. Periodate and iron(II) concentrations were varied over the ranges (0.125–2.50) × 10^{-2} *M* and (1.25–5.0) × 10^{-4} *M*, respectively.

The rate of the reaction was followed at 340 nm on a Durrum–Gibson stopped-flow spectrophotometer. At this wavelength an appreciable change in absorbance was observed. We were forced to follow the reaction at this wavelength because periodate

TABLE I. Kinetic Data.

$[H^+]$, M	10^4 [Fe(II)], M	10^2 $[L^-]_T$, M	k_{obs}, sec^{-1}
0.10	5.0	0.25	1.06
		0.50	1.32
		0.75	1.64
		1.00	1.72
		1.50	2.61
		2.00	3.47
		2.50	3.94
	2.5	0.125	0.69
		0.50	1.11
		0.75	1.37
		1.00	1.55
	1.25	0.125	0.43
		0.25	0.59
		0.50	0.82
		0.75	1.09
		1.00	1.31
0.20	5.0	0.25	0.71
		0.50	0.94
		0.75	1.07
		1.00	1.37
		1.50	1.71
		2.00	2.07
		2.50	2.44
		3.00	2.97
	2.5	1.00	0.92
		1.50	1.19
		2.00	1.45
	1.25	0.50	0.36
		1.00	0.57
		1.50	0.84
		2.00	1.03
0.40	5.0	0.25	0.44
		0.50	0.42
		0.75	0.58
		1.00	0.68
		1.50	1.03
		2.00	1.17
		2.50	1.34
	2.5	0.75	0.42
		1.00	0.50
		1.25	0.57
	1.25	0.25	0.26
		0.50	0.30
		0.75	0.35
		1.00	0.47
	0.5	0.125	0.31[b]
	1.0	0.125	0.43[b]
		0.25	0.57[b]

[a] $T = 25.0 \pm 0.1$ °C, $\lambda = 340$ nm, $I = 1.0\,M$ ($NaClO_4$). [b] $\lambda = 270$ nm.

absorbs appreciably in the UV region. Some side reactions are therefore expected due to formation of binuclear $[Fe_2(OH)_2]^{4+}$ which absorbs in this region [7]. Few runs were carried out at 270 nm with low periodate concentration where the rate of formation of Fe(III) was followed. Preliminary experiments

TABLE II. Variation of k_2'' and k_3 with $[H^+]$.

$[H]^+$	k_2'', sec^{-1}	10^{-4} k_3 M^{-2} sec^{-1}
0.10	89.0	7.8
0.20	39.5	7.2
0.40	13.5	6.9

indicated that no complex is formed between Fe(III) and periodate at the $[H^+]$ employed. The temperature of the reactants was equilibrated in the drive syringes by circulating water from a thermostat before the reaction was initiated.

Results

All the kinetic results are collected in Table I. The values of k_{obs} were obtained from the slopes of the linear parts of plots of $\log(A_t - A_\infty)$ *vs.* t (340 nm) or from those of $\log(A_\infty - A_t)$ *vs.* t (270 nm). Deviation from linearity beyond 70% of reaction was observed in all cases, the deviation increasing with increasing $[H^+]$ (see later).

The dependence of k_{obs} on [periodate] at $[Fe(II)]_0 = 5.0 \times 10^{-4}$ M and $[H^+]$ 0.10, 0.20 and 0.40 M is shown in Figure 1. At fixed $[H^+]$, the relation is described by eq. 1:

$$k_{obs} = k_1 + k_2[L^-]_T \tag{1}$$

where k_1 and k_2 correspond to the intercept and slope, respectively, and both are dependent on $[H^+]$, and $[L^-]_T$ represents total periodate concentration. Plots similar to Figure 1 were obtained at $[Fe(II)]_0$ 1.25×10^{-4} M and 2.5×10^{-4} M, but with both k_1 and k_2 increasing with increasing $[Fe(II)]_0$ at constant $[H^+]$. Figure 2 shows the variation of k_2 with $[Fe(II)]_0$ at various $[H^+]$ which agrees with eq. 2

$$k_2 = k_2' + k_3\,[Fe(II)]_0 \tag{2}$$

at fixed $[H^+]$. The magnitudes of k_2' and k_3 are obtained from the intercepts and the slopes of the plots of Figure 2 (collected in Table II). These results indicate that k_2' varies with $[H^+]$ according to eq. 3:

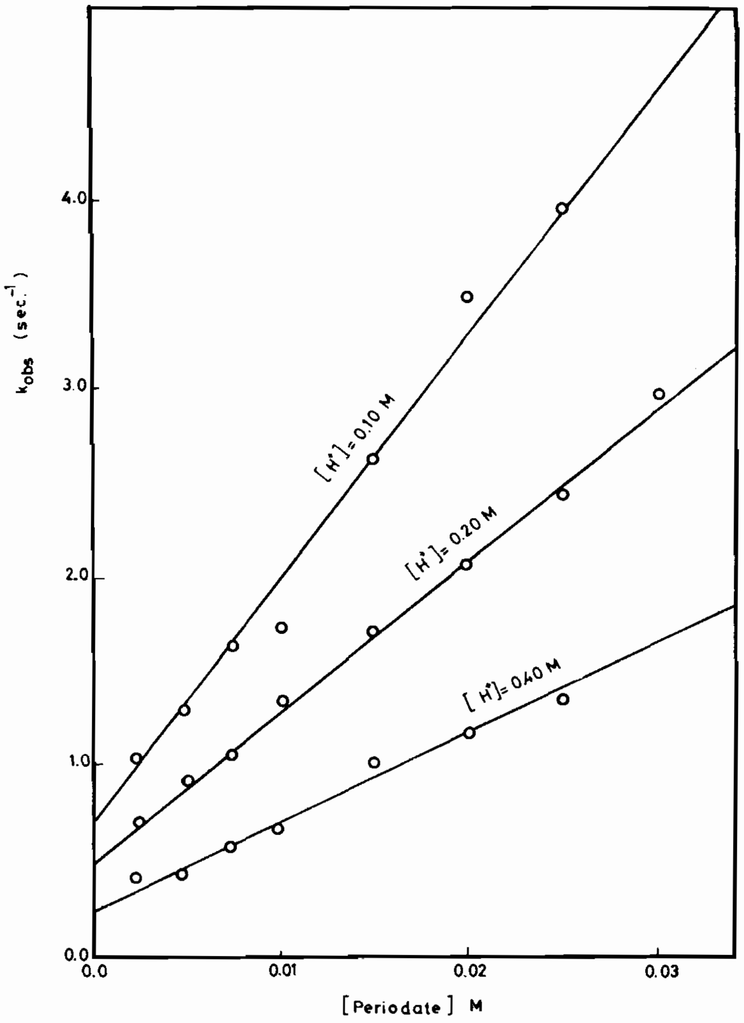
$$k_2' = k_2''/[H^+] \tag{3}$$

where $k_2'' = 7.5 \pm 1.5$ sec^{-1} at 25 °C and $I = 1.0M$ and k_3 (showing no dependence on $[H^+]$) and has a value $(7.3 \pm 0.5) \times 10^4$ M^{-2} sec^{-1} at 25 °C and $I = 1.0M$.

k_1 at constant $[H^+]$ varies with Fe(II) according to eq. 4 as deduced from Figure 3:

$$k_1 = k_0 + k_1'\,[Fe(II)]_0 \tag{4}$$

The value k_1' at hydrogen ion concentrations 0.10 and 0.20 M was calculated as 1.18×10^3 and 6.0×10^2 M^{-1} sec^{-1}, respectively at 25 °C and $I = 1.0M$. These values indicate an inverse first-order dependence on



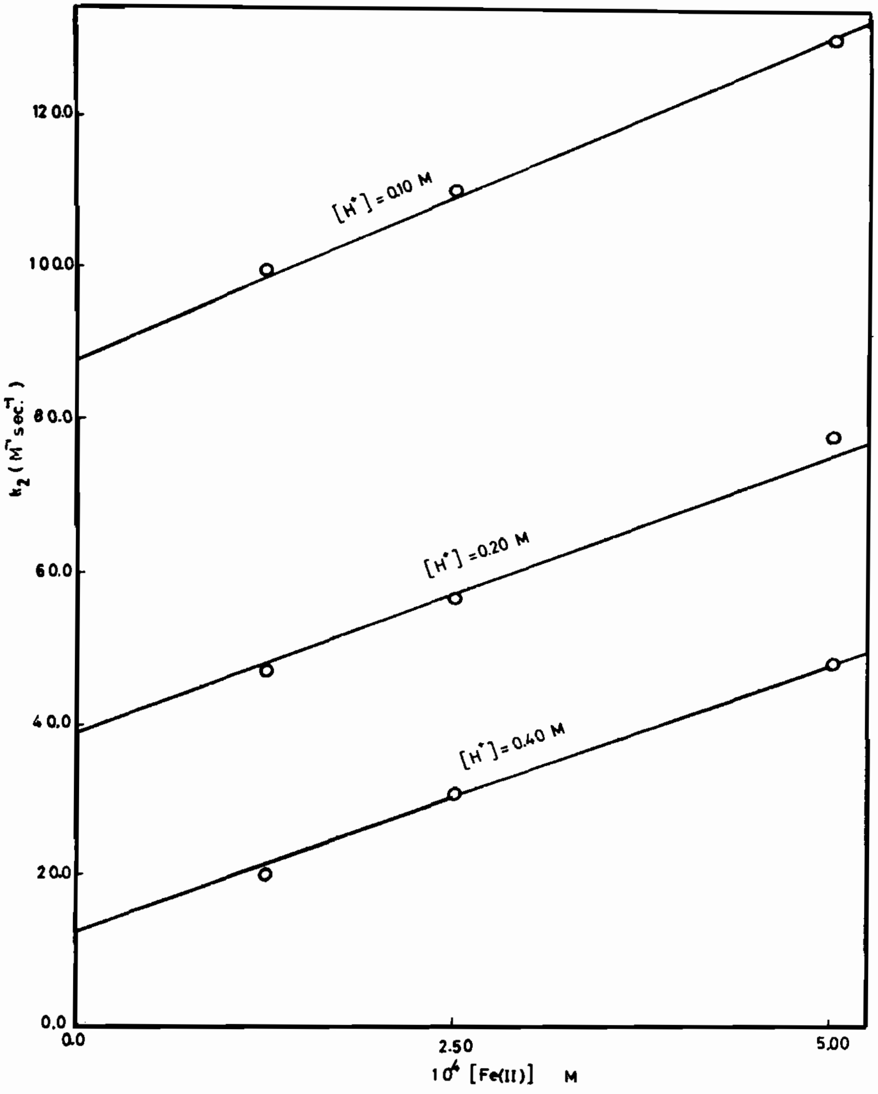


Figure 1. Plots of k_{obs} against [Periodate] at different hydrogen ion concentrations at 25 °C and I = 1.0 *M*.

Figure 2. Variation of k_2 M^{-1} sec^{-1} with [Fe(II)] at different [H⁺] at 25 °C and I = 1.0 *M*.

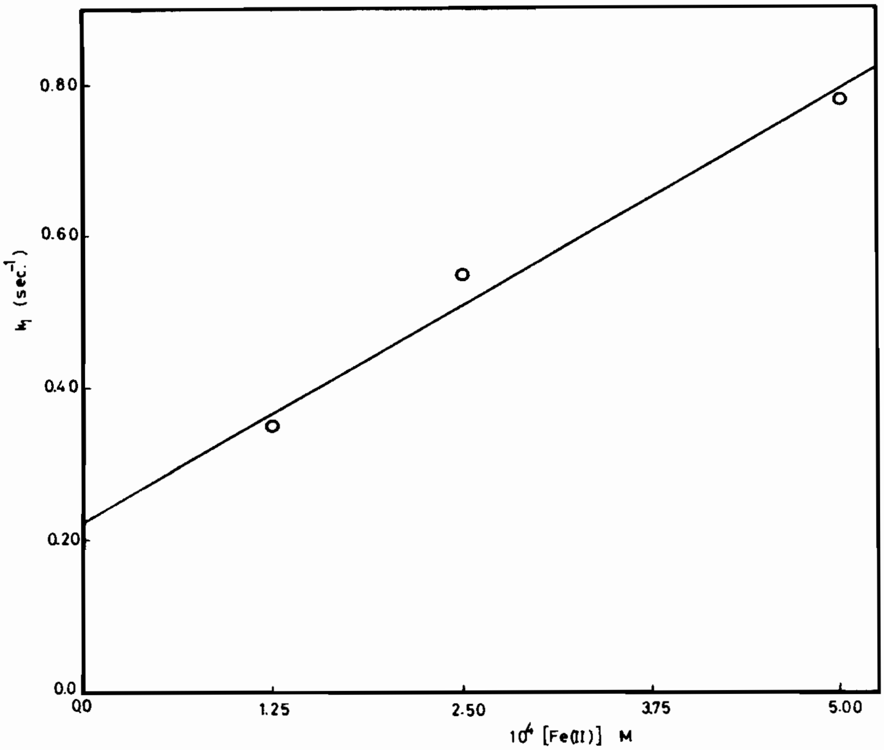


Figure 3. Variation of k_1 sec^{-1} with [Fe(II)] at $[H^+] = 0.10\ M$, temp. = 25 °C and I = 1.0 *M*.

$[H^+]$. k_0 seems to be independent of $[H^+]$ as it takes the values 0.23 and 0.24 sec^{-1} at 25 °C and I = 1.0 *M* at hydrogen ion concentrations 0.10*M* and 0.20*M*, respectively.

The rate law is thus described by eq. 5:

$$\text{Rate} = \{k_0 + k_1''/[H^+]\}[\text{Fe(II)}]^2 + \frac{k_2''[\text{Fe(II)}][L^-]_T}{[H^+]} + k_3[\text{Fe(II)}]^2[L^-]_T \qquad (5)$$

which accounts for all experimental results.

Discussion

The kinetic rate law indicated that oxidation of Fe(II) by periodate proceeds via two parallel pathways, one first order in both reactant concentrations and inversely proportional to $[H^+]$. The other pathway is first order in oxidant and second order in reductant concentrations and independent of $[H^+]$ in the range investigated. Taking into consideration the rapid equilibrium 6:

$$H^+ + L^- \rightleftharpoons HL \qquad K_1 \sim 150 \pm 10\ M^{-1} \qquad (6)$$

where L^- stands for IO_4^- and $H_4IO_6^-$ the periodate species that exist in aqueous solution, the following mechanism is proposed

$$\text{Fe(II)} + L^- \rightleftharpoons [\text{FeL}]^+, \qquad K_2 \qquad (7)$$

$$\text{Fe(II)} + \text{HL} \rightleftharpoons [\text{FeHL}]^{2+}, \qquad K_3 \qquad (8)$$

$$[\text{FeL}]^+ \xrightarrow{k_9} \text{Fe(III)} + \text{L(VI)} \qquad (9)$$

$$[\text{FeHL}]^{2+} + \text{Fe(II)} \xrightarrow{k_{10}} 2\text{Fe(III)} + IO_3^- \qquad (10)$$

$$\text{Fe(II)} + \text{L(VI)} \xrightarrow{\text{fast}} \text{Fe(III)} + IO_3^- \qquad (11)$$

The rate law 12 is derived from the above mechanism assuming that K_2 and K_3 are small, an assumption warranted by the adherence of the rate law to first order dependence on $[L^-]$:

$$\text{Rate} = \frac{k_9K_2[\text{Fe(II)}][L^-]_T}{1 + K_1[H^+]} + \{1 + 1/K_1[H^+]\}k_{10}K_3[\text{Fe(II)}]^2[L^-]_T \qquad (12)$$

Eq. 12 will reduce to 13 for the limiting conditions $K_1[H^+] \gg 1$ and $1 \gg 1/K_1[H^+]$:

$$\text{Rate} = \frac{k_9K_2[\text{Fe(II)}][L^-]_T}{K_1[H^+]} + k_{10}K_3[\text{Fe(II)}]^2[L^-]_T \qquad (13)$$

and by comparison with eq. 5 it is readily seen that $k_2'' = k_1K_2/K_3$ and $k_3 = k_{10}K_3$.

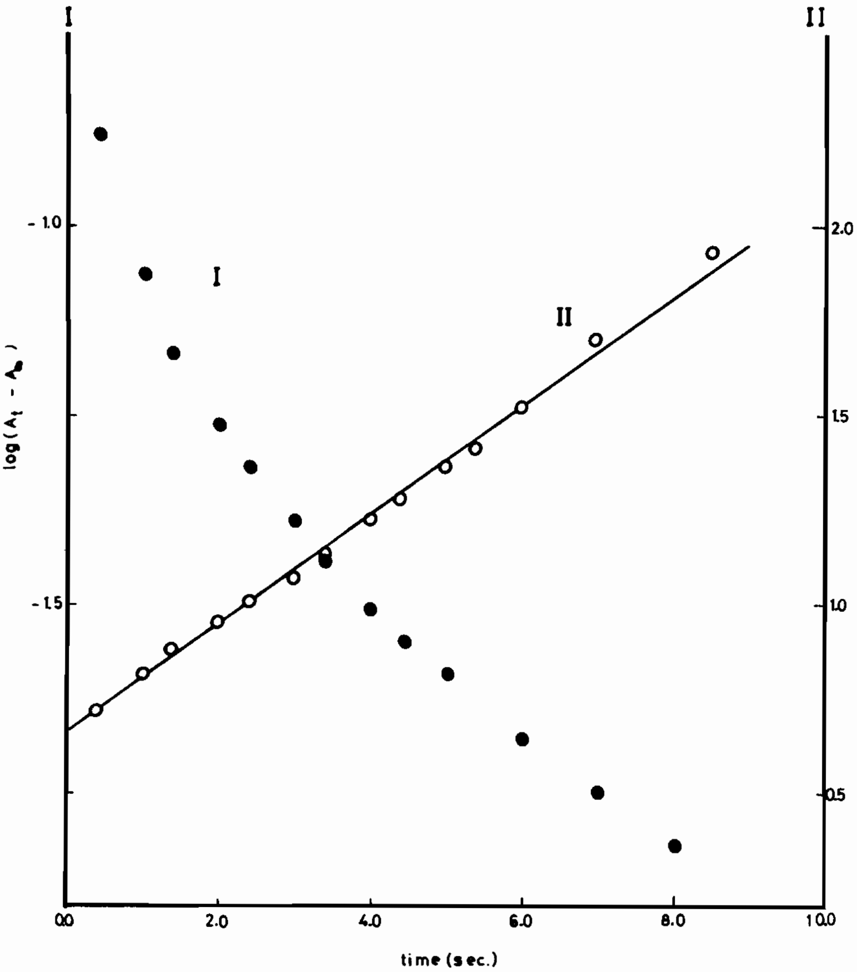


Figure 4. Departure from first-order dependence (I) and validity of second-order dependence (II) at $[H^+] = 0.80\ M$, $[Fe(II)] = 5.0 \times 10^{-4}\ M$, $[L^-]_T = 2.50 \times 10^{-3}\ M$, temp. 25 °C and $I = 1.0\ M$.

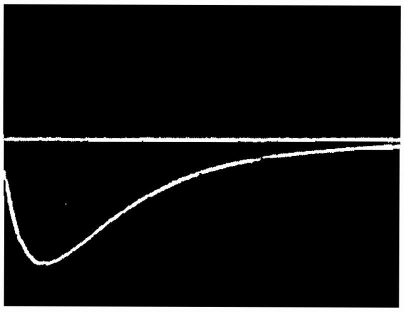


Figure 5. Stopped-flow trace showing a rapid formation and a slower dissociation of intermediates. Vertical axis 2% transmittance per major division and horizontal axis 0.2 sec per division. Horizontal line represents completion of reaction. $[Fe(II)] = 2.50 \times 10^{-4}\ M$, $[L^-]_T = 2.50 \times 10^{-2}\ M$, $[H^+] = 0.20\ M$, $I = 1.0\ M$ and temp. = 25 °C.

The proposed mechanism suggests that both one-electron (eq. 9) and two-electron transfer (eq. 10) operate in the reduction of periodate by Fe(II). The mechanism also indicates that one-electron transfer is associated with periodate ions (IO_4^- and/or $H_4IO_6^-$, whereas the two-electron transfer is associated with the acid form(s) (HIO_4 and/or H_5IO_6). Support for this is obtained from kinetics at high $[H^+]$ (~0.80*M*) where the term second order in [Fe(II)] dominates and the kinetics strictly obey second order dependence on [Fe(II)] as shown in Fig. 4. The work of Symons [1] is in accord with this as the polymerisation was observed in the pH range 1–4 where the term first order in [Fe(II)] is dominant.

The oxidation of Fe(II) by periodate seems to proceed by an inner-sphere mechanism. The stopped-flow traces indicated a rapid formation and a slower decomposition of an intermediate with an induction period (as shown in Figure 5). Furthermore Fe(II) is labile and substitution into its inner coordination shell is very likely with the periodate oxygen(s) acting as bridging atom)s). Indeed, an inner-sphere mechanism seems to be the preferable if not the only pathway in periodate oxidations. Thus, cyclic intermediates have been proposed for 1,2-diol oxidations [8], and oxygen atom transfer in iodide reaction with the formation of IO^- as a primary oxidation product [9]. In support of this hypothesis the oxidation of ($Fe(CN)_6^{4}$) [10], V(IV) [3] and ($CoEDTA^{2-}$) [11] is suggested to proceed *via* this mechanism. In the oxidation of the latter complex a primary Co(III) product other than hexadentate $CoEDTA^-$ has been identified spectrophotometrically. The failure of periodate to oxidise $Fe(phen)_3^{2+}$ to $Fe(phen)_3^{3+}$ is in keeping with an inner-sphere mechanism [12].

An explanation of the term independent of periodate concentration in eq. 5 is not obvious. It probably areises from a catalytic pathway involving a metal ion, such as Cu(II), present as an impurity. It has been reported that Cu(II) ions catalyse periodate oxidations [12].

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