

Kinetic and Mechanistic Studies on Oxidation of Ethylenediamine-*N, N'*-diacetato Chromium(III) Complex by Periodate Ion in Aqueous Solutions

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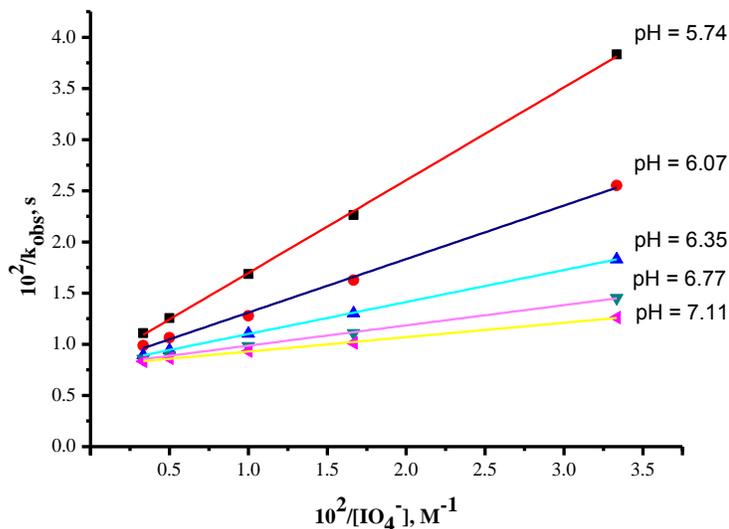
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Novelty and Highlights:

1. Chemistry of Cr(III) and Cr(VI) have received some attention in recent years. The ease of oxidation of chromium(III) complexes near the physiological pH value is a cause for concern as chromium(V), and chromium(VI) may be readily formed in this pH range. Chromium(III) complexes are reported to have anti diabetic activity.
2. Oxidation of the title complex by periodate ion has not been reported before.
3. The reaction exhibited first order dependence on the complex concentration and saturation kinetics with respect to periodate ion concentration.
4. The reaction proceeds via the inner-sphere mechanism.

Graphical Abstract

The rate law of oxidation of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})]^+$ by periodate ion displayed saturation kinetics and it is clear that the rate of the reaction increases with increasing pH values.



Kinetic and mechanistic studies on oxidation of ethylenediamine-*N*, *N'*-diacetato chromium(III) complex by periodate ion in aqueous solutions

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Abstract

The kinetics of the reaction between sodium periodate and $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ (edda = ethylenediamine-*N*, *N'*-diacetate) in aqueous solutions have been studied spectrophotometrically at 5.74 – 7.11 pH range, 20 – 40 °C and 0.20 M ionic strength. The reaction rate has been found to obey the following equation:

Rate = $k^{\text{et}}K_3[\text{Cr}^{\text{III}}]_{\text{T}}[\text{I}^{\text{VII}}]_{\text{T}}/\{1 + ([\text{H}^+]/K_1) + K_3[\text{I}^{\text{VII}}]_{\text{T}}\}$ where k^{et} is rate constant for the electron transfer process, K_1 is the dissociation constant of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ to $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})(\text{OH})] + \text{H}^+$ and K_3 is the pre-equilibrium formation constant. The thermodynamic activation parameters are reported. It is proposed that electron transfer proceeds via an inner- sphere mechanism with the hydroxo ligand of the chromium(III) complex bridging the two reactants.

Introduction

The oxidation of chromium from the trivalent to hexavalent states is an important environmental process because of the high mobility and toxicity of chromium(VI) [1]. Periodate oxidations have been reported to play an important role in biological determinants [2, 3]. There has been plenty of studies on the oxidation of several inorganic [4], and organic [5] substrates by periodate ion in aqueous medium. Metal complexes, which are relatively easily oxidized by IO_4^- , seem to fall into one of two classes; (i) labile complexes [6-11] or (ii) inert complexes that can offer a bridging ligand [12, 13]. The mechanism of oxidation of labile complexes is believed to be of the inner-sphere type, and in several cases direct evidence in support of this mechanism has been presented [14, 15]. The inert complexes $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, $[\text{Fe}^{\text{II}}(\text{CN})_2(\text{bipy})_2]$ and $[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$, that fit category (ii), are also readily oxidized by IO_4^- [7, 16-18]. The unusual second order dependence on $[\text{Cr}^{\text{III}}\text{cdta}(\text{H}_2\text{O})]^-$ and $[\text{Cr}^{\text{III}}\text{dtpa}(\text{H}_2\text{O})]^{2-}$ in the chromium(III)-periodate oxidation seems to support an inner-sphere mechanism [19]. The concurrent two one-electron transfer step proposed for this reaction requires the

inner-sphere mechanism. Additional support for this mechanism was also provided by the rate laws of some reactions. The rate law for the oxidation of $[\text{Co}^{\text{II}}\text{edta}]^{2-}$ by IO_4^- where (edta = ethylenediaminetetraacetate) is consistent with the formation of the precursor complex $[\text{edtaCo}^{\text{II}}\text{OIO}_3]^{3-}$ which precedes the electron transfer step [10]. The kinetics of oxidation of a number of chromium(III) complexes by IO_4^- have been reported. In most of these reactions, the hydroxo form of the chromium(III) complex is the most reactive species. The rate laws for the oxidation of $[\text{Cr}^{\text{III}}(\text{hedta})(\text{H}_2\text{O})]$ (hedta = N-(2-hydroxyethyl)ethylenediaminetriacetate), $[\text{Cr}^{\text{III}}(\text{ox})_2(\text{H}_2\text{O})]^-$ (ox = oxalate), $[\text{Cr}^{\text{III}}\text{G}_2(\text{H}_2\text{O})_2]$ (G = L-glutamate), $[\text{Cr}^{\text{III}}(\text{Hnta})(\text{asp})(\text{H}_2\text{O})]^-$, $[\text{Cr}^{\text{III}}(\text{Hnta})(\text{his})(\text{H}_2\text{O})]^-$, (nta = nitrilotriacetate, hist = histidine, asp = aspartate), $[\text{Cr}^{\text{III}}(\text{phen})_2(\text{H}_2\text{O})_2]^{3+}$ (phen = 1,10 phenanthroline) and $[\text{Cr}^{\text{III}}(\text{gly})_2(\text{H}_2\text{O})_2]^+$ (gly = glycinate) by IO_4^- displayed saturation kinetics [9, 20-25]. The kinetics, in each case, is interpreted in terms of formation of a precursor complex followed by a slower intramolecular electron transfer step. In the present study, we report our findings on the kinetics of oxidation of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ by IO_4^- .

The ease of oxidation of chromium(III) complexes near the physiological pH value is a cause for concern as chromium(V) and chromium(VI) may be readily formed in this pH range.

Experimental

Materials

All compounds used in this study were of reagent grade or Analar (BDH or Aldrich). $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ was prepared by the reported method [26]. Stock solutions of sodium metaperiodate were prepared by weight and wrapped with aluminum foil and kept in the dark. Solutions of periodate are known to undergo photochemical decomposition [27]. Buffer solutions were made up of $\text{NaH}_2\text{PO}_4/\text{NaOH}$ solutions of known concentrations. NaNO_3 was used to adjust ionic strength in the buffered solutions. Acrylonitrile (Aldrich) was used as received.

Kinetic procedure

The u.v-vis absorption spectrum of the oxidation products of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ by periodate, in the presence of phosphate buffers, were recorded on a Shimadzu UV-2600 spectrophotometer equipped with a thermostated cell-holder. Oxidation rates were measured by monitoring the absorbance of Cr(VI) at 370 nm. The Cr(III) complex and periodate solutions in the required buffers were allowed to equilibrate for 15 - 20 minutes in a water bath before the reaction was initiated. The pH of the reaction mixture was measured using a Chertsey (Surrey) 7065 pH-meter.

Pseudo-first order conditions were maintained in all runs by the presence of a large excess (>15-fold) of IO_4^- . The ionic strength was kept constant by the addition of NaNO_3 solution. The pH of the reaction mixture was found to be always constant during the reaction run.

Oxidation products

During the oxidation, the pink aqueous solution of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ changed gradually to yellow and its original absorption maxima, at 539 and 358 nm, were replaced by a single peak at 370 nm. The product of this reaction has been shown to produce a relatively stable Cr(VI). It was found that at the end of the reaction chromium(VI) was formed by the *sym*-diphenylcarbazide test.

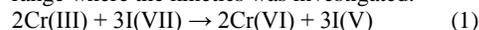
Stoichiometry

A known excess of Cr(III) complex was added to IO_4^- solution. The absorbance of Cr(VI) produced was measured at 370 nm after 24 h from the onset of the reaction. The quantity of Cr(III) consumed was calculated using the molar absorptivity of Cr(VI).

Results and Discussion

The $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ complex displayed absorption peaks at 539 nm and 358 nm. These peak positions are in

excellent agreement with the literature values [26]. The stoichiometry of the $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2] - \text{IO}_4^-$ reaction can be represented by Eq. (1). The ratio of IO_4^- initially present to chromium(VI) produced was 3.00 ± 0.07 . The stoichiometry is consistent with the observation that IO_3^- does not oxidize the chromium(III) complex over the pH range where the kinetics was investigated.



With periodate concentration in large excess over that of the complex, plots of $\ln(A_\infty - A_t)$ versus time were linear up to 85% of reaction where A_t and A_∞ are absorbances at time t and infinity, respectively. Pseudo-first order rate constants, k_{obs} , obtained from the slopes of these plots, are collected in Table 1. The results (Table 1) show that k_{obs} was unaffected when the concentration of the Cr(III) complex was varied at constant periodate concentration, indicating first order dependence on complex concentration $d[\text{Cr}^{\text{VI}}]/dt = k_{\text{obs}} [\text{Cr}^{\text{III}}]_T$ (2)

Table 1. Dependence of k_{obs} on the initial of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ at $[\text{IO}_4^-] = 0.01 \text{ M}$, $\text{pH} = 6.77$, $I = 0.20 \text{ M}$, $T = 20.0 \pm 0.1 \text{ }^\circ\text{C}$.

$10^4 [\text{Cr}^{\text{III}}], \text{M}$	$10^3 k_{\text{ot}}$
0.40	$10.15 \pm$
0.80	$10.18 \pm$
1.20	$10.16 \pm$
1.60	$10.17 \pm$
2.00	$10.18 \pm$

The variation of k_{obs} with $[\text{IO}_4^-]$ at various pH values is shown in Table 2 and (Fig. 1). It is obvious from these results that k_{obs} does not vary linearly with $[\text{IO}_4^-]$ at all pH ranges covered in this study. Indeed the variation with $[\text{IO}_4^-]$ is small indicating high association between the two reactants. It is also clear from the results in Table 2 that under constant reaction conditions, k_{obs} increases with increasing pH. Plots of $1/k_{\text{obs}}$ versus $1/[\text{IO}_4^-]$ are linear at all pH values covered in this study as shown in (Fig. 1). The dependence of k_{obs} varies with $[\text{IO}_4^-]$ according to Eq. (3) at constant reaction conditions. (Fig. 1) shows that *slope* values depend on $[\text{H}^+]$ whereas *intercept* values do not.

$$1/k_{\text{obs}} = 1/a[\text{IO}_4^-] + b/a \quad (3)$$

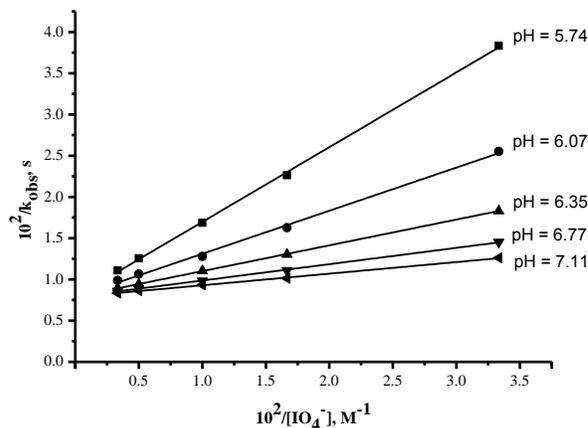


Fig. 1 Dependence of k_{obs} on $[IO_4^-]$ at several pH values, $[Cr(edda)(H_2O)_2^+] = 1.00 \times 10^{-4} M$, $T = 20^\circ C$ and $I = 0.20 M$. Values of a and b were obtained from the slope and the intercept as $(0.906 \pm 0.012) M^{-1}s^{-1}$ and $(79.0 \pm 2.05) M^{-1}$, respectively, at $20^\circ C$ and $pH = 5.74$.

Table 2. Dependence of k_{obs} on $[IO_4^-]$. $[Cr(edda)(H_2O)_2^+] = 1.00 \times 10^{-4} M$, $I = 0.20 M$, $T = 20.0 \pm 0.1^\circ C$.

$10^3 [IO_4^-], M$	$10^3 k_{obs}, s^{-1}$ at pH:				
	5.74	6.07	6.35	6.77	7.11
3.00	2.61 ± 0.10	3.93 ± 0.10	5.46 ± 0.10	6.88 ± 0.10	7.93 ± 0.20
6.00	4.42 ± 0.10	6.15 ± 0.10	7.67 ± 0.10	9.01 ± 0.20	9.88 ± 0.20
10.00	5.93 ± 0.10	7.82 ± 0.20	9.05 ± 0.20	10.17 ± 0.20	10.72 ± 0.30
20.00	7.96 ± 0.10	9.39 ± 0.10	10.61 ± 0.20	11.22 ± 0.20	11.59 ± 0.30
30.00	9.01 ± 0.20	10.12 ± 0.20	11.20 ± 0.20	11.64 ± 0.20	11.99 ± 0.20

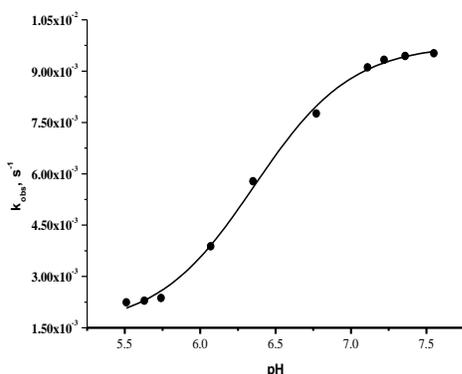


Fig. 2 Sigmoidal fitting of k_{obs} versus pH at $[Cr(edda)(H_2O)_2^+] = 1.00 \times 10^{-4} M$, $[IO_4^-] = 3.00 \times 10^{-3} M$, $T = 20.0^\circ C$ and $I = 0.20 M$

The effect of hydrogen ion concentration was investigated over the pH range 5.74 – 7.11. Table 2 shows that rate of reaction increases with the increasing pH value. In a weakly acidic medium the ethylenediaminediacetato chromium(III) complex may participate in the equilibrium shown in Eq. (4):



The value of K_1 obtained from the sigmoidal fitting of k_{obs} against pH , (Fig. 2), at $[IO_4^-] = 3.00 \times 10^{-3} M$, $T = 20.0^\circ C$ and $I = 0.20 M$ (4.47×10^{-7}) is in good agreement with the reported value (4.17×10^{-7}) [29]. The presence of $[H^+]$ dependence in the rate law suggests involvement of the deprotonated form of the chromium(III) complex, $[Cr^{III}edda(H_2O)OH]$, in the rate determining step.

From the reported equilibrium constants of aqueous periodate solutions [28], it may be concluded that, over the $[H^+]$ range used in this study, the periodate species likely to be present are IO_4^- , $H_4IO_6^-$, $H_3IO_6^{2-}$, which are in the equilibria

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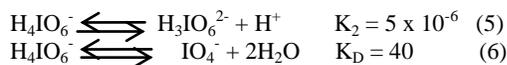


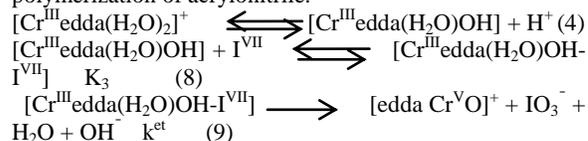
Table 3. Dependence of k_{obs} on ionic strength. $[\text{Cr}^{\text{III}}(\text{edda})_2(\text{H}_2\text{O})_2^+] = 1.00 \times 10^{-4} \text{ M}$, $[\text{IO}_4^-] = 3.00 \times 10^{-2} \text{ M}$,

I, M	$10^3 k_{\text{obs}}, \text{s}^{-1}$
0.10	3.93 ± 0.10
0.20	3.99 ± 0.20
0.50	3.89 ± 0.20
0.80	3.90 ± 0.10

pH = 6.07 ± 0.01 , I = 0.20 M, T = 20.0 ± 0.1 °C.

It is clear from the value of K_D that IO_4^- is not predominant species (I^{VII} will be used to represent H_4IO_6^- and $\text{H}_3\text{IO}_6^{2-}$). The experimental rate equation suggests a fast equilibrium step precedes the slow intramolecular electron transfer step.

A possible mechanism is described by Eqs. (7-10). The reaction seems to involve an inner sphere one-step two-electron transfer. This is supported by the absence of polymerization of acrylonitrile.



From the above mechanism, the rate of reaction is given by

$$\text{Rate} = k^{\text{et}}[\text{Cr}^{\text{III}}\text{edda}(\text{H}_2\text{O})\text{OH}-\text{I}^{\text{VII}}] \quad (11)$$

$$= k^{\text{et}}K_3[\text{Cr}^{\text{III}}\text{edda}(\text{H}_2\text{O})\text{OH}][\text{I}^{\text{VII}}] \quad (12)$$

If $[\text{Cr}^{\text{III}}]_{\text{T}}$ represents the total concentration of Cr^{III} species, then,

$$[\text{Cr}^{\text{III}}]_{\text{T}} = \frac{[\text{Cr}^{\text{III}}\text{edda}(\text{H}_2\text{O})\text{OH}][\text{H}^+]/K_1}{[\text{Cr}^{\text{III}}\text{edda}(\text{H}_2\text{O})\text{OH}] + K_3[\text{Cr}^{\text{III}}\text{edda}(\text{H}_2\text{O})\text{OH}][\text{I}^{\text{VII}}]} \quad (13)$$

Substitution for $[\text{Cr}^{\text{III}}\text{edda}(\text{H}_2\text{O})\text{OH}]$ from Eq. (13) in Eq. (12), gives

$$\text{Rate} = k^{\text{et}}K_3[\text{Cr}^{\text{III}}]_{\text{T}}[\text{I}^{\text{VII}}]_{\text{T}} / \{1 + ([\text{H}^+]/K_1) + K_3[\text{I}^{\text{VII}}]_{\text{T}}\} \quad (14)$$

Since the reaction is first order in $[\text{Cr}(\text{III})]$, the pseudo first order rate constant, k_{obs} is given by Eq. (15).

Table 4. Dependence of k_{obs} on $[\text{IO}_4^-]$. $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2^+] = 1.00 \times 10^{-4} \text{ M}$, pH = 5.74 ± 0.01 , I = 0.20 M at different temperatures.

$10^3 k_{\text{obs}}, \text{s}^{-1}$ at various temperatures °C ± 0.1:				
$10^3[\text{IO}_4^-], \text{M}$	20.0	25.0	30.0	40.0
3.00	2.61 ± 0.10	3.94 ± 0.10	6.20 ± 0.10	10.76 ± 0.20
6.00	4.42 ± 0.10	6.67 ± 0.10	8.82 ± 0.20	14.02 ± 0.30
10.00	5.93 ± 0.10	8.22 ± 0.20	11.39 ± 0.20	16.57 ± 0.40
20.00	7.96 ± 0.10	10.49 ± 0.20	13.87 ± 0.20	19.21 ± 0.50
30.00	9.01 ± 0.10	11.49 ± 0.20	14.59 ± 0.20	20.42 ± 0.40

$$k_{\text{obs}} = k^{\text{et}}K_3[\text{I}^{\text{VII}}]_{\text{T}} / \{1 + ([\text{H}^+]/K_1) + K_3[\text{I}^{\text{VII}}]_{\text{T}}\}$$

which on rearrangement, gives

$$1/k_{\text{obs}} = K_1 + [\text{H}^+] / \{k^{\text{et}}K_1K_3[\text{I}^{\text{VII}}]_{\text{T}}\} + 1/k^{\text{et}} \quad (16)$$

At constant $[\text{H}^+]$ Eq. (17) follows, in which A is a constant

$$1/k_{\text{obs}} = A / \{k^{\text{et}}K_1K_3[\text{I}^{\text{VII}}]_{\text{T}}\} + 1/k^{\text{et}} \quad (17)$$

Where $A = K_1 + [\text{H}^+]$, Eq. (17) is identical to the experimental results shown in Eq. (3), where $a = k^{\text{et}}K_1K_3/A$ and $b = K_1K_3/A$. Values of k^{et} , at temperatures used,

calculated from these relationships, by substitution $K_1 = 4.45 \times 10^{-7} \text{ M}$, are (1.27, 1.52, 1.72 and 2.21) $\times 10^{-2} \text{ s}^{-1}$ at 20.0, 25.0, 30.0 and 40.0 °C, respectively.

The effect of ionic strength on the oxidation rate was investigated. Results are shown in Table 3. It is clear from these results that, k_{obs} values were unaffected when the ionic strength was varied at constant reaction conditions. This can be attributed to the deprotonation of the complex.

The effect of temperature on oxidation rates was studied. Results are shown in Table 4 and (Fig. 3). It is obvious from these results that k_{obs} increases with increasing temperature. The enthalpy and entropy of activation, ΔH^\ddagger and ΔS^\ddagger , associated with k^{et} are determined using the Eyring equation, (Fig. 4), as $18.5 \pm 1.0 \text{ kJ mol}^{-1}$ and $-218.0 \pm 34.8 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The high negative entropy of activation is largely due to the result of the charge concentration on encounter complex formation which causes substantial mutual ordering of the solvated water molecules. The intramolecular electron transfer step is endothermic, hence the contributions of S^\ddagger and H^\ddagger to the rate constant seem to compensate each other. This suggests that the factors controlling ΔH^\ddagger must be closely related to those controlling ΔS^\ddagger ; therefore, the solvation state of the encounter complex would be important in determining ΔH^\ddagger . Thus the relatively small enthalpy of activation, ΔH^\ddagger , can be explained in terms of the formation of a more solvated complex.

From Eq. (16), it follows that the slope of the plots can be represented by Eq.(18). Slope = $[\text{H}^+]/k^{\text{et}}K_1K_3 + 1/k^{\text{et}}K_3$ (18)

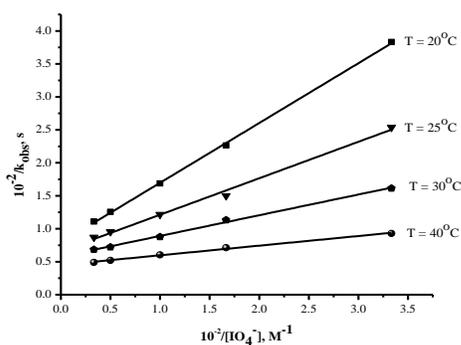


Fig. 3 Dependence of k_{obs} on $[\text{IO}_4^-]$ at several temperatures, $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2^+] = 1.00 \times 10^{-4} \text{ M}$, $\text{pH} = 5.74$ and $I = 0.20 \text{ M}$.

hence, the slope is dependent on $[\text{H}^+]$. This plot, (Fig. 5), can be given as the linear equation $y = mx + c$, with a correlation coefficient of 0.9968. Value of K_1 and K_3 were calculated from Eq.(18) and (Fig. 5) as $2.73 \times 10^{-7} \text{ M}$ and 658.3 M^{-1} , at 20°C and $I = 0.20 \text{ M}$, respectively.

This value of K_1 is in good agreement with that obtained from the sigmoidal fitting (4.40×10^{-7}) and with the reported value (4.17×10^{-7}) [27]. This indicates the validity of our proposed mechanism.

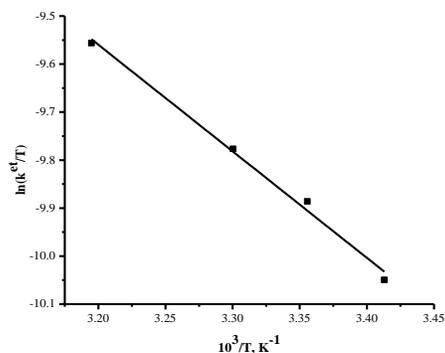


Fig. 4 Plot of Eyring equation at $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2^+] = 1.00 \times 10^{-4} \text{ M}$, $\text{pH} = 5.74$ and $I = 0.20 \text{ M}$.

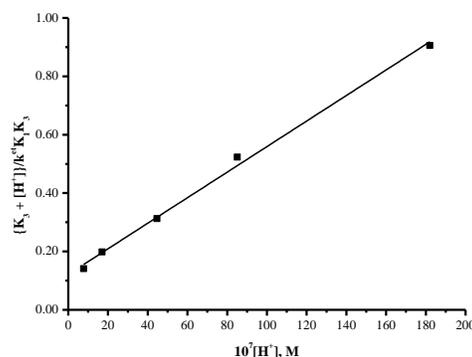


Fig. 5 Plot of $\{K_3 + [\text{H}^+]\}/k^{\text{et}}K_1K_3$ versus $[\text{H}^+]$ at $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2^+] = 1.00 \times 10^{-4} \text{ M}$, $T = 20.0^\circ\text{C}$, $I = 0.20 \text{ M}$.

Conclusions

From the above discussion, an inner-sphere mechanism is proposed for the oxidation of $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})_2]^+$ by periodate ion, in which the Cr^{IV} is coordinated to $[\text{Cr}^{\text{III}}(\text{edda})(\text{H}_2\text{O})(\text{OH})]$.

The oxidation process may proceed via one or two electron transfer, giving chromium(IV) or chromium(V), respectively, in the rate-determining step. This may then be followed by a fast step leading to chromium(VI). The fact that acrylonitrile was not polymerized by the reaction mixture seems to support a two electron transfer process. The high value of pre-equilibrium constant, K_3 , obtained in this reaction supports substitution on the periodate ion rather than on the chromium(III) complex.

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