



Kinetic studies on the oxidation of diethylenetriaminepentaacetato chromium(III) by periodate

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ABSTRACT

The kinetics of the oxidation of diethylenetriaminepentaacetato chromium (III), (Cr(III)-DTPA), by periodate were studied spectrophotometrically over pH range 6.10-7.15 at 14-22°C. The reaction follows first order with respect to Cr(III)DTPA and $[IO_4^-]$ and inversely dependent on $[H^+]$. The mechanism involves the formation of an intermediate between the monohydroxochromium(III) complex and periodate which decomposes in rate determining step. The values of the intramolecular electron transfer, the formation constant of the intermediate and the hydrolysis constant of the complex were calculated. The activation parameters were calculated.

Introduction

Metal complexes which are relatively easily oxidized by periodate in aqueous solution, seem to be classified (i) labile complexes^[1,2] and (ii) inert complexes that can offer bridge ligand^[3,4]. The mechanism of oxidation of labile complexes is believed to be inner-sphere type, and direct evidence was supported this mechanism^[1,2]. In case of oxidation of $[Cr(III)(EDTA)(H_2O)]$ by periodate^[2], it was proposed that the oxidation was proceeded via one or two electron transfer giving Cr(IV) or Cr(V), in the rate determining step followed by fast step leading to Cr(VI). The inner sphere process is also believed to be operating in oxidation of inert complexes^[3,4]. Oxidation of chromium complexes by periodates showed a first-order dependency on both the chromium complex and the oxidant^[5-11]. The unusual second order dependence on $[Cr(H_2O)_6]^{3+}$ in chromium periodate reaction seems to support an inner-sphere mechanism^[4,12]. The two electron transfer step proposed for this mechanism where the hydroxyl form was considered to be the reactive chromium(III) species.

In this work, we report the extension of these studies to oxidize chromium(III)-DTPA complex by periodate ion. The conjugate base of DTPA has high affinity to form complexes with transition metals leaving the iminodiacetate group uncomplexed^[13]. The difference in the course of the present study with that studied earlier was attributed to the difference in the anionic charge surrounding the central ion which plays an important role on the reaction rate. The experiments were carried out at different pH values and different

temperatures in order to promote differences as well as similarities in the redox process with that of aminopolyphosphonate complexes^[7]. The effect on the precursor formation constant and the electron transfer rate constant has been studied.

Materials and Methods

KIO_4 , $Cr(NO_3)_3 \cdot 9H_2O$, KNO_3 and DTPA were of pure grade and were used without further purification. The stock solution of chromium (III) was prepared and determined spectrophotometrically as chromate. The stock solution of DTPA was standardized by titration with Zn salt solution in hexamethylenetetraamine buffer (pH = 6) with xylenol orange as an indicator. A solution of Cr(III)DTPA complex was prepared by leaving the mixture of $Cr(NO_3)_3 \cdot 9H_2O$ with a slight excess of DTPA concentration for 24 h at pH range 6.10-7.15. Spectrophotometric measurements were made to insure complete formation of the complex and the absence of uncomplexed chromium(III). The concentration of chromium(III) complex in the reaction was kept at 0.2 mmol dm^{-3} .

Kinetic measurements

All kinetic measurements were carried out using a Unicam Helios α spectrophotometer equipped with a water-jacketed cell holder. The reactants were thermostated for 15 min., then mixed thoroughly and quickly transferred to an absorption cell. The formation of chromium (VI) was followed by monitoring the absorbance at $\lambda_{max} = 370 \text{ nm}$ as a function of time. Pseudo first-order conditions were maintained in all runs by using a large excess of periodate over the chromium(III) complex. The pH of the reaction was

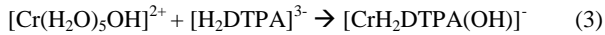
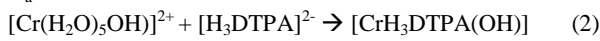
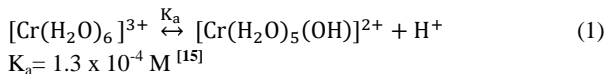
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adjusted using buffer solution and measured using a radiometer M62 pH-meter fitted with a combined glass calomel electrode. Measurements were recorded at an ionic strength of 0.2 mol dm⁻³ using KNO₃ solution.

Results and discussion

Addition of a colourless solution of potassium periodate to the chromium(III) DTPA complex results in disappearance of the peaks of the latter at 390 nm and 550 nm, and formation of a yellow species, identified by its spectrum as chromium(VI) as shown in (Fig.1). Table 1 illustrates that under an experimental conditions H₂DTPA³⁻ and H₃DTPA²⁻ were found to be the dominant species^[14], whereas the hydroxo-species of chromium(III) ion, [Cr(H₂O)₅OH]²⁺ was the dominant species for the chromium(III) ion therefore,



The inverse dependence of the reaction rate on the hydrogen ion concentration confirms that reactive species is [Cr H₂DTPA(OH)]⁻ for the reduction of IO₄⁻ in which the complex is bridged to IO₄⁻ through the hydroxo ligand. No reaction occurs between chromium (III) DTPA complex with IO₃⁻ which indicates that IO₃⁻ is the final product for the present reaction. This is consistent with early reported ^[5-6, 10-11].

The oxidation kinetics of the chromium (III) complex by periodate was studied over pH range 6.10 to 7.15 over range of periodate and complex concentrations. The kinetics of the reaction was studied under pseudo-first order condition with the concentration of periodate greatly exceeding than that of the chromium (III) complex. The conventional plots of ln (A_∞-A_t) versus time for at least three half-lives were found to be two linear stages with short reaction time and high rate constant followed by a second long reaction time with slower rate constant as shown in (Fig. 2). The observed rate constants k_{1obs} and k_{2obs} were calculated from the slopes of the first and second straight lines obtained respectively and are listed in Table 2. The constancy of the observed rate constants (k_{1obs} and k_{2obs}) over the Cr(III)DTPA concentration (1.8-2.4 x 10⁻⁴ mol dm⁻³) is in agreement with a first order kinetics.

The first order plots which is consistent with only one reaction with two different rates is probably attributed to tendency of chromate anion to associate with DTPA complex thus competing with periodate ion for the available site on the chromium coordination sphere ^[16]. This suggestion is supported by the following:

1. The reaction did not proceed in the presence of iodate instead of periodate.
2. In the presence of hydrogen peroxide instead of periodate, the same behavior was observed where the plot of ln (A_∞-A_t) versus time leads to two linear stages, (Fig. 3), as observed in presence of periodate. Therefore the inflection shown in presence of periodate illustrates that iodate anion

produced from the reduction of periodate does not compete the periodate ion for the available sites on the chromium (III) coordination sphere.

3. Linear parallel change between values of log k_{1obs} and log k_{2obs} versus the pH of the reaction, (Fig. 4), indicates a single reaction with rate constants characteristic to the slow and fast parts of the reaction.
4. Linear change of k_{1obs} versus k_{2obs}, (Fig. 5), also indicates single reaction with different rate constants.

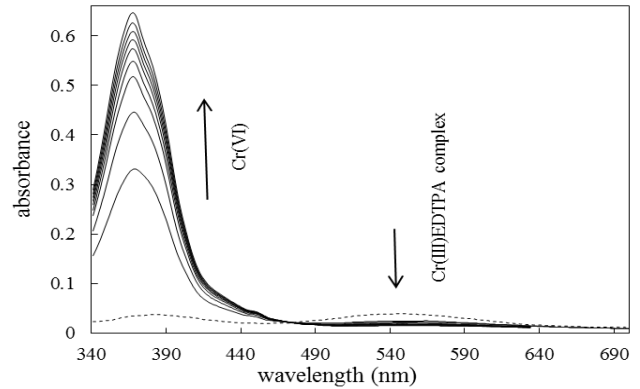


Fig. 1: Absorption spectrum of Cr(III)DTPA complex and periodate mixture at different time.

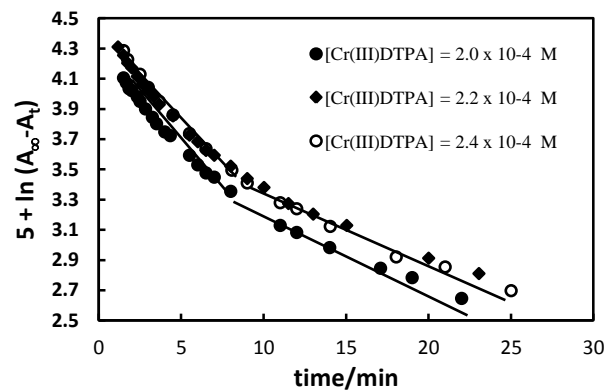


Fig. 2: Pseudo-first order plots of the reaction between Cr(III)-DTPA complex and KIO₄, [KIO₄] = 1.997 x 10⁻³ mol dm⁻³, Temp = 17 °C, pH = 6.6.

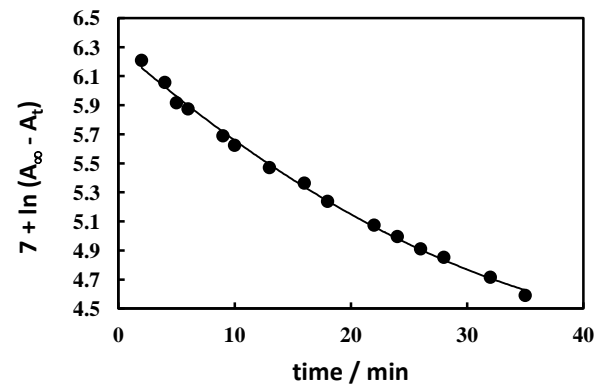


Fig. 3: Pseudo-first order plot of the reaction between Cr(III)-DTPA complex and H₂O₂, Temp = 42 °C, [Cr(III)-DTPA] = 4 x 10⁻⁴ mol dm⁻³, [H₂O₂] = 3.67 x 10⁻² mol dm⁻³.

Table 1: Acid protonation constants for H₅DTPA [14].

log k _{o11} = 9.87	log k _{o31} = 4.2	log k _{o51} = 2.18
log k _{o21} = 8.64	log k _{o41} = 2.9	

Table 2: Kinetic data of oxidation of Cr(III) DTPA by KIO₄.

Complex x 10 ⁴ /mol dm ⁻³	KIO ₄ x 10 ³ /mol dm ⁻³	Temp/ ^o C	pH	k _{1obs} x 10 ³ /s ⁻¹	k _{2obs} x 10 ³ /s ⁻¹
2	1.997	14	6.1	0.529	0.244
			6.3	0.785	0.335
			6.5	1.107	0.450
			6.7	1.642	0.635
			6.9	2.360	1.011
2	1.997	17	6.2	0.883	0.339
			6.4	1.243	0.487
			6.6	1.438	0.725
			6.8	2.859	1.219
			7.0	3.810	1.644
2	1.997	22	6.2	1.001	0.467
			6.4	1.285	0.670
			6.7	3.282	1.368
			7.0	5.213	2.263
			7.15	6.460	2.689
2	1.614	17	6.4	1.073	0.431
			6.6	1.492	0.622
			6.8	2.134	0.997
			7.0	3.148	1.314
2	1.997	17	6.2	0.883	0.339
			6.4	1.243	0.487
			6.6	1.438	0.725
			6.8	2.859	1.219
			7.0	3.810	1.644
2	2.300	17	6.2	0.909	0.335
			6.4	1.453	0.532
			6.6	2.092	0.868
			6.8	3.029	1.244
			7.0	4.123	1.741
2	2.774	17	6.2	0.995	0.367
			6.4	1.507	0.553
			6.6	2.174	0.903
			6.7	2.899	1.408
2	3.026	17	6.2	1.146	0.447
			6.4	1.665	0.722
			6.7	3.070	1.325
			6.8	4.024	1.652
1.8	1.997	17	6.4	1.153	0.425
2.0			1.243	0.487	
2.2			1.385	0.510	
2.4			1.409	0.537	
1.8	1.997	17	6.6	1.802	0.691
2.0			1.938	0.725	
2.2			2.132	0.965	
2.4			2.396	1.023	

Table 3: Summary of kinetic data and activation parameters for the oxidation of chromium (III) DTPA by periodate.

pH	First part		Second part	
	k/s^{-1}	$K_2/mol^{-1}dm^3$	$k s^{-1}$	$K_2/mol^{-1}dm^3$
6.2	2.771×10^{-3}	0.516×10^3	0.59×10^{-3}	1.347×10^3
6.4	4.002×10^{-3}	0.4103×10^3	1.03×10^{-3}	0.814×10^3
6.6	17.37×10^{-3}	0.090×10^3	2.15×10^{-3}	0.452×10^3
	$\Delta H^* = 50.63 \text{ kJ mol}^{-1}$		$\Delta H^* = 70 \text{ kJ mol}^{-1}$	
	$\Delta S^* = -76.7 \text{ J K}^{-1} \text{ mol}^{-1}$		$\Delta S^* = -16.6 \text{ J K}^{-1} \text{ mol}^{-1}$	

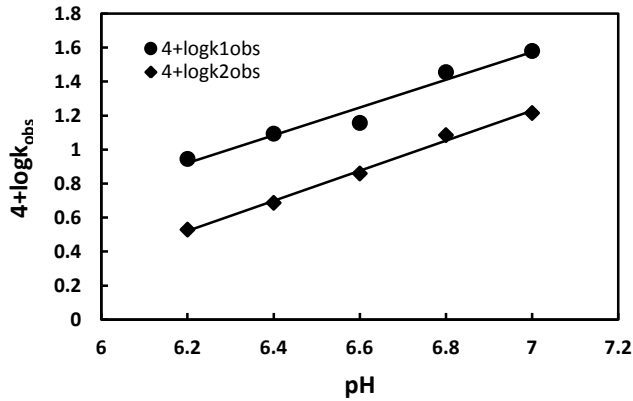


Fig. 4: Variation of $\log k_{1obs}$ and $\log k_{2obs}$ with pH, $[Cr(III)\text{-DTPA}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[KIO_4] = 1.997 \times 10^{-3} \text{ mol dm}^{-3}$ and Temp = 17°C.

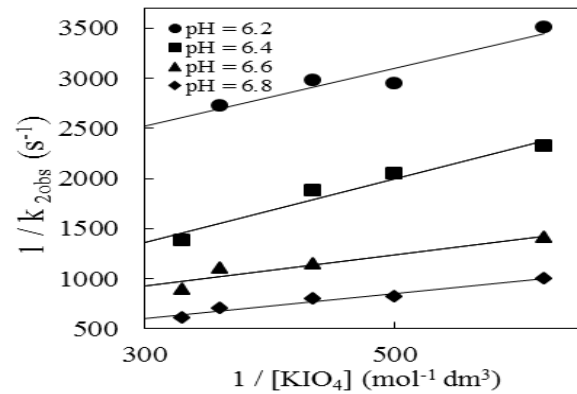
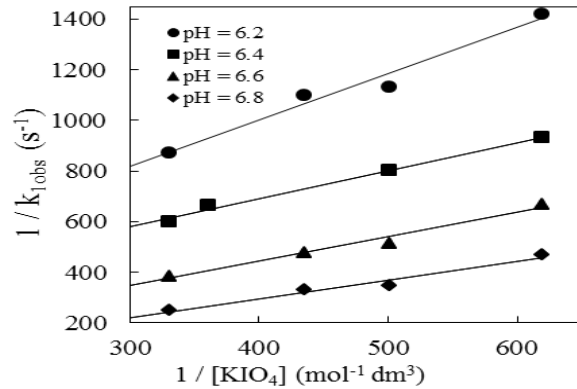


Fig. 6: The variation of $1/k_{1obs}$ and $1/k_{2obs}$ with $1/[KIO_4]$ at various pH values. Temp = 17°C, $[Cr(III)\text{-DTPA}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$.

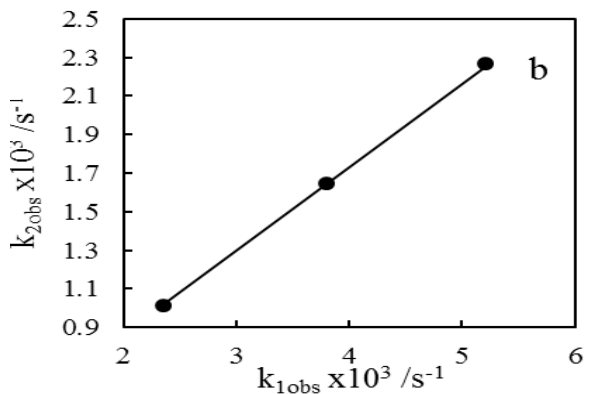
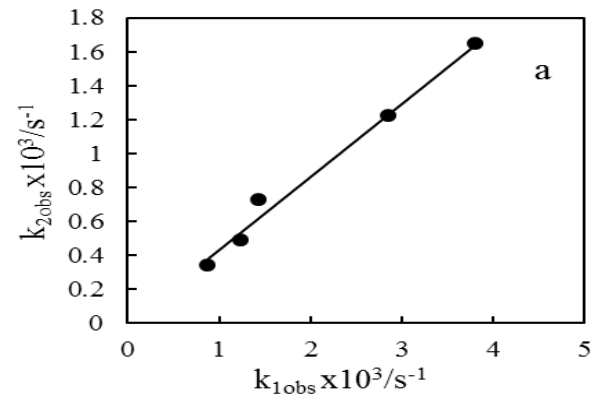
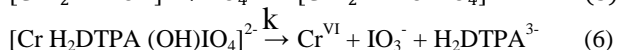
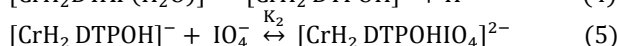
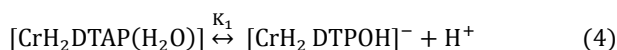


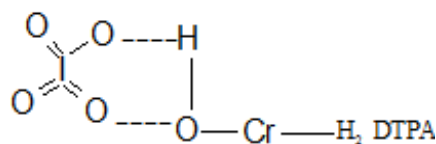
Fig. 5: Variation of k_{1obs} with k_{2obs} $[Cr(III)\text{-DTPA}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[KIO_4] = 1.997 \times 10^{-3} \text{ mol dm}^{-3}$, a-Temp.= 17°C and different pH, b- pH=7 and different temp.

When all experimental conditions were kept constant except the periodate concentration, the observed first order rate constant is directly proportional to the concentration of periodate and a linear relationship was obtained when observed rate constant was plotted versus periodate concentration reaching a limiting value of high periodate concentration. The variation k_{obs} with $[IO_4^-]$ are small indicating high association between the two reactants. A Michealis-Menten plot with respect to periodate concentrations resulted in linear relationship with non-zero intercept by plotting of k_{obs}^{-1} versus $1/[IO_4^-]$ (Fig. 6).

The dependence of the observed rate constants on the pH of the medium is presented in (Fig. 7), where straight lines measurable intercepts were obtained when k_{obs}^{-1} values were plotted versus $[H^+]$ at different temperatures. A mechanism consistent with the observed kinetics is

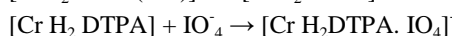
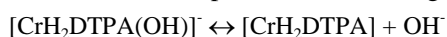


An inner sphere mechanism is proposed for oxidation of the Cr(III)DTPA complex with periodate, in which the hydroxo complex is the bridged to periodate (scheme 1).

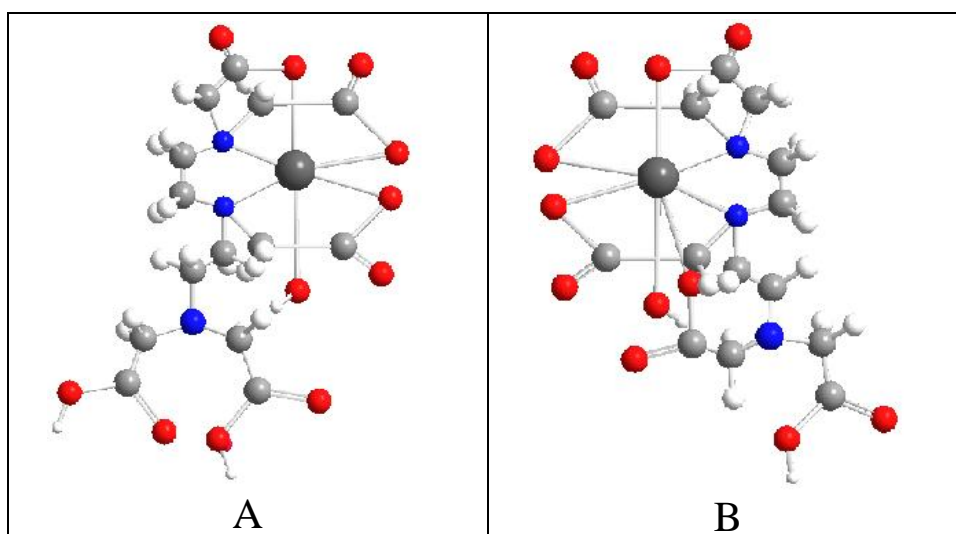


(Scheme 1)

This proposal is supported by the inverse dependence of the rate on the hydrogen ion concentration. Therefore the periodate replaces the hydroxyl group and the substitution takes place in the two stages;



The labilizing effect of the free carboxylate of the Cr(III) DTPA complex, (scheme 2), through its inductive effect reflects the easy rupture of Cr – OH bond and facilitate the insertion of periodate in the coordination sphere of chromium (III). Ogino et al [17] showed that with the quinquedentate Cr-EDTA complex there is a rapid equilibration with acetate ligand (replacement of a coordinated H_2O by CH_3COO^- anion), whereas with the structurally related quinquedentate Cr-MEDTA (META is N-methyl-ethyl-NN'N'-triacetic acid), the methyl group is unable to labilise the coordinated water molecule. The labilisation effect of the carboxylate was attributed to a transient six dentate coordination of EDTA [16]. This suggests that bond breaking and bond formation processes are taking place through a common entering IO_4^- and leaving coordinated OH^- .



(Scheme 2): A- Cr-DTPA complex, B- transient Cr-DTPA complex

From the above mechanism, the rate of reaction can be represented as follows:

$$\text{rate} = k [\text{CrH}_2\text{DTPA}(\text{OH}) \cdot \text{IO}_4^{2-}] \quad (7)$$

$$= kK_2[\text{CrH}_2\text{DTPA}(\text{OH})^-][\text{IO}_4^-] \quad (8)$$

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

$$[\text{Cr(III)}]_{\text{T}} = [\text{CrH}_2\text{DTPA}(\text{OH})^-] + [\text{CrH}_2\text{DTPA}(\text{H}_2\text{O})] + [\text{CrH}_2\text{DTPA}(\text{OH}) \cdot \text{IO}_4^{2-}] \quad (9)$$

$$= [\text{CrH}_2\text{DTPA}(\text{OH})^-] + \left\{ \frac{[\text{CrH}_2\text{DTPA}(\text{OH})^-][\text{H}^+]}{K_1} + K_2[\text{CrH}_2\text{DTPA}(\text{OH})^-][\text{IO}_4^-] \right\}$$

$$[\text{Cr(III)}]_{\text{T}} = [\text{CrH}_2\text{DTPA}(\text{OH})^-] \left\{ 1 + \frac{[\text{H}^+]}{K_1} + K_2[\text{IO}_4^-] \right\} \quad (10)$$

$$= [\text{CrH}_2\text{DTPA}(\text{OH})^-] \left\{ \frac{K_1 + [\text{H}^+] + K_1K_2[\text{IO}_4^-]}{K_1} \right\} \quad (11)$$

$$\therefore \text{rate} = \frac{kK_1K_2[\text{Cr(III)}]_{\text{T}}[\text{IO}_4^-]}{K_1 + [\text{H}^+] + K_2K_1[\text{IO}_4^-]} \quad (12)$$

$$k_{\text{obs}} = \frac{kK_1K_2[\text{IO}_4^-]}{K_1 + [\text{H}^+] + K_1K_2[\text{IO}_4^-]} \quad (13)$$

Equation (13) can be rearranged to give:

$$\frac{1}{k_{\text{obs}}} = \frac{K_1 + [\text{H}^+]}{kK_2K_1[\text{IO}_4^-]} + \frac{1}{k} \quad (14)$$

From (eq. 14) and (Fig. 6), it follows that the slopes of the plots can be represented by:

$$\text{slope} = \frac{K_1 + [\text{H}^+]}{kK_2K_1} = \frac{1}{kK_2} + \frac{[\text{H}^+]}{kK_2K_1} \quad (15)$$

It is obvious, from (eq. 15) and (Fig. 6) that the slope is dependent upon $[\text{H}^+]$.

This plot is shown in (Fig. 8) which indicates the validity of the proposed mechanism. The K_1 value was calculated from (eq. 15) and (Fig. 8) as $\text{p}K_1 = 6.31$. The rate constant for the intramolecular electron transfer, k , and the equilibrium constant for the formation of the activated complex K_2 , at different pH values are listed in Table 3, together with the ΔH^* and ΔS^* values. Table 3 illustrates that K_2 (eq.5) decreases as the pH increases, due to the increase of chromate ions concentration with

increasing pH value (k_{obs} is directly proportional to pH). This is supported that chromate ions are responsible for the inflection of straight line. Linear isokinetic plot for oxidation of hydroxochromium(III) complexes by periodate, (Fig. 9) indicates that they follow the same mechanism.

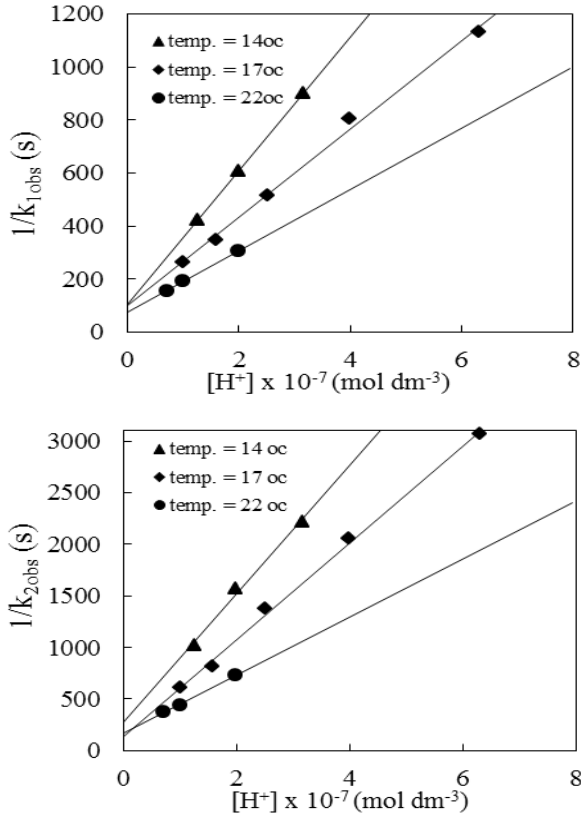


Fig. 7: The inverse dependence of $k_{1\text{obs}}$ and $k_{2\text{obs}}$ on the concentration of the hydrogen ion at various temperature, $[\text{KIO}_4] = 1.997 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Cr(III)-DTPA}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$.

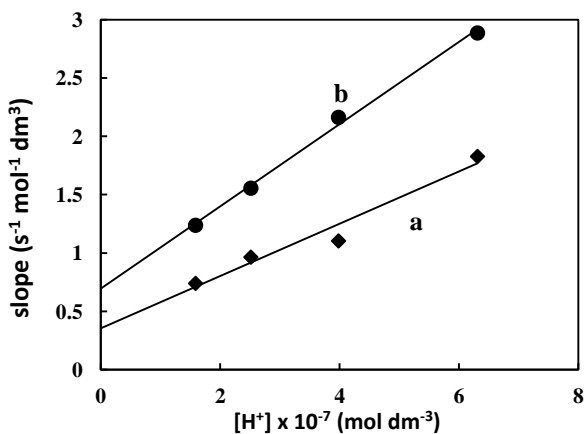


Fig. 8: Plot of $1/kK_2 + [\text{H}^+] / kK_1K_2$ versus hydrogen ion concentration. Temp = 17 °C, $[\text{Cr(III)-DTPA}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, a-short reaction time, b-long reaction time.

In the oxidation of Cr(III)NTMP (NTMP nitrilotris (methylenephosphonic acid) by periodate [7], the rate constant was equal $0.236 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25°C and pH = 6.75 comparing to a value of $1.64 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 22°C and pH = 6.7 for the present study. The higher value

for the reaction of Cr(III)DTPA complex with periodate than that for Cr(III)NTMP complex was due to:

- i- the lower negative charge of the Cr(III)DTPA (-1) than that for Cr(III)NTMP(-3).
- ii- the bulkiness of the tetrahedral phosphonate groups compared to the planer carboxylate which retards the reaction rate.

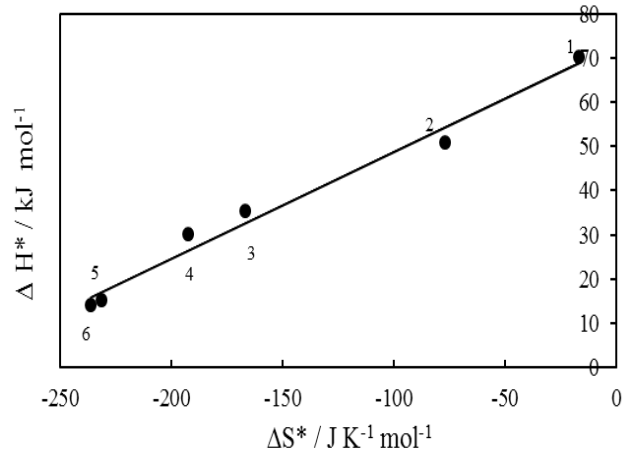


Fig. 9: Isokinetic plot for oxidation of chromium(III)-complexes by periodate, (1,2) this work, (3) [9], (4) [4], (5) [6], (6) [8].

Conclusion

The oxidation of diethylenetriaminepentaacetato chromium (III), (Cr(III)-DTPA), by periodate is assigned an inner-sphere mechanism. A common mechanism for the oxidation of (Cr(III)-DTPA by periodate is proposed and is supported by the excellent isokinetic relationship between ΔH^* and ΔS^* for oxidation of hydroxochromium(III) complexes by periodate indicates that they follow the same mechanism.

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