June 2009 Volume 4 Issue 2

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 4(2), 2009 [59-67]

Kinetics and mechanism of oxidation of a ternary nitrilotriacetatochromium(III) complexes involving L-histidine and DL-aspartic as a secondary ligands by periodate

Hassan A.Ewais[1]*, Mohamed A.Habib[2]

[1]Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef City, (EGYPT)

[2]Chemistry Department Faculty of Science, Al-Tahadi University, Serit, (LYBIA)

E-mail : hshalby2002@yahoo.com

Received: 17th May, 2009 ; Accepted: 22nd May, 2009

ABSTRACT

The oxidation of$[Cr^{III}(NTA)(Hist)(H_2O)]^-$ and$[Cr^{III}(NTA)(Asp)(H_2O)]^-$ (NTA = nitrilotriacetic acid, Hist = L-histidine and Asp=DL-aspartic acid) by periodate in aqueous medium has been studied spectrophotometrically over 15.0-35.0^{0}C range. The reaction is first order with respect to both$[IO_4^-]$ and the complex concentration, and the rate increases over the pH range 3.40-4.45 in both cases. The experimental rate law is consistent with a mechanism in which both the deprotonated forms,$[Cr^{III}(NTA)(Hist)(OH)]^{2-}$ and$[Cr^{III}(NTA)(Asp)(OH)]^{2-}$ are significantly more reactive than the conjugate acids. It is proposed that electron transfer proceeds through an inner-sphere mechanism via coordination of IO_4^- to chromium(III). A common mechanism for the oxidation of some chromium(III) complexes by periodate is proposed, and this is supported by an excellent isokinetic relationship between ΔH^* and ΔS^* values for these reactions.

KEYWORDS

Nitrilotriacetatochromium(III)-complexes;
Periodate oxidation;
Inner-sphere mechanism;
Isokinetc relationship.

INTRODUCTION

Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases such as nitrilotriactic acid (NTA) and iminodiacetic (IDA) acid with some transition metals have attracted much interest as they can display exceptionally high stability and may be biologically relevant[1,2]. The use of transition metal complexes of nitrilotriacetic acid have been widely adopted in biology, and are gaining increasing use in biotechnology, particularly in the protein purification technique known as immobilized metal-ion chromatography[3]. The chromium (III)-complexes of α-amino acid are biologically available, depends on the complexing ability of the ligands for chromium against OH^-. The chromium aids in the transportation of amino acids through the cell membrane[4].

The biological oxidation of chromium from the trivalent to hexavalent states is an important environmental process because of the high mobility and toxicity of chromium(VI)[5]. Recently, Cr(III) oxidation to Cr(V) and/or Cr(VI) in biological systems came into consideration as a possible reason of anti-diabetic activities of some Cr(III) complexes, as well as of long-term toxicities of such complexes[6]. The specific interactions of Cr(III) ions with cellular insulin receptors[7], are caused by intra-or extracellular oxidations of Cr(III) to Cr(V) and/or Cr(VI) compounds, which act as protein tyrosine phosphatase (PTP) inhibitors.

Periodate oxidations have been reported to play an important role in biological determinants[8-10]. Studies of the kinetics of periodate oxidations on a series of dextran oligomers, polymers and some dimeric carbohydrates[8] were investigated to show the dependence of the kinetic rates on the molecular weight. Caffeic acid (3,4-dihydroxy cinnamic acid) was oxidized by means of sodium periodate that mimics the mechanism of polyphenol oxidase, the reaction leads to the formation of the antioxidant product 2-s-cysteinyl caffeic adduct which exhibits slightly improved antiradical activity in relation with the parent molecule (Caffeic acid)[9].

The imidazol-modified M-salophen/$NaIO_4$ oxidizing system can be applied to oxidize a large number of primary aromatic amines in high to good yield at short times and room temperature[10]. Also, an efficient oxidation of Hantzsch 1,4-dihydropyridines to their corresponding pyridine derivatives with $(Bu_4N)IO_4$ catalyzed by[Mn(TPP)Cl], was reported[11]. Inner-sphere mechanism for oxidation of chromium(III)-complex of some amino acids[12,13], and some nucleosides[14-16] by periodate also has been proposed with the hydroxo group acting as bridging ligand, or through the substitution of coordinated H_2O by$[IO_4]^-$.

Oxidation of ternary nitrilotriacetatocobalt(II)-complexes involving succinate, malonate, tartarate, maleate and benzoate as a secondary ligands by periodate has been investigated[17-19]. In all cases, initial cobalt(III) products were formed, and these changed slowly to the final cobalt(III) products. It is proposed that the reaction follows an inner-sphere mechanism, which suggested relatively faster rates of ring closure compared to the oxidation step. Because, an I^{VI} in the initial product is probably substituted by water molecule with a very slow rate due to inertness of Co^{III} and Co^{II}-OIO_3 bond is being stronger than Co-H_2O bond. But, the kinetics of oxidation of cobalt(II) complexes of propylenediaminetetraacetate (PDTA)[20], 1,3-diamino-2-hydroxypropanetetraacetate (HPDTA)[20], diethyl enetriamine- pentaacetate (DPTA)[21], trimethylene diaminetetraacetate (TMDTA)[22] and ethyleneglycol, bis(2-aminoethyl)ether,N,N,N',N'-tetraacetate (EGTA)[22] by periodate gave only the final product.

Periodate oxidations of the chromium(III) complex of nitrilotriacetic acid[23], 2-aminopyridine[24] and iminodiacetic acid[25] were carried out. In all cases the electron transfer proceeds through an inner-sphere mechanism via coordination of IO_4^- to chromium(III).

In order to gather more information, I thought it was important to investigate the kinetics and mechanism of the oxidation of a ternary complexes of chromium(III) involving nitrilotriacetic acid as a primary ligand and L-histidine or DL-aspartic acid as a secondary ligands by periodate to study the effect of secondary ligands on the stability of$[Cr^{III}(NTA)(H_2O)_2]$[23] towards oxidation.

EXPERIMENTAL

Materials and solutions

The ternary nitrilotriacetatochromium(III) complexes involving L-histadiene and DL-aspartic acid as a secondary ligands were prepared by the reported method[26]. All chemicals used in this study were of reagent grade (Analar, BDH, Sigma). Buffer solutions were prepared from NaCl and HCl of known concentration. $NaNO_3$ was used to adjust ionic strength in the different buffered solution. Doubly distilled H_2O was used in all kinetic runs. A stock solution of $NaIO_4$ (Aldrich) was prepared by accurate weighing and wrapped in aluminum foil to avoid photochemical decomposition[27].

Kinetic procedures

The UV-visible absorption spectra of the products of oxidation of$[Cr^{III}(NTA)(Hist)(H_2O)]^-$ and$[Cr^{III}(NTA)(Asp)(H_2O)]^-$ by IO_4^- were followed spectrophotometrically for a definite period of time using the JASCO UV-530 spectrophotometer. All reactants were thermally equilibrated for ca 15 min. in an automatic circulation thermostat, thoroughly mixed and quikly transferred to an absorption cell. The oxidation rates were measured by monitoring the absorbance of Cr^{VI} at 350 nm, on a Jenway 3600 spectrophotometer, where the absorption of the oxidation products is maximal at the reaction pH. The pH of the reaction mixture was measured using a G-C825 pH-meter.

Pseudo-first-order conditions were maintained in all runs by the presence of a large excess (>10-fold) of IO_4^-. The ionic strength was kept constant by the addition of $NaNO_3$ solution. The pH of the reaction mixture

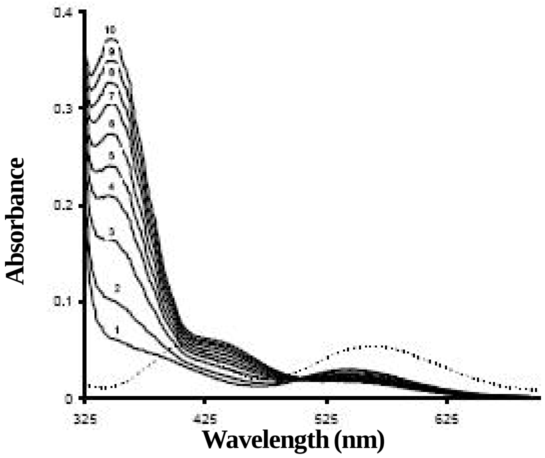

Figure 1: Absorbance spectra of reaction mixtures versus time. Curves (1)-(10) were recorded at 2, 5, 10, 15,20,25,30, 35, 40 and 50 min. respectively, from the time of initiation; [complex] = 2.5 × 10^{-4} M, [IO_{4^-}] =0.02 M, I = 0.2 M, pH = 4.05 and T = 30^0C Curve (…………) spectrum of the complex (1.0 × 10^{-3} M) at the same pH

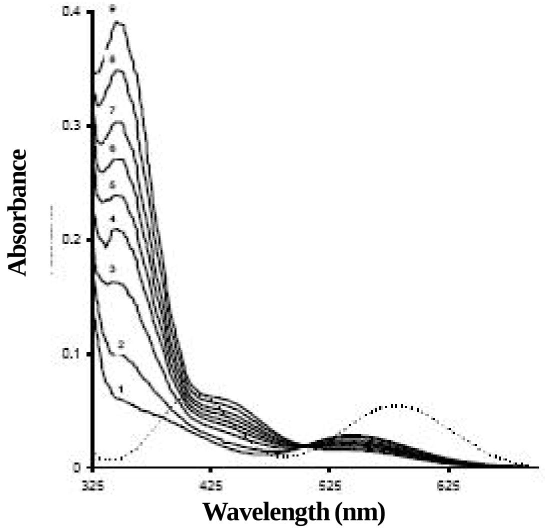

Figure 2: Absorbance spectra of reaction mixtures versus time. Curves (1)-(9) were recorded at 2, 5, 10, 15,20,25,30, 40 and 50 [complex = 2.5 × 10^{-4} M, [IO_4^-] = 0.02 M, I = 0.2 M, pH = 4.05 and T = 30^0C. Curve (…………) spectrum of the complex (1.0 × 10^{-3} M) at the same pH

was found to be constant during the reaction run.

Oxidation products

The ultraviolet visible absorption spectra of the oxidation products of[Cr^{III}(NTA)(Hist)(H_2O)]$^-$ and[Cr^{III}(NTA)(Asp)(H_2O)]$^-$ by periodate were recorded over time on JASCO UV- 530 spectrophotometer (Figures 1 and 2). The data show that the chromium(III)-complex peaks at 560 and 575 nm for[Cr^{III}(NTA)(Hist)(H_2O)]$^-$ and[Cr^{III}(NTA)(Asp)(H_2O)]$^-$ have disappeared and has been replaced by a peak at 350 nm. The presence of one isosbestic point at 500 and 504 nm in the absorption spectra as shown in figures 1 and 2, respectively, was taken as the criterion for the presence of two absorbing species in equilibrium.

Stoichiometry

A known excess of Cr^{III} complex was added to IO_4^- solution, the absorbance of Cr^{VI} produced was measured at 350 nm after 24 hour from the onset of the reaction. The quantity of Cr^{III} consumed was calculated using the molar absorptivity of Cr^{VI} at the employed pH.

Test for free radical

In order to verify the presence of the free radicals in the reaction, the following test was performed. A reaction mixture containing acrylonitrile was kept for 24 h in an inert atmosphere. On diluting the reaction mixture with methanol since no precipitate was formed hence this suggests that there no possibility of free radical intervention in the reaction.

RESULTS

Kinetics of oxidation of[Cr^{III}(NTA)(Hist)(H_2O)]$^-$

Oxidation of[Cr^{III}(NTA)(Hist)(H_2O)]$^-$ by periodate was studied over the (3.40-4.45) pH range, 0.20 mol dm^{-3} ionic strength, (0.50-5.0) × 10^{-2} mol dm^{-3} periodate concentration range, (1.25-6.25) × 10^{-4} mol dm^{-3} complex concentration range, and (15.0-35.0)^{0}C.

The stoichiometry of the[Cr^{III}(NTA)(Hist)(H_2O)]$^-$/ IO_4^- reaction can be represented by Equation (1).

$$2Cr^{III} + 3I^{VII} \rightarrow 2Cr^{VI} + 3I^{V} \qquad (1)$$

The ratio of I^{VII} initially present to Cr^{VI} produced was 1.50, the stoichiometry is consistent with the observation that IO_3^- does not oxidize the Cr^{III} complex over the pH range where the kinetics was investigated.

Plots of ln (A_∞-A_t) versus time were linear up to 90 % from the beginning of reaction where A_t and A_∞ are absorbance 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 chromium(III)-complex was var-

TABLE 1: Dependence of the rate, k_{obs} ($\times 10^4$, s^{-1}) on[$Cr^{III}(NTA)(Hist)(H_2O)]^{-a}$, [$IO_4^-$] and temperature at pH = 4.05

10^2[IO_4^-](mol dm^{-3})	10^4 k_{obs} (s^{-1})T = 15°C	20°C	25°C	30°C	35°C
0.5	1.20 ±0.02	1.70±0.01	1.92±0.03	2.68±0.05	3.56±0.03
1.0	2.10±0.01	3.10±0.04	3.75±0.05	4.71±0.08	7.30±0.10
1.5	2.95±0.04	-	5.78±0.08	6.58±0.15	9.26±0.08
2.0	3.86±0.06	6.03±0.07	7.15±0.11	9.11±0.24	11.60±0.23
3.0	5.75±0.05	8.53±0.06	9.31±0.09	13.86±0.35	18.38±0.37
4.0	6.95±0.07	11.15±0.12	12.48±0.20	17.45±0.40	26.60±0.55
5.0	9.05±0.10	13.68±0.25	17.33±0.31	23.81±0.62	31.05±0.80

[a][$Cr^{III}(NTA)(Hist)(H_2O)^-$] = 2.50 × 10^{-4} mol dm^{-3}; I[a] = 0.20 mol dm^{-3}; 10^4 k_{obs} = 7.08±0.03, 7.44±0.02, 6.90±0.05 and 7.32±0.04 s^{-1} at 10^{-4}[$Cr^{III}(NTA)(Hist)(H_2O)^-$] = 1.25, 3.75, 5.0 and 6.25 mol dm^{-3}, respectively at 25.0°C, and[IO_4^-] = 0.02 mol dm^{-3}. While at I = 0.3, 0.4, 0.5 and 0.6 mol dm^{-3}, 25.0°C, [a][$Cr^{III}(NTA)(Hist)(H_2O)^-$] and[$IO_4^-$] = 0.02 mol dm^{-3}, 10^4k_{obs} = 7.73±0.05, 8.0±0.07, 8.40±0.08 and 9.15±0.07 s^{-1}, respectively

TABLE 2 : Effect of pH on k_{obs} at[$Cr^{III}(NTA)(Hist)(H_2O)]^-$ = 2.50 × 10^{-4} mol dm^{-3} I = 0.20 mol dm^{-3}, and T = 25°C

10^2 [IO_4^-] (mol dm^{-3})	10^4 k_{obs}s^{-1} pH = 3.40	pH=3.72	pH=4.05	pH=4.27	pH=4.45
0.5	0.36±0.01	0.74±0.01	1.92±0.03	3.25±0.05	4.41±0.02
1.0	0.75±0.01	1.26±0.03	3.75±0.02	6.21±0.12	8.91±0.07
1.5	1.05±0.02	2.20±0.05	5.78±0.08	8.63±0.21	13.96±0.25
2.0	1.38±0.04	2.55±0.02	7.15±0.18	11.70±0.39	21.30±0.37
3.0	--	4.18±0.07	9.31±0.24	17.13±0.63	--
4.0	2.16±0.03	5.51±0.10	12.48±0.33	24.43±0.80	24.65±0.54
5.0	3.16±0.05	6.25±0.16	17.33±0.47	--	26.80±1.0

ied at constant periodate concentration, indicating first-order dependence on complex concentration.

At constant[H^+] and ionic strength, $1/k_{obs}$ varies linearly with 1/[IO_4^-] at different temperatures (Figure 3), and the kinetics of the reaction are described by Equation (2):

$$d[Cr^{VI}]/dt = \{a[IO_4^-]_T / 1 + b[IO_4^-]_T\}[Cr^{III}]_T \quad (2)$$

$$k_{obs} = a[IO_4^-]_T / (1 + b[IO_4^-]_T) \quad (3)$$

or

$$1/k_{obs} = 1/a\,[IO_4^-]_T + b/a \quad (4)$$

Plots of $1/k_{obs}$ *versus* 1/[IO_4^-] at different pH values (3.40-4.45) (Figure 4), show that the reaction rate increased as the pH increased over the range studied (TABLE 2). The rate of reaction increases by the increasing the ionic strength of the solution (TABLE 1). This phenomenon has been attributed to the fact that the reaction takes place between the same charged species.

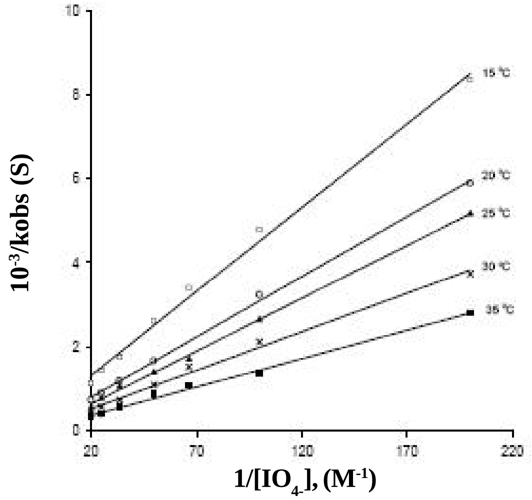

Figure 3: Plot of 1/kobs versus 1/[IO_{4-}] at different temperatures

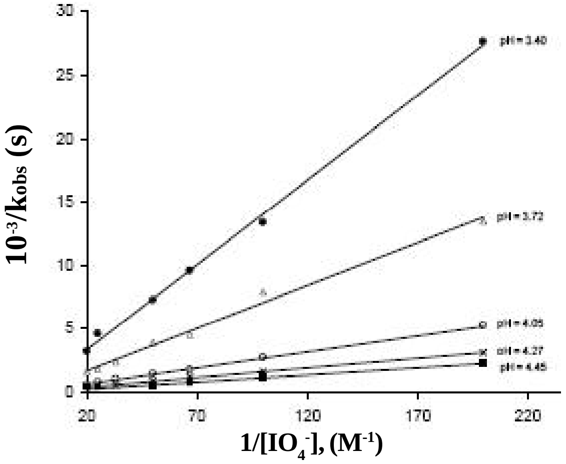

Figure 4: Plot of $1/k_{obs}$ versus 1/[IO_4^-] at different pH

Kinetics of oxidation of[$Cr^{III}(NTA)(Asp)(H_2O)]^-$

Under the same experimental condition for the oxidation[$Cr^{III}(NTA)(Asp)(H_2O)]^-$, the kinetics of oxidation of the[$Cr^{III}(NTA)(Asp)(H_2O)]^-$ by periodate were studied. The overall stoichiometry of[Cr^{III}(NTA)(Asp)(H_2O)]$^-$/[IO_4]$^-$ reaction can be represented by Equation (1). The concentration of periodate initially present to chromium(VI) produced was found to be 3.0 : 2.0.

First-order plots of ln (A_∞-A_t) *versus* time were found to be linear up to 85 % from the beginning of the

TABLE 3: Variation of k_{obs} with different concentrations of periodate and different temperatures $[Cr^{III}(NTA)Asp)(H_2O)]^{-b}$ = 2.50×10^{-4} mol dm^{-3}, $[IO_4^-]$ at pH = 4.05 and I = 0.20 mol dm^{-3}

$10^2[IO_4^-]$ mol dm^{-3}	10^4 k_{obs} (s^{-1}) T = 15 °C	20°C	25°C	30°C	35°C
0.5	1.03±0.02	1.38±0.01	1.58±0.03	1.87±0.02	3.04±0.05
1.0	1.85±0.01	2.46±0.02	3.20±0.01	3.48±0.02	6.23±0.14
1.5	2.51±0.03	3.50±0.02	4.15±0.04	4.81±0.08	8.25±0.30
2.0	2.98±0.02	4.50±0.06	5.64±0.04	6.33±0.25	9.80±0.45
3.0	4.46±0.02	6.40±0.09	8.32±0.17	10.15±0.38	13.50±0.61
4.0	5.05±0.04	8.05±0.20	--	11.43±0.53	19.55±0.80
5.0	5.53±0.07	9.50±0.37	11.50±0.31	17.32±0.62	24.37±0.70

$^b[Cr^{III}(NTA)(Asp)(H_2O)]$= 2.50 × 10^{-4} mol dm^{-3}, I^b = 0.20 mol dm^{-3}, 10^4k_{obs} = 5.58±0.04, 6.08±0.02, 5.87±0.05 and 5.90±0.07 s^{-1} at $10^{-4}[Cr^{III}$ (NTA) $(Asp)H_2O)^-]$ = 1.25, 3.75, 5.0 and 6.25 mol dm^{-3}, respectively at 25.0°C, and$[IO_4^-]$ = 0.02 mol dm^{-3}. While at I = 0.3, 0.4, 0.5 and 0.6 mol dm^{-3}, 25.0°C, $^b[Cr^{III}(NTA)(Asp)(H_2O)^-]$ and$[IO_4^-]$ = 0.02 mol dm^{-3}, 10^4k_{obs} = 6.62±0.03, 7.75±0.06, 8.70±0.04 and 9.50±0.05s^{-1}, respectively

TABLE 4 : Effect of pH on k_{obs} at$[Cr^{III}(NTA)(Asp)(H_2O)]^-$ = 2.50 × 10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 25°C

$10^2[IO_4^-]$ moldm^{-3}	10^4 k_{obs} (s^{-1}) pH 3.40	3.72	4.05	4.27	4.45
0.5	0.46±0.01	0.76±0.01	1.58±0.04	3.30±0.02	5.00±0.06
1.0	1.16±0.01	1.48±0.03	3.20±0.09	6.06±0.06	8.91±0.10
1.5	--	1.96±0.01	4.15±0.07	8.23±0.15	11.10±0.23
2.0	1.73±0.03	2.72±0.02	5.64±0.18	9.78±0.28	12.80±0.33
3.0	2.15±0.02	4.36±0.08	8.31±0.32	13.1±0.43	14.80±0.80
4.0	3.30±0.04	5.98±0.12	--	17.35±0.61	19.50±1.00
5.0	5.75±0.07	7.46±0.24	11.50±0.55	20.85±0.70	30.00±1.42

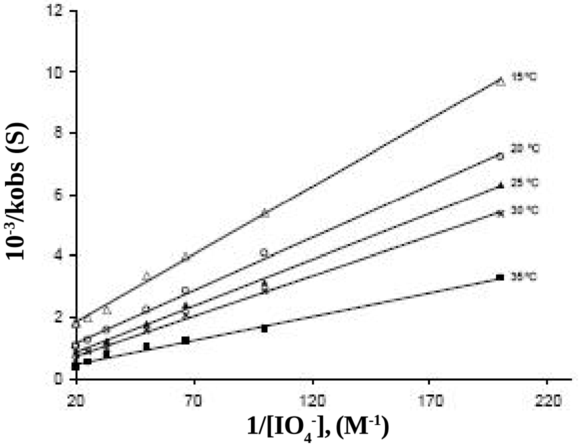

Figure 5: Plot of $1/k_{obs}$ versus $1/[IO_4^-]$ at different temperatures

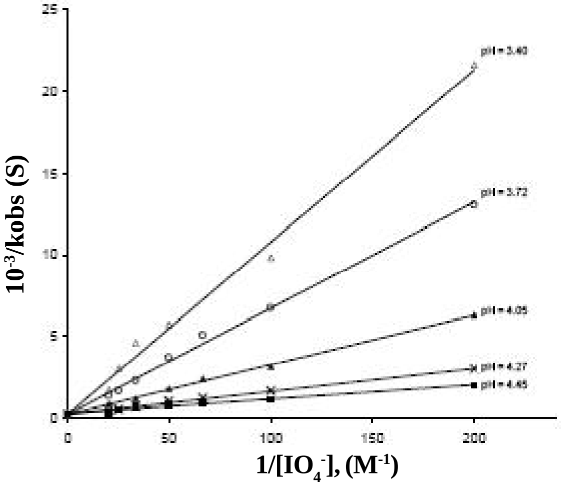

Figure 6: Plot of $/k_{obs}$ versus $1/[IO_4^-]$ at different pH

reaction. Observed rate constants, k_{obs}, were obtained from the slopes of these plots, are collected in TABLE 3. The magnitude of the observed pseudo-first-order rate constant, k_{obs}, was found to independent of the chromium(III)-complex concentration as shown in TABLE 3. This indicates the pseudo-first-order dependence on complex concentration.

At constant$[H^+]$ and ionic strength, $1/k_{obs}$ varies linearly with $1/[IO_4^-]$ at different temperatures (Figure 5), and the kinetics of the reaction are described by Equation (4)

At constant temperature $1/k_{obs}$ varies linearly with $1/[IO_4^-]$ at different pHs (3.40 – 3.45) (Figure 6), show that the rate of reaction increases with increasing pH (TABLE 4). TABLE 3 indicates that the reaction rate is increases with increasing of ionic strength.

DISCUSSION

The system which consists of a metal ion and more than one type of ligand is defined as ternary complexes such as$[Cr^{III}(NTA)(Hist)(H_2O)]^-$, and $[Cr^{III}(NTA)(Asp)$

$(H_2O)]^-$, where nitrilotriacetic acid is functioning as tridentate through two carboxylic groups and one imino group while L-histadiene or DL-aspartic acid as a secondary ligands are a bidentate. The oxidation of$[Cr^{III}$ $(NTA)(Hist)(H_2O)]^-$ by periodate may be proceeding through an inner-sphere mechanism. The assignment of an inner-sphere mechanism for this reaction seems to be supported by the fact that$[IO_4]^-$ is capable of acting as a ligand as demonstrated by its coordination by copper(III)[28] and nickel(IV)[29], in which the coordinated H_2O is substituted by I^{VII}[13].

In acidic aqueous medium the chromium(III) complex may be involved in the equilibrium shown in Equation (5):

$$[Cr^{III}(NTA)(Hist)(H_2O)]^- \rightleftharpoons [Cr^{III}(NTA)(Hist)(OH)]^{2-} + H^+ \; K_1 \quad (5)$$

K_1 can be determined potentiometrically and has the value 5.0×10^{-4} at 25^{0}C From the pH range and K_1 value, suggests involvement of the deprotonated form of the chromium(III)-complex in the rate-determining step. There is a possibility for the coordination of IO_4^-, since substitution of H_2O ligand by IO_4^- is likely to occur[14,16].

The kinetic data may be interpreted in terms of a mechanism involving rapid pre-equilibrium oxidant-chromium(III) complex formation followed by a slow intramolecular electron transfer step. A possible mechanism is described by Equations (6-10):

$$[Cr^{III}(NTA)(Hist)(H_2O)]^- \rightleftharpoons [Cr^{III}(NTA)(Hist)(OH)]^{2-} + H^+ \; K_1 \quad (6)$$

$$[Cr^{III}(NTA)(Hist)(H_2O)]^- + [IO_4^-] \rightleftharpoons [Cr^{III}(NTA)(Hist)(OIO_3)]^{2-} + H_2O \; K_2 \quad (7)$$

$$[Cr^{III}(NTA)(Hist)(OH)]^{2-} + [IO_4^-] \rightleftharpoons [Cr^{III}(NTA)(Hist)(OH)(OIO_3)]^{3-} K_3 \quad (8)$$

$$[Cr^{III}(NTA)(Hist)(OIO_3)]^{2-} \xrightarrow{k_1} \text{Products} \quad (9)$$

$$[Cr^{III}(NTA)(Hist)(OH)(OIO_3)]^{3-} \xrightarrow{k_2} \text{Products} \quad (10)$$

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

$$d[Cr^{VI}]/dt = (k_1K_2 + k_2K\,K_1/[H^+]) [Cr^{III}(NTA)(Hist)(H_2O)]^-[IO_4^-] \quad (11)$$

If we assume that$[Cr^{III}]_T$ represents all the different forms of chromium(III), then:

$$[Cr^{III}]_T = [Cr^{III}(NTA)(Hist)(H_2O)]^- \{1 + (K_1/[H^+]) + [IO_4^-](K_2 + (K_1K_3/[H^+])\} \quad (12)$$

Substituting$[Cr^{III}(NTA)(Hist)(H_2O)]^-$ from Equation (12) into Equation (11) gives:

$$d[Cr^{VI}]/dt = (k_1K_2 + k_2\,K_3\,K_1/[H^+])[IO_4^-][Cr^{III}]_T / \{1 + (K_1/[H^+]) + (K_2 + K_1K_3/[H^+])[IO_4^-]\} \quad (13)$$

$$k_{obs} = [IO_4^-]\{k_1K_2 + (k_2K_1K_3/[H^+])\} / \{1 + (K_1/[H^+]) + (K_2 + K_1K_3/[H^+])[IO_4^-]\} \quad (14)$$

$$k_{obs} = \{(k_1K_2[H^+] + k_2K_1K_3)[IO_4^-]\} / \{[H^+] + K_1 + (K_2[H^+] + K_1K_3)[IO_4^-]\} \quad (15)$$

Since, the deprotonated form, $[Cr^{III}(NTA)(Hist)(OH)]^{2-}$, is considered to be more reactive form than its conjugate acid, we can assume that $K_3 >> K_2$ and that Equation (15) may be reduced to Equation (16).

$$k_{obs} = k_2K_1K_3[IO_4^-] / \{[H^+] + K_1 + (K_2[H^+] + K_1K_3)[IO_4^-]\} \quad (16)$$

Upon rearrangement

$$1/k_{obs} = 1/[IO_4^-]\{([H^+]/k_2K_1K_3) + (1/k_2K_3)\} + \{(K_2[H^+]/k_2K_1K_3) + (1/k_2)\} \quad (17)$$

At constant$[H^+]$, Equation (17) is identical to the experimental rate law shown in Equation (3) where,

$$a = (k_2K_1K_3)/(K_1 + [H^+]) \text{ and } b = (K_2[H^+] + K_1K_3)/(K_1 + [H^+])$$

Plot of both $1/a = K_1 + [H^+] / k_2K_1K_3$ and $b/a = (K_2[H^+] + K_1K_3) / k_2K_1K_3$ versus$[H^+]$ are linear according to the equation $y = mx + c$ with correlation coefficient of $r = 0.9953$ and 0.9876, respectively. The K_1 value was calculated by dividing the intercept by the slope of a plot 1/a versus$[H^+]$ as 8.64×10^{-4} mol dm^{-3} at 25^{0}C. The intramolecular electron transfer rate constant, k_2, was calculated from the intercept of a plot b/a versus$[H^+]$ as 3.20×10^{-2} s^{-1}. The value of K_2 calculated by dividing the slope of both b/a and 1/a versus$[H^+]$ by as 5.22 mol^{-1} dm^3. Substituting the value of k_2 gives K_3 from the intercept of plot of 1/a versus$[H^+]$ as 10.98 mol^{-1} dm^3. The value of K_1 is in a good agreement with that obtained potentiometrically ($K_1 = 5.0 \times 10^{-4}$) and the value of K_3 (10.98) is more than K_2 (5.22) provides a good basis for the suggested mechanism. This indicates the validity of our proposed mechanism.

Thermodynamic activation parameters, ΔH^* and ΔS^* associated with constant (a) in Equation (2), were obtained from a least-squares fit to the transition state theory equation as 36.5±3.3 kJ mol^{-1} and -149±11.2 JK^{-1} mol^{-1} respectively. Both ΔH^* and ΔS^* are composite values including formation of$[Cr^{III}(NTA)(Hist)(OH)(OIO_3)]^{3-}$ in the intramolecular electron-transfer step.

In case of$[Cr^{III}(NTA)(Asp)(H_2O)]^-$, the observed $[H^+]$ dependence suggested the involvement of the deprotonated from of the chromium(III) complex,

$Cr^{III}(NTA)(Asp)(OH)]^{2-}$ in the rate determining step. So, in acid medium$[Cr^{III}(NTA)(Asp)(H_2O)]^-$, may participate in the equilibrium shown in Equation (18):

$$[Cr^{III}(NTA)(Asp)(H_2O)]^- \rightleftharpoons [Cr^{III}(NTA)(Asp)(OH)]^{2-} + H^+ \ K_4 \qquad (18)$$

K_4 was measured potentiometrically has the value 4.46×10^{-5} at 25^0C. From the pH (3.40 - 4.45) and the K_4 value, it is clear that $[Cr^{III}(NTA)(Asp)(OH)]^{2-}$ may be the reactive species. Also, from the results in TABLE 3, show that the rate of reaction increases with increasing of ionic strength. This behavior is expected since the reaction takes place between the same charged species. Therefore$[Cr^{III}(NTA)(Asp)(OH)]^{2-}$ may be the reactive species. An inner-sphere process may still be accommodated through replacement of coordinated H_2O in$[Cr^{III}(NTA)(Asp)(H_2O)]^-$ by IO_4^-[13].

A possible mechanism is described by Equations 19 - 147.

$$[Cr^{III}(NTA)(Asp)(H_2O)]^- \rightleftharpoons [Cr^{III}(NTA)(Asp)(OH)]^{2-} + H^+ \ K_4 \qquad (19)$$

$$[Cr^{III}(NTA)(Asp)(OH)]^{2-} + I^{VII} \rightleftharpoons [Cr^{III}(NTA)(Asp)(OH)(I^{VII})]^{3-} \ K_5 \qquad (20)$$

$$[Cr^{III}(NTA)(Asp)(OH)(I^{VII})]^{3-} \xrightarrow{k_3} \text{Products} \qquad (21)$$

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

$$d[Cr^{VI}]/dt = k_3K_5[Cr^{III}(NTA)(Asp)(OH)]^{2-}[I^{VII}] \qquad (22)$$

If$[Cr^{III}]_T$ represents the total concentration of Cr^{III} species, then.

$$[Cr^{III}]_T = [Cr^{III}(NTA)(Asp)(OH)]^{2-} \{[H^+]/K_4 + 1 + K_5[I^{VII}]_T\} \qquad (23)$$

Substitution for$[Cr^{III}(NTA)(Asp)(OH)]^{2-}$ from Equation (23) into Equation (22) gives.

$$d[Cr^{VI}]/dt = k_3K_5[Cr^{III}]_T[I^{VII}]_T /\{1 + [H^+] / K_4 + K_5[I^{VII}]_T\} \qquad (24)$$

and

$$k_{obs} = k_3K_5[I^{VII}]_T / \{1 + [H^+] / K_4 + K_5[I^{VII}]_T\} \qquad (25)$$

which on rearrangment, gives

$$1/k_{obs} = (K_1 + [H^+])/k_3K_4K_5[I^{VII}]_T + 1/k_3 \qquad (26)$$

At constant$[H^+]$, Equation (26) follows, in which A is a constant:

$$1/k_{obs} = A / k_3K_4K_5[I^{VII}]_T + 1/k_3 \qquad (27)$$

which is identical to the experimental results shown in Equation (3) where $a = k_3K_4K_5/A$ and $b = K_4K_5 /A$.

The values of 10^3k_3 at the temperature used, calculated from Equation (27), are 1.05, 2.19, 3.93, 5.02 and 6.30 $mol^{-1}\ dm^3\ s^{-1}$ at 15, 20, 25, 30 and 35, respectively. The thermodynamic activation parameters associated with k_3 obtained from a least-squares fit to the transition state theory equation are $\Delta H = 64.6\pm8.5$ $kJ\ mol^{-1}$ and $\Delta S = -76.0\pm7.7\ JK^{-1}mol^{-1}$.

From Equation (27), it follows that the slope of the plots can be represented by Equation (28):

$$\text{Slope} = [H^+] / k_3K_4K_5 + 1/ k_3K_5 \qquad (28)$$

It is obvious from Equation (28) that the slope is dependent on$[H^+]$. This is plot can be given as the linear equation y = mx + c, with a correlation coefficient of 0.9890. The values of K_4 and K_5 were calculated from Equation (28) as $3.72\times10^{-5}\ mol\ dm^{-3}$ and 490 $mol^{-1}\ dm^3$, at 25^0C and $I = 0.20\ mol\ dm^{-3}$, respectively. Value of K_4 is in good agreement with that obtained potentiometrically ($K_1 = 4.45 \times10^{-5}$).

In comparison with the oxidation of$[Cr^{III}(NTA)(H_2O)_2]$[23] under the same conditions, the deprotonated complexes are significantly found to be more reactive than their conjugated acids. The value of the intramolecular electron transfer rate constant, $k^{e.t.}$, for the oxidation reaction increases in the order:$[Cr^{III}(NTA)(H_2O)_2] > [Cr^{III}(NTA)(Hist)(H_2O)]^- > [Cr^{III}(NTA)(Asp)(H_2O)]^-$ at 25^0C (TABLE 5). This means that the stability of these complexes toward oxidation increase in the following order:$[Cr^{III}(NTA)(Asp)(H_2O)]^- > [Cr^{III}(NTA)(Hist)(H_2O)]^- > [Cr(NTA)(H_2O)_2]$. This may be due to the presence of the amino acid as a secondary ligand in the ternary complexes, increase the stability of chromium(III) towards oxidation than binary complex,$[Cr^{III}(NTA)(H_2O)_2]$.

The small ΔH* values and large negative activation entropies reasonably could reflect some nonadibatically in the electron transfer process[30]. Both ΔH* and ΔS* then may be expected to systematically increases as the orientation of the oxidant in the precursor complex is alter so as to enhance overlap between donor and acceptor redox orbitals and consequently the probability of adiabatic electron transfer[30]. The relatively low value of ΔH* for$[Cr^{III}(NTA)(Hist)(H_2O)]^-$ is due to its composite value including formation which may be exothermic and intramolecular electron transfer which may be endothermic.

Enthalpies and entropies of activation for the oxidation of chromium(III) complexes by periodate are collected in TABLE 5. ΔH* and ΔS* for the oxidation of these complexes were calculated related to intramolecular electron transfer steps except

TABLE 5: Enthalpies and entropies of activation for the oxidation of some chromium(III) complexes by periodate

Complex	10^3 k^{et} (s^{-1})	ΔH* (KJ/mol)	-ΔS* (J/Kmol)	Ref.	Figure 7 key
$[Cr^{III}(TOH)(H_2O)]$	2.95	76±2.1	38.7±7.1	33	1
$[Cr^{III}(NTA)(Asp)(H_2O)]^-$	3.93	64.6±8.5	76±7.7	This work	2
$[Cr^{III}(Ud)(Asp)(H_2O)_3]^{2+}$	0.70	59.5±9.2	107±35.2	22	3
$[Cr^{III}(NTA)(Hist)(H_2O)]^-$	32.0	36.5±3.3	149±11.2	This work	4
$[Cr^{III}(Ud)(H_2O)_3]^{3+}$	9.31	37.8±3.1	158.3±39.3	22	5
$[Cr^{III}(HIDA(Val)(H_2O)]$	1.22	41.7±1.5	162.5±3.3	34	6
$[Cr^{III}(Arg)_2(H_2O)_2]^+$	3.46	30±2	192±12.4	13	7
$[Cr^{III}(NTA)(H_2O)_2]$	62.0	14.0±2.4	221±8.8	23	8
$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$	1.82	15.9±1.2	227±5	34	9
$[Cr^{III}(HIDA)_2(H_2O)]$	10.9	12.3±1	240.7±7	25	10

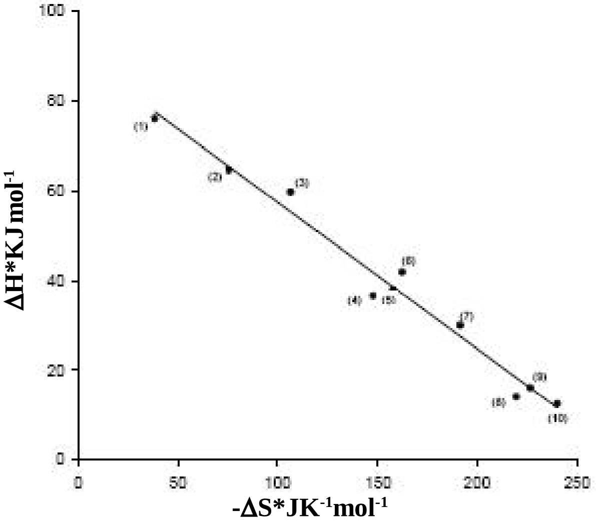

Figure 7: Enthalpies and entropies of activation of some chromium(III)-complexes

for$[Cr^{III}(HIDA)_2(H_2O)]$, $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ and$[Cr^{III}(NTA)(Hist)(H_2O)]^-$, ΔH* and ΔS* are composite values including the enthalpy of formation of the precursor complexes and the intramolecular electron transfer steps. A plot of ΔH* versus ΔS* for these complexes is shown in figure 7, and an excellent linear relationship was obtained. Similar linear plots were found for a large number of redox reactions[30,31] and for each reaction series a common rate-determining step is proposed. The isokinetic relation lends support a common mechanism for the oxidation of chromium(III) complexes, reported here, by periodate. This consists of a periodate ion coordination to the chromium(III) complexes in step preceding the rate-determining intramolecular electron transfer within the precursor complex.. Isokinetic compensation between ΔH* and ΔS* in a series of related reactions usually implies that one interaction between the reactants varies within the series, the remainder of the mechanism being invariant[32]. The electron transfer reactivities of these complexes with periodate are comparable, as the coordination of periodate with these complexes are identical. All of this suggests that the excellent correlation often observed between ΔS* and ΔH* mainly reflects the fact that both thermodynamic parameters are in reality two measures of the same thing, and that measuring a compensation temperature is just a rather indirect way of measuring the average temperature at which the experiments were carried out. As this temperature will often be in a range that the experimenter expects to have some biological significance, it is not surprising if the compensation temperature turns out to have a biologically suggestive value[33].

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