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Inner-sphere oxidation of ternary iminodiacetatochromium(III) complexes involving DL-valine and L-arginine as secondary ligands. Isokinetic relationship for the oxidation of ternary iminodiacetato-chromium(III) complexes by periodate

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Abstract

Background: In this paper, the kinetics of oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ (HIDA = iminodiacetic acid, Val = DL-valine and Arg = L-arginine) were studied. The choice of ternary complexes was attributed to two considerations. Firstly, in order to study the effect of the secondary ligands DL-valine and L-arginine on the stability of binary complex $[Cr^{III}(HIDA)(IDA)(H_2O)]$ towards oxidation. Secondly, transition metal ternary complexes have received particular focus and have been employed in mapping protein surfaces as probes for biological redox centers and in protein capture for both purification and study.

Results: The results have shown that the reaction is first order with respect to both $[IO_4^-]$ and the complex concentration, and the rate increases over the pH range 2.62 – 3.68 in both cases. The experimental rate law is consistent with a mechanism in which both the deprotonated forms of the complexes $[Cr^{III}(IDA)(Val)(H_2O)_2]$ and $[Cr^{III}(IDA)(Arg)(H_2O)_2]$ are significantly more reactive than the conjugate acids. The value of the intramolecular electron transfer rate constant for the oxidation of $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$, k_3 (1.82×10^{-3} s^{-1}), is greater than the value of k_1 (1.22×10^{-3} s^{-1}) for the oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ at 45.0°C and $I = 0.20$ mol dm^{-3}. It is proposed that electron transfer proceeds through an inner-sphere mechanism *via* coordination of IO_4^- to chromium(III).

Conclusion: The oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ by periodate may proceed through an inner-sphere mechanism via two electron transfer giving chromium(VI). The value of the intramolecular electron transfer rate constant for the oxidation of $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$, k_3, is greater than the value of k_1 for the oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$. A common mechanism for the oxidation of ternary iminodiacetatochromium(III) complexes by periodate is proposed, and this is supported by an excellent isokinetic relationship between ΔH^* and ΔS^* values for these reactions.

Background

Periodate oxidations have been reported to play an important role in biochemical studies [1,2]. They are used in the spectrophotometric determination of glucose and fructose in invert sugar syrups [1]. Alpha-amino acids in proteins can be determined by measuring the ammonia produced through oxidation with periodate in carbonate medium [2]. Periodate oxidation exerts a number of biological effects including the enhancement of lymphocyte activation and increased frequency of effecter to target cell binding [3]. Also, periodate has been used in the modification of human serum transferrin by conjugation to an oligosaccharide [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 extra-cellular oxidations of Cr(III) to Cr(V) and/or Cr(VI) compounds, which act as protein tyrosine phosphatase (PTP) inhibitors. The oxidation of some Cr(III) complexes by H_2O_2 in neutral or weakly basic aqueous media (pH 7.0–9.0), lead to polynuclear species formed on hydrolysis of Cr(III) complexes in neutral aqueous solutions [8]. The relative reactivities of various Cr(III) complexes towards H_2O_2 may correlate with their reported activities as insulin activators [9]. The use of large doses $[Cr(pic)_3]$ supplements may lead to improvements in glucose metabolism for type 2 diabetics; there is a growing concern over the possible genotoxicity of these compounds [10]. The current perspective discusses chemical transformations of Cr(III) nutritional supplements in biological media, with implications for both beneficial and toxic actions of Cr(III) complexes, which are likely to arise from the same biochemical mechanisms, dependent on concentrations of the highly reactive Cr (IV/V/VI) species, formed in the reactions of Cr(III) with biological oxidants [10].

It has been reported that chromium(III) can catalyze the oxidation by periodate [11,12]. Catalysis is believed to be caused by chromium(VI) produced by the relatively rapid oxidation of chromium(III) by periodate [12]. Oxidations of hexacyanoferrate(II), hexaaquoiron(II) and octacyanomolybdate(IV) by periodate are reported to proceed *via* an inner-sphere mechanism [13-15]. In all cases, IO_4^- was reduced to IO_3^- [13-16]. The unusual second-order dependence on $[Cr(H_2O)_6]^{3+}$ in the chromium(III)-periodate reaction seems to support an inner-sphere mechanism [17]. The kinetics of oxidation of the chromium(III) complex of DL-aspartic acid [18], 2-aminopyridine [19]

and iminodiacetic acid [20] by periodate were carried out. In all cases the electron transfer proceeds through an inner-sphere mechanism via coordination of IO_4^- to chromium(III).

Inner-sphere oxidation of ternary nitrilotriacetatocobalt(II) complexes involving succinate, malonate, tartarate and maleate as a secondary ligands by periodate has been investigated [21,22]. 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.

The kinetics of oxidation of cobalt(II) complexes of propylenediaminetetraacetate (PDTA) [23], 1,3-diamino2-hydroxypro-panetetraacetate (HPDTA) [23], diethylenetriaminepentaacetate (DPTA) [24], trimethylenediaminetetraacetate (TMDTA) [25] and ethyleneglycol, bis(2-aminoethyl)ether, *N,N,N',N'*-tetraacetate (EGTA) [25] by periodate gave only the final cobalt(III) product.

Ternary complexes of oxygen-donor ligands and heteroaromatic *N*-bases such as iminodiacetic (IDA) acid and nitrilotriactic acid (NTA) with some transition metals have attracted much interest as they can display exceptionally high stability and may be biologically relevant [26,27]. The use of transition metal complexes of iminodiacetic 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 [28].

Experimental
Materials and methods
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 solutions. 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 [29].

$[Cr^{III}(HIDA)(Val)(H_2O)_2]NO_3$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]NO_3$ were prepared by a previous reported method [30]. The elemental analysis data of these complexes are: Found: C, 26.82; H, 4.76; N, 10.20. $C_9H_{20}O_{11}N_3$ Calcd: C, 27.13; H, 5.03; N, 10.55 and Found: C, 26.70; H, 5.08; N, 17.80. $C_{10}H_{24}O_{11}N_6$ Calcd: C, 26.31; H, 5.26; N, 18.42 respectively. To confirm the formula of the complexes, IR spectra and TGA data were carried out. In the IR spectra, bands in the (3565 – 3382) cm^{-1} region, were attributed to ν (OH) of the water mole-

cules. The OH- of the carboxylic group disappeared and a new (νCOO-) appeared in the region (1467 – 1426) cm^{-1} indicating that the carboxylic group of the ligands participates in the coordination with the metal ions through deprotonation. All the spectra of the complexes studied showed asym-(νCOO-Co) band in the region (1586 – 1649) cm^{-1}.

The thermogram of the complex $[Cr^{III}(HIDA)(Val)(H_2O)_2]NO_3$ shows that weight loss (15.42) at 163°C corresponds to the loss of two coordinated water molecule and one carbonyl group (calc. 15.83). The thermogram of the complex $[Cr^{III}(HIDA)(Arg)(H_2O)_2]NO_3$ shows that weight loss (18.08) at 207°C corresponds to the loss of two coordinated water molecule and one carboxylic group (calc. 17.76).

Kinetic procedures

The UV-visible absorption spectra of the products of oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ 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 quickly transferred to an absorption cell. The oxidation rates were measured by monitoring the absorbance of Cr^{VI} at 355 nm, on a Milton-Roy 601 spectrophotometer, where the absorption of the oxidation products is maximal at the reaction pH. The pH of the reaction mixture was measured using a Chertsey 7065 pH-meter. The temperature of the reacting solution was controlled, using an automatic circulation thermostat. The thermostat was provided with a special pumping system for circulating water at regulated temperature in the cell holder. The average stabilizing accuracy as measured in the thermostat liquid was ± 0.1°C

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 was found to be constant during the reaction run.

Oxidation products

The ultraviolet visible absorption spectra of the oxidation products of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ by periodate were recorded over time on a JASCO UV-530 spectrophotometer (Figures 1 and 2). The data shows that the chromium(III)-complex peaks at 542 and 545 nm for $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ have disappeared and have been replaced by a peak at 355 nm. The presence of one
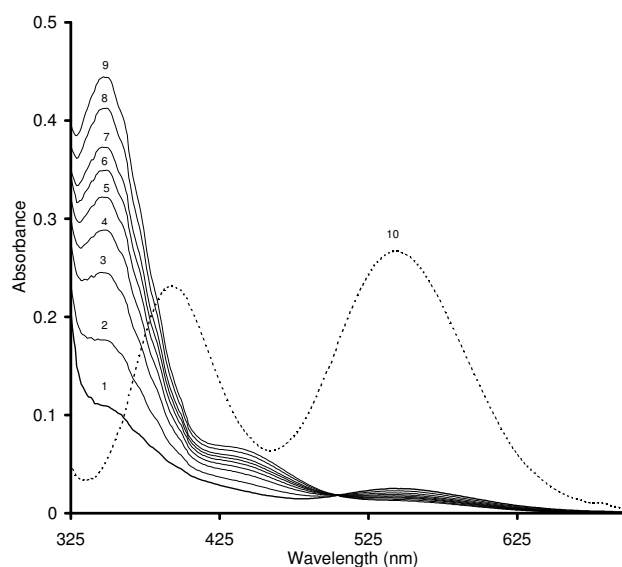

Figure 1
Change in absorbance as a function of time. Curves (1)-(9) were recorded at 2, 5, 10, 15, 20, 25, 30, 40 and 50 min. respectively, from the time of initiation; [complex] = 5.0 × 10^{-4} mol dm^{-3}, [IO$_4^-$] = 0.02 mol dm^{-3}, I = 0.2 mol dm^{-3} (NaNO$_3$), pH = 2.92 and T = 45.0°C. Curve (10) spectrum of [Cr^{III}(HIDA)(Val)(H$_2$O)$_2^+$] (5.0 × 10^{-2} mol dm^{-3}) at the Same pH.

isosbestic point at 501 and 503 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, and the absorbance of Cr^{VI} produced was measured at 355 nm after 24 hours 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 hours in an inert atmosphere. On diluting the reaction mixture with methanol, since no precipitate was formed this suggests no possibility of free radical intervention in the reaction.

Results
Kinetics of oxidation of [Cr^{III}(HIDA)(Val)(H$_2$O)$_2$]$^+$
Oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ by periodate was studied over the (2.62 – 3.68) pH range, 0.20 mol dm^{-3}ionic strength, (0.50 – 5.0) × 10^{-2} mol dm^{-3} periodate
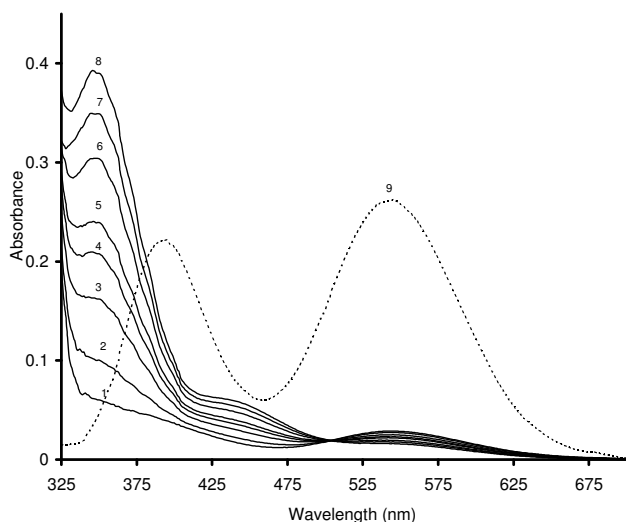
Figure 2
Change in absorbance as a function of time. Curves
(1)-(8) were recorded at 2, 5, 10, 15, 20, 32, 45 and 60 min.
respectively, from the time of initiation; [complex] = 5.0 ×
10^{-4} mol dm^{-3}, $[IO_4^-]$ = 0.02 mol dm^{-3}, I = 0.20 mol dm^{-3}
($NaNO_3$), pH = 2.92 and T = 45.0°C. Curve (9) spectrum of
$[Cr^{III}(HIDA)(Arg)(H_2O)_2^+]$ (5.0 × 10^{-2} mol dm^{-3}) at the same
pH.

concentration range, (1.25 – 6.25) × 10^{-4} mol dm^{-3} complex concentration range, and (25.0 – 55.0)°C.

The stoichiometry of the $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+/IO_4^-$ reaction can be represented by Equation (1):

$$2Cr^{III} + 3I^{VII} \rightarrow 2Cr^{VI} + 3I^{V}$$
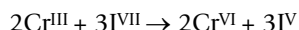
The ratio of I^{VII} initially present to Cr^{VI} produced was 1.50 ± 0.05. The stoichiometry is consistent with the observation that IO_3^- does not oxidize the Cr^{III}-complex over the pH range where the kinetics were investigated.

Plots of ln (A_∞-A_t) *versus* time were linear up to 85% from the beginning of reaction where A_t and A_∞ are absorbance at time t and infinity, respectively (Figure 3). Pseudo-first-order rate constants, k_{obs}, obtained from the slopes of Figure 3, are collected in Table 1. The results (Table 1) show that k_{obs} was unaffected when the concentration of the chromium(III)-complex was varied 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 4), and the kinetics of the reaction are described by Equation (2):

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

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

or

$$1/k_{obs} = 1/a [IO_4^-]_T + b/a$$

Values of constant (a) and (b) were obtained from the slope and intercept in Figure 4. Plots of $1/k_{obs}$ *versus* $1/[IO_4^-]$ at different pH values (2.62–3.68) (Figure 5), show that the reaction rate increased as the pH increased over the range studied (Table 2). The reaction rate is independent of the ionic strength when varied between 0.20 – 0.50 mol dm^{-3}.

Kinetics of oxidation of $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$
Under the same experimental conditions as for the oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$, the kinetics of oxidation of $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ by periodate were studied. The overall stoichiometry of the $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+/[IO_4^-]$ 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 for greater than 85% from the beginning of the reaction. Observed rate constants, k_{obs}, 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 be 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 6), 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 (2.38 – 3.34) (Figure 7), showing that the rate of reaction increases with increasing pH (Table 4). The reaction rate is independent of the ionic strength when varied between 0.20 – 0.50 mol dm^{-3}.

Discussion
The system which consists of a metal ion and more than one type of ligand is defined as a ternary complex such as $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$, where iminodiacetic acid is functioning as a tridentate through two carboxylic groups and one imino group, while DL-valine or L-arginine as secondary ligands are bidentate.

The oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ by periodate may be proceeding through an inner-sphere mechanism.
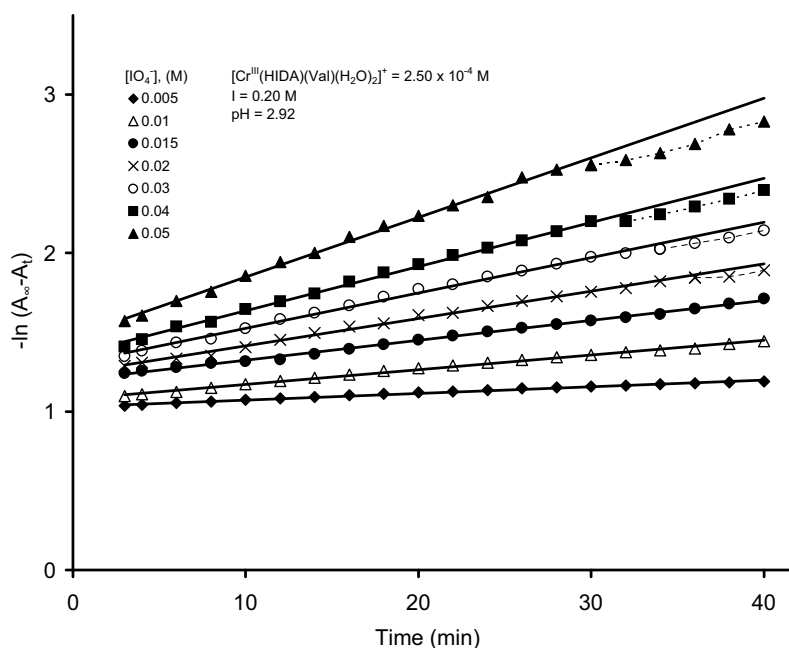
Figure 3
Pseudo-first-order plots for the reaction of [Cr^{III}(HIDA)(Val)(H$_2$O)$_2$]$^+$ with periodate at T = 45°C.

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) [31] and nickel(IV) [32], in which the coordinated H$_2$O is substituted by I^{VII} [20].

In acid medium the chromium(III)-complex is in equilibrium:
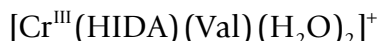
$$[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$$

K$_1$ was measured potentiometrically and had the value 1.92×10^{-3} at 45°C and *I* = 0.20 mol dm^{-3}. From the pH (2.62 – 3.68) and the K$_1$ value, it is clear that

[Cr^{III}(IDA)(Val)(H$_2$O)] may be the reactive species. Also, the rate of reaction is independent of ionic strength. This behavior is expected since the reaction takes place between charged and uncharged species. Therefore [Cr^{III}(IDA)(Val)(H$_2$O)] may be the reactive species.

Of the possible hydrates of I(VII) oxide, only paraperiodic acid, H$_5$IO$_6$$^-$, exists as a solid in equilibrium with its aqueous solution, so the acidic periodate solutions contain two species, IO$_4$$^-$ and H$_5$IO$_6$. The proportion of H$_5$IO$_6$ increases with a decrease in pH. This acid undergoes the following equilibria [33]:
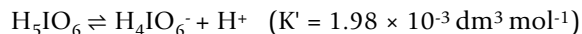
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad (K' = 1.98 \times 10^{-3}\ dm^3\ mol^{-1})$$

Table 1: Variation of rate constant, k_{obs}, with different concentrations of periodate and different temperatures.
[Cr^{III}(HIDA)(Val)(H$_2$O)$_2$$^+$]^a = 2.50 × 10^{-4} mol dm^{-3} at pH = 2.92 and I = 0.20 mol dm^{-3}.

10^2 [IO$_4$$^-$] mol dm^{-3}	10^4 k_{obs} (s^{-1}) T = 25°C	35°C	40°C	45°C	50°C	55°C
0.5	0.80 ± 0.02	1.08 ± 0.03	1.17 ± 0.04	1.31 ± 0.05	1.54 ± 0.06	1.74 ± 0.05
1.0	1.38 ± 0.03	1.80 ± 0.04	2.02 ± 0.03	2.25 ± 0.04	2.57 ± 0.07	3.00 ± 0.10
1.5	1.69 ± 0.03	2.26 ± 0.02	2.75 ± 0.04	3.02 ± 0.03	3.31 ± 0.05	3.82 ± 0.15
2.0	2.05 ± 0.02	2.69 ± 0.05	2.96 ± 0.06	3.49 ± 0.06	4.18 ± 0.08	4.65 ± 0.22
3.0	2.43 ± 0.05	3.15 ± 0.04	3.68 ± 0.08	4.18 ± 0.08	4.81 ± 0.13	5.52 ± 0.30
4.0	2.77 ± 0.07	3.89 ± 0.05	4.46 ± 0.09	5.13 ± 0.11	6.52 ± 0.20	7.35 ± 0.50
5.0	3.24 ± 0.06	4.27 ± 0.07	5.08 ± 0.12	5.62 ± 0.15	7.09 ± 0.32	8.40 ± 0.60

^{a} [Cr^{III}(HIDA)(Val)(H$_2$O)$_2$$^+$] = 2.50 × 10^{-4} mol dm^{-3}; 10^{4}k$_{obs}$ = 3.35 ± 0.04, 3.54 ± 0.07, 3.46 ± 0.06 and 3.50 ± 0.05 s^{-1} at 10^4
[Cr^{III}(HIDA)(Val)(H$_2$O)$_2$$^+$] of 1.25, 3.75, 5.00 and 6.25 mol dm^{-3}, respectively at 45°C and [IO$_4$$^-$] = 0.02 mol dm^{-3}.

Figure 4
Plot of 1/k_{obs} versus 1/[IO_4^-] at different temps.

$$H_4IO_6^- \rightleftharpoons 2H_2O + IO_4^- \quad (K'' = 0.025)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad (K''' = 5.0 \times 10^6 \, dm^3 \, mol^{-1})$$

It was reported that at pH = 4.2, 99.8% of periodate is present as $H_4IO_6^-$ and IO_4^- and 0.2% as H_5IO_6 [34].

A possible mechanism is described by Equations 9–11:

$$[Cr^{III}(HIDA)(Val)(H_2O)_2]^+ \rightleftharpoons [Cr^{III}(IDA)(Val)(H_2O)] + H^+ \quad K_1$$

$$[Cr^{III}(IDA)(Val)(H_2O)] + I^{VII} \rightleftharpoons [Cr^{III}(IDA)(Val)(I^{VII})]^- + H_2O \quad K_2$$

$$[Cr^{III}(IDA)(Val)(I^{VII})]^- \rightarrow Products \quad k_1$$

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

$$d[Cr^{VI}]/dt = k_1[Cr^{III}(IDA)(Val)(I^{III})]^-$$
$$= k_1K_2[Cr^{III}(IDA)(Val)(H_2O)][I^{VII}]$$

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

$$[Cr^{III}]_T = [Cr^{III}(IDA)(Val)(H_2O)][H^+] / K_1$$
$$+ [Cr^{III}(IDA)(Val)(H_2O)]$$
$$+ K_2[Cr^{III}(IDA)(Val)(H_2O)][I^{VII}]_T$$

Substitution for $[Cr^{III}(IDA)(Val)(H_2O)]$ from Equation (13) into Equation (12) gives:

$$rate = k_1K_2[Cr^{III}]_T[I^{VII}]_T / \{1 + [H^+]/K_1 + K_2[I^{VII}]_T\}$$

and

$$k_{obs} = k_1K_2[I^{VII}]_T / \{1 + [H^+]/K_1 + K_2[I^{VII}]_T\}$$

which on rearrangment, gives:

$$1/k_{obs} = (K_1 + [H^+])/k_1K_1K_2[I^{VII}]_T + 1/k_1$$

At constant [H^+], Equation (17) follows, in which (A) is a constant:

$$1/k_{obs} = A/k_1K_1K_2[I^{VII}]_T + 1/k_1$$

which is identical to the experimental results shown in Equation (4) where $a = k_1K_1K_2/A$ and $b = K_1K_2/A$. The calculated values of 10^3k_1 are 0.41, 0.50, 0.56, 0.83, 1.22 and
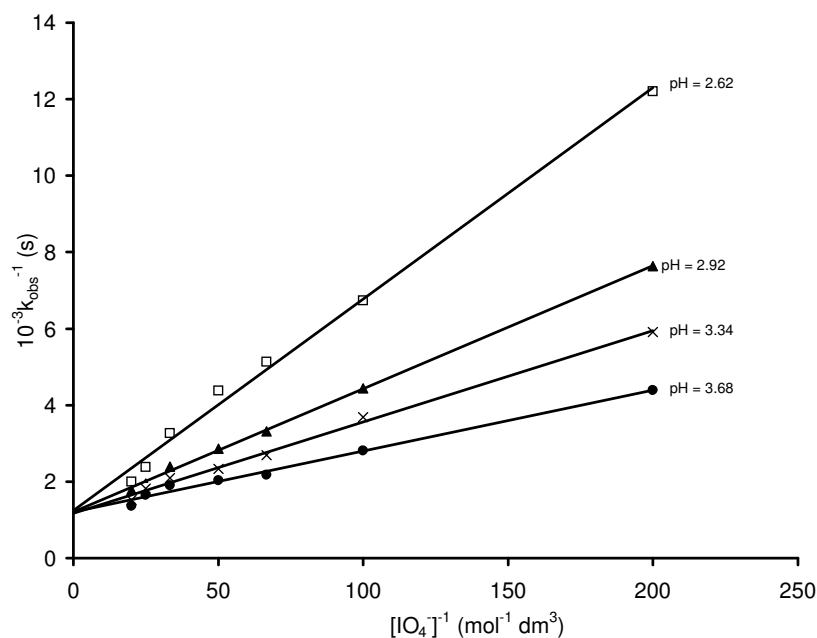
Figure 5
Plot of 1/k_{obs} versus 1/[IO$_4^-$] at different pH's.

1.37 s^{-1} at 25.0, 35.0, 40.0, 45.0, 50.0 and 55.0°C respectively. The activation parameters associated with k_1 obtained from a least-squares fit to the transition state theory equation are $\Delta H^* = 41.7 \pm 1.5$ kJ mol^{-1} and $\Delta S^* = -162.5 \pm 3.3$ JK^{-1} mol^{-1}.

From Equation (16), it follows that the slope of the plots can be represented by Equation (18):

$$\text{Slope} = [H^+]/k_1K_1K_2 + 1/k_1K_2$$

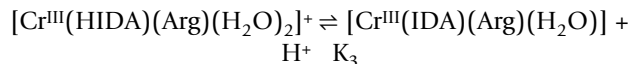It is clear from Equation (18) that the slope is dependent on [H$^+$]. This plot can be given as the linear equation $y = mx + c$, with a correlation coefficient of 0.9887. The values of K_1 and K_2 were calculated from Equation (18) as 0.78 ×

Table 2: Effect of pH on k_{obs} (s^{-1}) at [Cr^{III}(HIDA)(Val)(H$_2$O)$_2^+$] = 2.50 × 10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 45°C.

10^2 [IO$_4^-$] mol dm^{-3}	10^4 k_{obs} (s^{-1}) pH 3.68	3.34	2.92	2.62
0.5	2.28 ± 0.04	1.69 ± 0.02	1.31 ± 0.05	0.82 ± 0.02
1.0	3.55 ± 0.07	2.72 ± 0.03	2.25 ± 0.04	1.48 ± 0.02
1.5	4.58 ± 0.10	3.72 ± 0.04	3.02 ± 0.03	1.95 ± 0.04
2.0	4.93 ± 0.14	4.29 ± 0.07	3.49 ± 0.06	2.28 ± 0.07
3.0	5.25 ± 0.21	4.76 ± 0.12	4.18 ± 0.08	3.07 ± 0.10
4.0	6.06 ± 0.28	5.49 ± 0.17	5.13 ± 0.11	4.20 ± 0.15
5.0	7.35 ± 0.40	6.58 ± 0.26	5.62 ± 0.15	5.00 ± 0.23

10^{-3} mol dm^{-3} and 90.0 mol^{-1} dm^3, at 45°C and $I = 0.20$ mol dm^{-3}. The value of K_1 is in good agreement with that obtained potentiometrically ($K_1 = 1.92 \times 10^{-3}$) at 45°C and $I = 0.20$ mol dm^{-3}.

In the case of [Cr^{III}(HIDA)(Arg)(H$_2$O)$_2$]$^+$, the protonated and deprotonated forms of the chromium(III)-complex are involved in the rate-determining step. In acidic aqueous medium the chromium(III)-iminodiacetic acid-arginine complex may be included in the equilibrium shown in Equation (19):

$$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+ \rightleftharpoons [Cr^{III}(IDA)(Arg)(H_2O)] + H^+ \quad K_3$$

K_3 was measured potentiometrically and had the value 0.50×10^{-3} at 45°C and $I = 0.20$ M. There is a possibility for the coordination of IO$_4^-$, since substitution of H$_2$O ligand by IO$_4^-$ is likely to occur [18].

The mechanistic pathway for the oxidation of chromium(III)-iminodiacetic acid-L-arginine complex by periodate over the studied pH range may be represented by:
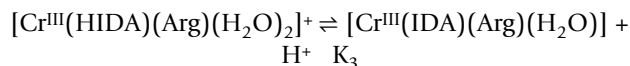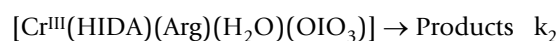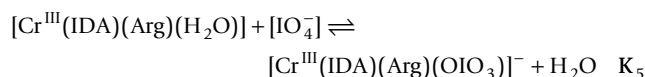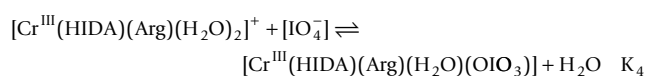
$$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+ \rightleftharpoons [Cr^{III}(IDA)(Arg)(H_2O)] + H^+ \quad K_3$$

Table 3: Dependence of the rate, k_{obs} ($\times 10^4$, s^{-1}) on [Cr^{III}(HIDA)(Arg)(H$_2$O)$_2$$^+$]^b, [IO$_4$$^-$] and temperature at pH = 2.92 and I = 0.20 mol dm^{-3}.

10^2 [IO$_4$$^-$] (mol dm^{-3})	25°C	35°C	40°C	45°C	50°C	55°C
0.5	0.60 ± 0.02	0.75 ± 0.04	0.80 ± 0.01	0.92 ± 0.03	1.23 ± 0.02	1.33 ± 0.04
1.0	1.20 ± 0.01	1.43 ± 0.03	1.55 ± 0.02	1.83 ± 0.03	2.07 ± 0.05	2.42 ± 0.07
1.5	1.64 ± 0.03	2.00 ± 0.05	2.22 ± 0.03	2.57 ± 0.06	2.62 ± 0.07	3.25 ± 0.15
2.0	1.95 ± 0.06	2.48 ± 0.09	2.78 ± 0.08	3.30 ± 0.09	3.33 ± 0.08	3.83 ± 0.35
3.0	2.76 ± 0.04	3.33 ± 0.15	3.90 ± 0.12	4.27 ± 0.13	4.50 ± 0.15	5.00 ± 0.50
4.0	3.35 ± 0.05	3.83 ± 0.21	5.45 ± 0.18	6.23 ± 0.20	6.67 ± 0.30	6.92 ± 0.50
5.0	3.97 ± 0.08	5.00 ± 0.30	5.83 ± 0.25	6.67 ± 0.35	7.50 ± 0.40	8.23 ± 0.80

^{b} [Cr^{III}(HIDA)(Arg)(H$_2$O)$_2$$^+$] = 2.50 × 10^{-4} mol dm^{-3}; $10^4 k_{obs}$ = 3.19 ± 0.07, 3.22 ± 0.10, 3.37 ± 0.08 and 3.25 ± 0.06 s^{-1} at 10^4 [Cr^{III}(HIDA)(Arg)(H$_2$O)$_2$$^+$] of 1.25, 3.75, 5.0 and 6.25 mol dm^{-3}, respectively at 45°C and [IO$_4$$^-$] = 0.02 mol dm^{-3}.

$$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+ + [IO_4^-] \rightleftharpoons$$
$$[Cr^{III}(HIDA)(Arg)(H_2O)(OIO_3)] + H_2O \quad K_4$$

$$[Cr^{III}(IDA)(Arg)(H_2O)] + [IO_4^-] \rightleftharpoons$$
$$[Cr^{III}(IDA)(Arg)(OIO_3)]^- + H_2O \quad K_5$$

$$[Cr^{III}(HIDA)(Arg)(H_2O)(OIO_3)] \rightarrow Products \quad k_2$$

$$[Cr^{III}(IDA)(Arg)(OIO_3)]^- \rightarrow Products \quad k_3$$

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

$$d\,[Cr^{III}]/dt = (k_2K_4 + k_3K_3K_5/[H^+])$$
$$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+[IO_4^-]$$

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

$$[Cr^{III}]_T =$$
$$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+\{1 + (K_3/[H^+]) + K_4[IO_4^-] + (K_3K_5/[H^+])[IO_4^-]\}$$

Substituting $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ from Equation (26) into Equation (25) gives:

$$d[Cr^{III}]/dt = (k_2K_4 + k_3K_5K_3 / [H^+])[IO_4^-][Cr^{III}]_T /$$
$$\{1 + (K_3/[H^+]) + (K_4 + K_3K_5/[H^+])[IO_4^-]\}$$

Figure 6
Plot of 1/k_{obs} versus 1/[IO$_4$$^-$] at different temps.
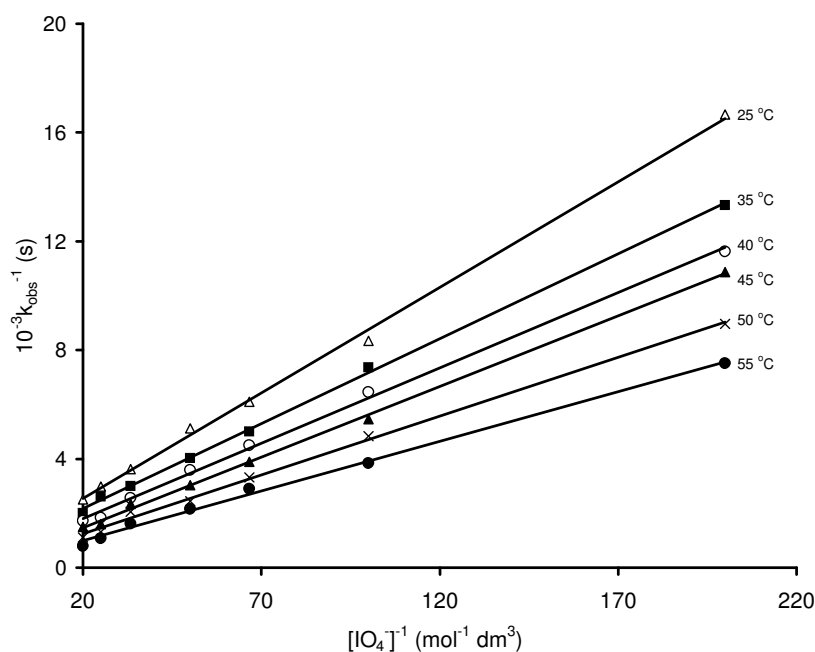
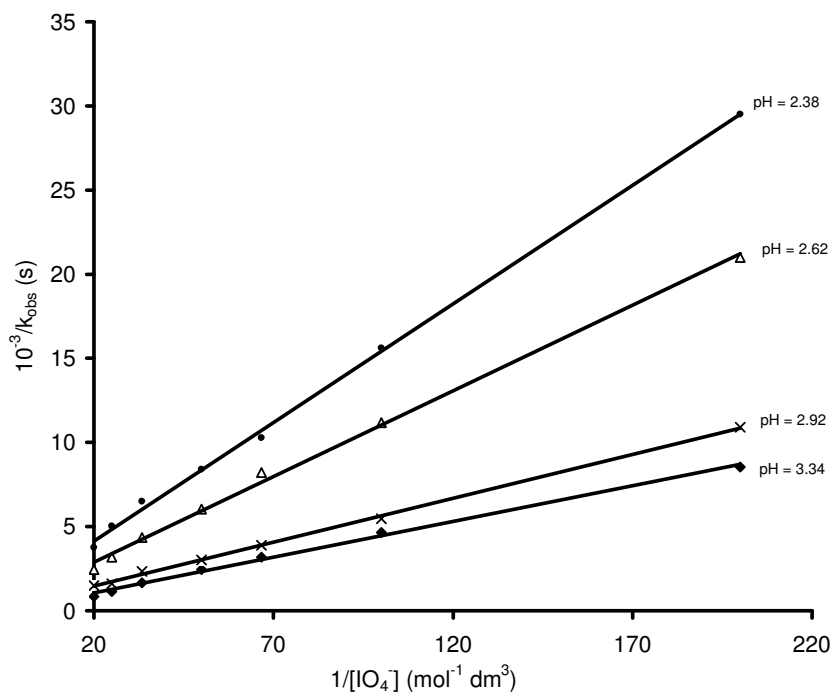**Figure 7**
Plot of $1/k_{obs}$ versus $1/[IO_4^-]$ at different pH's.

Hence:

$$k_{obs} = \{(k_2 K_4 [H^+] + k_3 K_3 K_5) [IO_4^-]\}/\{ [H^+] + K_3 + (K_4 [H^+] + K_3 K_5) [IO_4^-]\}$$

Since, the deprotonated form $[Cr^{III}(IDA)(Arg)(H_2O)]$ is considered to be the more reactive form than its conjugate acid, we can assume that $K_5 \gg K_4$ and that Equation (28) may be reduced to Equation (29):

Table 4: Effect of pH on k_{obs} at $[Cr^{III}(HIDA)(Arg)(H_2O)_2^+]$ = 2.50 × 10^{-4} mol dm^{-3} I = 0.20 mol dm^{-3}, and T = 45°C.

$10^2 [IO_4^-]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) pH = 3.34	pH = 2.92	pH = 2.62	pH = 2.38
0.5	1.00 ± 0.04	0.92 ± 0.03	0.42 ± 0.01	0.35 ± 0.02
1.0	2.15 ± 0.06	1.83 ± 0.03	0.83 ± 0.01	0.60 ± 0.03
1.5	2.78 ± 0.08	2.57 ± 0.06	1.48 ± 0.03	1.03 ± 0.03
2.0	3.65 ± 0.12	3.30 ± 0.09	2.00 ± 0.06	1.35 ± 0.04
3.0	4.52 ± 0.2	4.27 ± 0.13	2.30 ± 0.05	2.00 ± 0.05
4.0	6.42 ± 0.3	6.23 ± 0.20	5.00 ± 0.09	3.33 ± 0.07
5.0	10.4 ± 0.7	6.67 ± 0.35	5.90 ± 0.15	3.92 ± 0.10

$$k_{obs} = k_3 K_3 K_5 [IO_4^-]/\{[H^+] + K_3 + (K_4 [H^+] + K_3 K_5) [IO_4^-]\}$$

Upon rearrangement:

$$1/k_{obs} = 1/[IO_4^-]/([H^+]/k_3 K_3 K_5) + (1/k_3 K_5) + \{(K_4 [H^+]/k_3 K_3 K_5) + (1/k_3)\}$$

At constant $[H^+]$, Equation (30) is identical to the experimental rate law shown in Equation (4) where:

$$a = (k_3 K_3 K_5)/(K_3 + [H^+]) \text{ and } b = (K_4 [H^+] + K_3 K_5)/(K_3 + [H^+])$$

Plots of both $1/a = K_3 + [H^+]/k_3 K_3 K_5$ and $b/a = (K_4 [H^+] + K_3 K_5)/k_3 K_3 K_5$ *versus* $[H^+]$ are linear according to Equation $y = mx + c$ with correlation coefficient of r = 0.9864 and 0.9951, respectively. The K_3 value was calculated by dividing the intercept by the slope of a plot $1/a$ *versus* $[H^+]$ as 1.0×10^{-3} mol dm^{-3} at 45°C. The intramolecular electron transfer rate constant, k_3, was calculated from the intercept of plot b/a *versus* $[H^+]$ as 1.82×10^{-3} s^{-1}. The value of K_4 was calculated by dividing the slope of both b/a and $1/a$ *versus* $[H^+]$ as 29.2 mol^{-1} dm^3. Substituting the value of k_3 gives K_5 from the intercept of plot of $1/a$ *versus* $[H^+]$ as 291 mol^{-1} dm^3. The value of K_3 is in a good agreement with that obtained potentiometrically ($K_3 = 0.50 \times 10^{-3}$) and the

value of K_5 (291) is more than K_4 (29.2), providing a good basis for the suggested 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 15.9 ± 1.2 kJ mol^{-1} and -277 ± 5 JK^{-1} mol^{-1} respectively.

The oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)-(H_2O)_2]^+$ by periodate may proceed through an inner-sphere mechanism via one or two electron transfer giving chromium(IV) or chromium(V) respectively in the rate determining step leading to chromium(VI). The fact that acrylonitrile was not polymerized seems to support a two electron transfer process.

Kinetics of oxidation of Cr(III) to Cr(VI) in acidic medium (pH = 2–4) using periodate are biologically important [35]. Since carbohydrates reduce Cr(VI) to a significant extent only in strongly acidic media, it is likely that the first Cr(V) complexes formed in biological systems upon the addition of Cr(VI) are those of strong reductants, such as GSH or ascorbate [5].

In comparison with the oxidation of $[Cr^{III}(HIDA)(IDA)(H_2O)]$ [20] 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_1, for the oxidation reaction increases in the order: $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ > $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ > $[Cr^{III}(HIDA)(IDA)(H_2O)]$ at 45°C (Table 5). This means that the stability of these complexes towards oxidation increases in the following order: $[Cr^{III}(HIDA)(IDA)(H_2O)]$ > $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ > $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$

This may be due to the presence of the amino acid as a secondary ligand in the ternary complexes, and decreases the stability of chromium(III) towards oxidation than binary complex, $[Cr^{III}(HIDA)(IDA)(H_2O)]$ [20].

The high negative entropies of activation for this reaction may be largely the result of the charge concentration on complex formation, which causes substantial mutual ordering of the solvated water molecules [36]. The intramolecular electron transfer steps are endothermic as indicated by the positive ΔH^* values. The contributions of ΔH^* and ΔS^* to the rate constant seem to compensate each other. This fact suggests that the factors controlling ΔH^* must be closely related to those controlling ΔS^*. Therefore, the solvation state of the encounter complex would be important in determining ΔH^* [36]. The relatively low value of ΔH^* for $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ 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 $[Cr^{III}(HIDA)(IDA)(H_2O)]$, $[Cr^{III}(HIDA)(Asp)(H_2O)_2]^+$ [37], $[Cr^{III}(HIDA)-(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ with periodate are collected in Table 5. A plot of ΔH^* versus ΔS^* for these complexes is shown in Figure 8. The small change in the rates of the oxidation of iminodiacetatochromium(III) complexes (Table 5) are shown to arise from parallel changes ΔH^* and ΔS^*. Similar linear plots were found for a large number of redox reactions [38,39] and for each reaction series a common rate-determining step is proposed. An excellent linear relationship is seen; this isokinetic relationship lends support to a common mechanism for the oxidation of chromium(III) complexes, reported here, by periodate. This consists of periodate ion coordination to the chromium(III) complexes in step preceding the rate-determining intramolecular electron transfer within the precursor complex.

Conclusion

The oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$ and $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$ by periodate may proceed through an inner-sphere mechanism via two electron transfer giving chromium(VI). The value of the intramolecular electron transfer rate constant for the oxidation of $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$, k_3, is greater than the value of k_1 for the oxidation of $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$. A common mechanism for the oxidation of a ternary iminodiacetatochromium(III) complexes by periodate is proposed, and this is supported by an excellent isokinetic relationship between ΔH^* and ΔS^* values for these reactions.

Table 5: Values of ΔH* and ΔS* for the oxidation of some chromium(III) complexes by periodate.

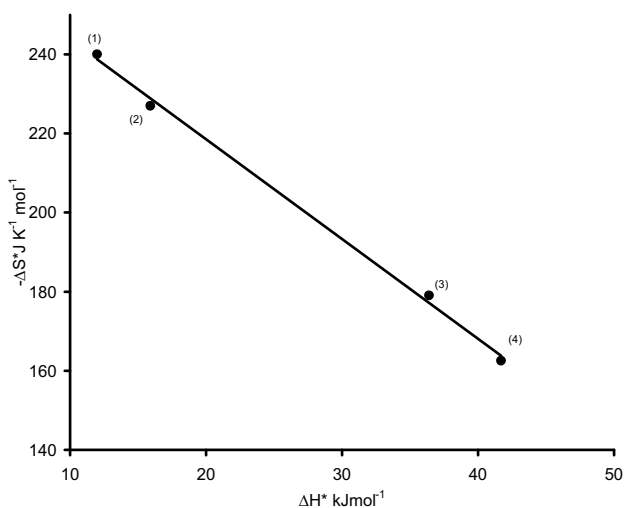| complex	$10^3\, k_1$ (s^{-1})	ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (JK^{-1} mol^{-1})	Reference
$[Cr^{III}(HIDA)(IDA)(H_2O)]$	1.09	12.3 ± 1	240 ± 7	15
$[Cr^{III}(HIDA)(Asp)(H_2O)_2]^+$	3.38	36.4 ± 3	179 ± 9	28
$[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$	1.22	41.7 ± 1.5	162.5 ± 3.3	This work
$[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$	1.82^c	15.9 ± 1.2	227 ± 5	This work

$^c k_1 = k_3$

Figure 8
Isokinetic relationship for the oxidation of a ternary iminodiacetatochromium(III) complexes. (1) $[Cr^{III}(HIDA)(IDA)(H_2O)]^+$, (2) $[Cr^{III}(HIDA)(Arg)(H_2O)_2]^+$, (3) $[Cr^{III}(HIDA)(Asp)(H_2O)_2]^+$, (4) $[Cr^{III}(HIDA)(Val)(H_2O)_2]^+$.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

HAE suggested the problem and carried out literature survey, undertaking the microanalysis, discussion of the results, writing the article and publication. FDD carried out the experimental parts. AAAK contributed in the discussion of the results.

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