Open Journal of Inorganic Chemistry, 2018, 8, 91-104
http://www.scirp.org/journal/ojic
ISSN Online: 2161-7414
ISSN Print: 2161-7406

Periodate Oxidation of a Ternary Complex of Nitrilotriacetatochromium(III) Involving ß-Alanine as Co-Ligand

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How to cite this paper: Ewais, H.A., Abdel-Salam, A.H., Basaleh, A.S. and Habib, M.A. (2018) Periodate Oxidation of a Ternary Complex of Nitrilotriacetatochromium(III) Involving ß-Alanine as Co-Ligand. *Open Journal of Inorganic Chemistry*, **8**, 91-104.
https://doi.org/10.4236/ojic.2018.84008

Received: September 5, 2018
Accepted: October 12, 2018
Published: October 15, 2018

Abstract

The kinetics of the periodate oxidation of chromium(III)-complex, $[Cr^{III}(NTA)(Ala)(H_2O)]$-(NTA = Nitrilotriacetate and Ala = ß-alanine) to Cr(VI) have been carried out for the temperature range 15˚C - 35˚C under pseudo-first order conditions, $\left[IO_4^-\right] \gg$ [complex]. Reaction obeyed first order dependence with respect to $\left[IO_4^-\right]$ and [Cr(III)], and the rate of reaction increases with increasing of pH for the range 3.40 - 4.45. Experimentally, the mechanism of this reaction is found to be consistent with the rate law in which the hydroxo species, $[Cr^{III}(NTA)(Ala)(OH)]^{2-}$ is considerably much more reactive than their conjugate acid. ΔH^* and ΔS^* have been calculated. It is proposed that electron transfer occurs through an inner-sphere mechanism *via* coordination of IO_4^- to chromium(III).

Keywords

Nitrilotriacetatochromium(III), Ternary Complex, Periodate Oxidation, Inner-Sphere Mechanism, Thermodynamic Activation Parameters

1. Introduction

The Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases such as nitrilotriacetic acid (NTA) and iminodiacetic acid (IDA) with 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 NTA is gaining increasing use in biotechnology, particularly in the protein purification technique known as immobilized metal-ion chromatography [3]. The chromium(III) complexes of *a* amino acids are biologically available, depending on the complexing ability of the ligands for chromium against OH^-. Chromium can also aid in the transportation of amino acids through the cell membrane [4]. The biological oxidation of chromium from the trivalent to the hexavalent state 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 for the anti-diabetic activities of some Cr(III) complexes, as well as the long-term toxicities of such complexes [6]. The specific interactions of chromium ions with cellular insulin receptors [7] are a consequence of 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 processes [8] [9] [10].

Studies of the kinetics of periodate oxidations on a series of dextran oligomers, polymers and some dimeric carbohydrates [8] revealed a dependence of the kinetic rates on the molecular weight. The oxidation of caffeic acid (3,4-dihydroxy cinnamic acid) by sodium periodate was found to mimic the mechanism of polyphenol oxidase. The antioxidant product 2-s-cysteinyl caffeic acid exhibits slightly improved antiradical activity compared to the parent molecule (caffeic acid) [9]. The imidazol-modified M-salophen/$NaIO_4$ system can be applied to oxidize a large number of primary aromatic amines in good yield at short times and room temperature [10].

An inner-sphere mechanism for oxidation of chromium(III) complexes of some amino acids [11] [12] [13] and nucleosides [14] [15] [16] by periodate 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, tartrate, maleate and benzoate as secondary ligands by periodate has been investigated [17] [18] [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, involving a ring closure step that is faster than the oxidation step. The I^{VI} in the initial product is probably substitutional by water at a very slow rate due to the substituted inertness of Co(III) and also the Co(II)-OIO_3 bond being stronger than Co-H_2O bond. The oxidation of cobalt(II) complexes of propylenediaminetetraacetate (PDTA) [20], 1,3-diamino-2-hydroxypropanetetraacetate (HPDTA) [20], diethylenetriamine-pentaacetate (DPTA) [21], trimethylenediaminetetraacetate (TMDTA) [22] and ethyleneglycol,bis(2-aminoethyl)ether,N,N,N0,N0-tetraacetate (EGTA) [22] by periodate gave only the final product. Periodate oxidations of the chromium(III) complexes of NTA [23], 2-aminopyridine [24] and IDA [25] were studied. In all cases, the electron transfer proceeds through an inner-sphere mechanism *via* coordination of IO_4^- to chromium(III).

In this paper, we report on the kinetics and mechanism of the periodate oxidation of ternary complexes of chromium(III) involving NTA as primary ligand and ß-alanine as a secondary ligand, in order to study the effect of secondary ligand on the stability of $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ [23] toward oxidation.

2. Experimental

2.1. Materials and Methods

The ternary complexes of chromium(III) involving nitrilotriacetato and *β*-alanine was prepared according to the report method [26]. All chemicals used in this study were of analar grade (BDH, Aldrich and Sigma). Buffer solutions were prepared from CH_3COONa (Sigma 99%) and CH_3COOH (BHD 99.9%) of known concentration. $NaNO_3$ (Aldrich 99.99%) 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 99.9%) was prepared by accurate weighing and wrapped in aluminum foil to avoid photochemical decomposition [27].

2.2. Instrumentation

UV-vis spectrophotometer model JASCO UV-530 was used to record the electronic spectra of the investigated complexes. The oxidation of complex, $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ by IO_4^- were followed spectrophotometrically. The absorption measurements for the oxidation of reaction products are maximum at the reaction pH. Automatic circulation thermostat was used to regulate the temperature of solution. The average stabilizing accuracy was ±0.1˚C. Large excess of IO_4^- (>10-fold) was used in all measurements to get the pseudo-first order situation. $NaNO_3$ solution was utilized to make a constant ionic strength. It is noticed that during the course of the reaction the pH of the reaction is constant.

2.3. Kinetic Measurements

The UV-Visible absorption spectra of the products of oxidation of the complex $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ by IO_4^- was followed spectrophotometrically for a measured period of time using a JASCO UV-530 spectrophotometer. All reactants were thermally equilibrated for ca 15 min in an automatic circulation thermostat, then mixed thoroughly and quickly 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 maintaining a large excess (>10-fold) of IO_4^- over complexes. 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 runs. Potentiometric measurements were performed with a Metrohm 702

SM titrino, using Irving and Rossotti techniques [28].

3. Results and Discussion

The UV-Visible spectra of the oxidation product of the complex, $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ by periodate were recorded over time on a JASCO UV-530 spectrophotometer (**Figure 1**). The spectrum gives a maxima at 564 and 410 nm for $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ complex which disappeared and replaced by a single peak at 350 nm due to the formation of chromium (VI). The presence of one isosbestic point at 501 nm in the absorption spectra (**Figure 1**) indicates the presence of two absorbing species in equilibrium. To measure the stoichiometry, a known excess of Cr(III) complex was added to IO_4^- solution and the absorbance of Cr(VI) produced was measured at 350 nm after 24 h. The quantity of Cr(III) consumed was calculated using the molar absorptivity of Cr(VI) at the utilized pH.

The oxidation of $[Cr^{III}(NTA)(Ala)(H_2O)]$-complex by periodate was carried out in the pH range 3.40 - 4.45, 0.2 M ionic strength, $\left[IO_4^-\right]$ range (0.5 - 5.0) × 10^{-2} M and with temperature range 15˚C - 35˚C (±0.1˚C). The stoichiometry of the reaction can be represented by Equation (1):

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

where Cr(III) and I(VII) represent total chromium(III)-complex and periodate, respectively. The concentration ratio of IO_4^- initially present to Cr(VI)

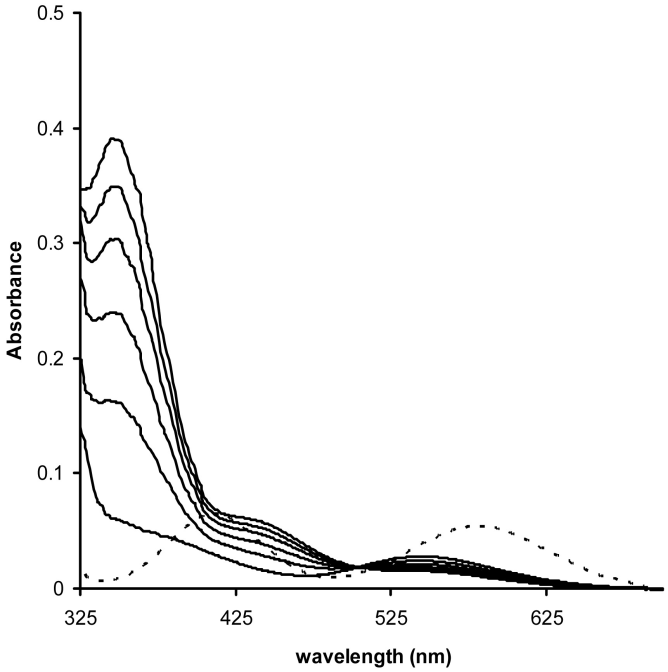

Figure 1. Absorbance spectra of reaction mixtures at interval times; [complex] = 2.5 × 10^{-4} mol·dm^{-3}, $\left[IO_4^-\right]$ = 0.02 mol·dm^{-3}, I = 0.2 mol·dm^{-3}, pH = 4.05 and T = 30˚C. Curve (…………) spectrum of the complex (2.5 × 10^{-4} mol·dm^{-3}) at the same pH.

produced was found to be 3:2. The stoichiometry is also consistent with the observation that IO_3^- does not oxidize the Cr(III)-complex over the studied pH range. **Table 1** shows pseudo-first order rate constants, k_{obs}. Data obtained exhibits that k_{obs} does not have any effect, when we change the concentration of $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ complex with constant IO_4^- concentration of 2.0 × 10^{-2} mol·dm^{-3}, pH = 4.05, ionic strength 0.20 mol·dm^{-3}, temperature 25˚C and at different concentrations of complex over the range (1.25 - 6.25) × 10^{-4} mol·dm^{-3}, confirming that this reaction is first order and related to the concentration of Cr(III) complex, $[Cr^{III}(NTA)(Ala)(H_2O)]^-$. This behavior is represented by Equation (2).

$$\text{Rate} = k_{obs}\left[\text{Cr}^{\text{III}}\left(\text{NTA}\right)\left(\text{Ala}\right)\left(\text{H}_2\text{O}\right)\right]^- \qquad (2)$$

The effect of periodate on the rate of the reaction of $Cr^{III}(NTA)(Ala)(H_2O)]^-$ was studied over the temperature range (15˚C - 35˚C). The variation of rate constant, k_{obs}, with different concentrations of $\left[IO_4^-\right]$ at different temperatures are summarized in **Table 1**. Plotting k_{obs} against $\left[IO_4^-\right]$, was found to be linear without intercept as shown in **Figure 2**. The dependence of k_{obs} on $\left[IO_4^-\right]$ is thus described by Equation (3):

$$k_{obs} = k_1\left[IO_4^-\right] \qquad (3)$$

The dependence of the reaction rate on pH was investigated over the 3.40 - 4.45 pH range at constant $\left[IO_4^-\right]$ = 2.0 × 10^{-2} mol·dm^{-3}, $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ = 2.5 × 10^{-4} mol·dm^{-3}, I = 0.20 mol·dm^{-3} and T = 25˚C. The kinetic data are graphically represented in **Figure 3**. Variation of the k_{obs} with pH is summarized in (**Table 2**), which indicates that the reaction rate increases with increasing pH values. Plot of k_{obs} against $\left[IO_4^-\right]$ at different pH values are given in **Figure 3**. From **Figure 3**, it was found that, the slopes are dependent on pH (**Table 3**). Plot of these slopes (k_1) versus 1/H$^+$ are linear with slope (k_3) and an intercept (k_2) according to Equation (4).

$$k_1 = k_2 + k_3/\left[H^+\right] \qquad (4)$$

Table 1. Dependence of k_{obs} on $\left[IO_4^-\right]$ at pH = 4.05, $[Cr^{III}(NTA)(Ala)(H_2O)]^{-a}$ = 2.5 × 10^{-4} mol·dm^{-3}, and I = 0.2 mol·dm^{-3} at different temperatures.

$10^2\left[IO_4^-\right]$ (mol·dm^{-3})	10^4 k_{obs} (s^{-1}) 15˚C	20˚C	25˚C	30˚C	35˚C
0.5	0.500	0.88	1.20	1.51	2.31
1.0	1.25	1.95	2.96	3.48	6.23
1.5	2.51	3.25	4.15	4.81	8.50
2.0	2.98	4.5	5.65	6.33	12.00
3.0	4.46	6.68	8.31	10.15	13.50
4.0	-	8.80	9.86	12.25	-
5.0	7.25	10.20	12.75	-	20.05

Table 2. Effect of pH on k_{obs} at $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ = 2.5×10^{-4} mol·dm^{-3}, I = 0.2 mol·dm^{-3}, and T = 25˚C.

$10^2[IO_4^-]$ (mol·dm^{-3})	10^4k_{obs} (s^{-1}) pH = 3.40	pH = 3.72	pH = 4.05	pH = 4.27	pH = 4.45
0.5	0.66	0.83	1.20	1.66	3.60
1.0	0.88	1.51	2.96	5.51	-
1.5	1.20	2.28	4.14	6.4	8.45
2.0	1.58	2.66	5.65	10.51	12.16
3.0	2.95	4.01	8.31	15.5	19.01
4.0	4.16	5.66	9.86	19.03	22.56
5.0	5.00	7.58	12.75	23.68	31.20

Table 3. Values of (k_1) at different temperatures.

T(˚C)	$10^3/T$(K^{-1})	10^2k_1 (mol^{-1}·dm^3·s^{-1})	$-\ln k_1/T$(mol^{-1}·dm^3·s^{-1}·K^{-1})
15	3.47	1.42	9.92
20	3.41	2.13	9.53
25	3.35	2.64	9.33
30	3.30	3.21	9.15
35	3.25	4.05	8.93

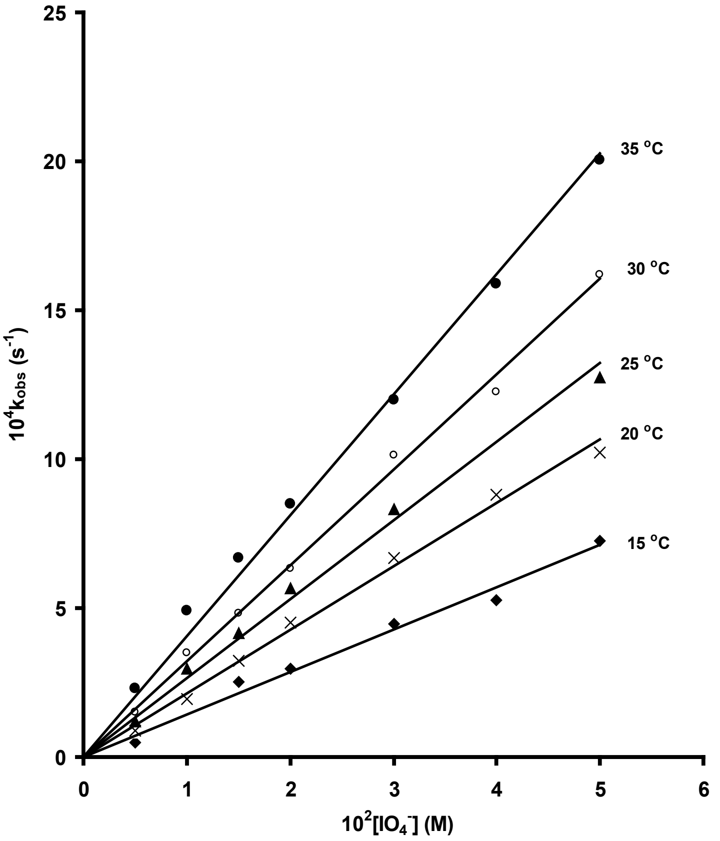

Figure 2. Plot of k_{obs} versus $[IO_4^-]$ at different temperatures.

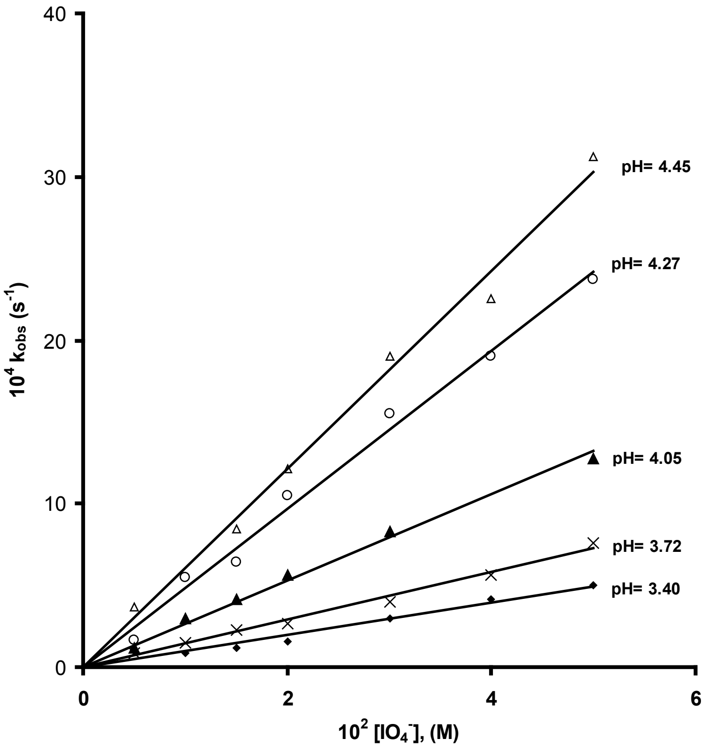

Figure 3. Plot of k_{obs} versus $\left[IO_4^-\right]$ at different pH.

The values of k_2 and k_3 were obtained from the intercept and slope as 4.28 × 10^{-3} $mol^{-1}\cdot dm^3\cdot s^{-1}$ and 2.09 × 10^{-6} s^{-1} respectively at $T = 25^\circ C$.

From Equations (2), (3) and (4), the rate law for the oxidation of $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ by periodate is given by Equation (5):

$$d\left[Cr^{VI}\right]/dt = \left[IO_4^-\right]\left[Cr^{III}(NTA)(Ala)(H_2O)\right]^-\left(k_2 + k_3/\left[H^+\right]\right) \quad (5)$$

and

$$k_{obs} = \left(k_2 + k_3/\left[H^+\right]\right)\left[IO_4^-\right] \quad (6)$$

Table 3 shows the values of k_1 which obtained from the slopes of **Figure 2** at different temperatures. From these results, thermodynamic activation parameters ΔH^* and ΔS^* associated with constant (k_1) in Equation (3) were calculated using Eyring approximation. ΔH^* and ΔS^* are equal to 35.75 $kJ\cdot mol^{-1}$ and −155.3 $J\cdot K^{-1}\cdot mol^{-1}$ respectively. According to the data reported, The effect of hydrogen ion concentration was investigated over the pH range 3.40 - 4.45, we noticed that in acidic aqueous medium the chromium(III) complex may be involved in the equilibrium shown in Equation (7).

$$\left[Cr^{III}(NTA)(Ala)(H_2O)\right]^- \rightleftharpoons \left[Cr^{III}(NTA)(Ala)(OH)\right]^{2-} + H^+ \qquad K_1 \quad (7)$$

The value of K_1 can be determined potentiometrically and has the value 1.70 × 10^{-5} at 25˚C. From the pH range and K_1 value, it may be suggested that the involvement of the deprotonated form of the chromium(III)-complex in the rate-determining step. There are possibilities for the coordination of IO_4^- due to the following reasons. Firstly, the H_2O ligand in $[Cr^{III}(NTA)(Ala)(H_2O)]^-$ may be labile and hence substitution by IO_4^- is likely [29] [30] [31]. Secondly, periodate ion is capable of acting as a ligand, as evidenced from its coordination to copper(III) [32] and nickel(IV) [33]. Also there is a direct relationship between the reaction rate and ionic strength, where the values of $10^4 k_{obs}$ obtained at I = 0.30, 0.40, 0.50 and 0.60 mol·dm^{-3}, pH = 4.05, $[IO_4^-]$ = 0.02 mol·dm^{-3} and T = 25˚C are 5.83, 6.05, 6.27 and 6.57, respectively which is attributed to the reaction between similar charged species. It may be concluded that from the reported equilibrium constants of aqueous periodate solutions over the pH range used that, the periodate species likely to be present are IO_4^-, $H_4IO_6^-$ and $H_3IO_6^{2-}$ [34], according to the equilibria, Equations (8)-(10):

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad \left(K_2 = 1.98\times10^{-3}\ \text{dm}^3\cdot\text{mol}^{-1}\right) \tag{8}$$

$$H_4IO_6^- \rightleftharpoons 2H_2O + IO_4^- \quad \left(K_3 = 0.025\right) \tag{9}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad \left(K_4 = 5.0\times10^{6}\ \text{dm}^3\cdot\text{mol}^{-1}\right) \tag{10}$$

From K_4 value, $H_3IO_6^{2-}$ is not the predominant species (IO_4^- will be used to represent $H_4IO_6^-$).

The mechanistic pathway for the oxidation of nitrilotriacetatetrisodium salt chromium(III) complex by periodate over the studied pH range may be represented by Equations (11)-(23):

$$\left[Cr^{III}(NTA)(Ala)(H_2O)\right]^- \rightleftharpoons \left[Cr^{III}(NTA)(Ala)(OH)\right]^{2-} + H^+ \quad K_1 \tag{11}$$

$$\begin{aligned}&\left[Cr^{III}(NTA)(Ala)(H_2O)\right]^- + \left[IO_4^-\right]\\ &\rightleftharpoons \left[Cr^{III}(NTA)(Ala)(OIO_3)\right]^{2-} + H_2O \quad K_5\end{aligned} \tag{12}$$

$$\begin{aligned}&\left[Cr^{III}(NTA)(Ala)(OH)\right]^{2-} + \left[IO_4^-\right]\\ &\rightleftharpoons \left[Cr^{III}(NTA)(Ala)(OH)(OIO_3)\right]^{3-} \quad (K_6)\end{aligned} \tag{13}$$

$$\left[Cr^{III}(NTA)(Ala)(OIO_3)\right]^{2-} \xrightarrow{k_4} \text{Products} \tag{14}$$

$$\left[Cr^{III}(NTA)(Ala)(OIO_3)(OH)\right]^{3-} \xrightarrow{k_5} \text{Products} \tag{15}$$

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

$$\begin{aligned}d\left[Cr^{VI}\right]/dt = {}& k_4\left[Cr^{III}(NTA)(Ala)(OIO_3)\right]^{2-}\\ &+ k_5\left[Cr^{III}(NTA)(Ala)(OH)(OIO_3)\right]^{3-}\end{aligned} \tag{16}$$

Since

$$\left[Cr^{III}(NTA)(Ala)(OIO_3)\right]^{2-} = K_5\left[Cr^{III}(NTA)(Ala)(H_2O)\right]^-\left[IO_4^-\right] \tag{17}$$

and

$$\left[Cr^{III}(NTA)(Ala)(OH)(OIO_3)\right]^{3-} = K_6\left[Cr^{III}(NTA)(Ala)(OH)\right]^{2-}\left[IO_4^-\right] \tag{18}$$

Substitution in Equations (17) and (18) in Equation (16) leads to:

$$\begin{aligned}\mathrm{d}\left[\mathrm{Cr^{VI}}\right]/\mathrm{d}t = {} & K_2k_4\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{H_2O})\right]^-\left[\mathrm{IO_4^-}\right] \\ & + k_5K_6\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{OH})\right]^{2-}\left[\mathrm{IO_4^-}\right]\end{aligned} \tag{19}$$

Since

$$\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{OH})\right]^{2-} = K_1\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{H_2O})\right]^-/\left[\mathrm{H^+}\right] \tag{20}$$

Substitution Equation (20) in Equation (19) we obtained:

$$\begin{aligned}\mathrm{d}\left[\mathrm{Cr^{VI}}\right]/\mathrm{d}t = {} & K_5k_4\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{H_2O})\right]^-\left[\mathrm{IO_4^-}\right] \\ & + \left(k_5K_6K_1/\left[\mathrm{H^+}\right]\right)\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{H_2O})\right]^-\left[\mathrm{IO_4^-}\right]\end{aligned} \tag{21}$$

On rearrangement:

$$\mathrm{d}\left[\mathrm{Cr^{VI}}\right]/\mathrm{d}t = \left(k_4K_5 + k_5K_6K_1/\left[\mathrm{H^+}\right]\right)\left[\mathrm{Cr^{III}}(\mathrm{NTA})(\mathrm{Ala})(\mathrm{H_2O})\right]^-\left[\mathrm{IO_4^-}\right] \tag{22}$$

Hence,

$$k_{\mathrm{obs}} = \left[\mathrm{IO_4^-}\right]\left\{k_4K_5 + \left(k_5K_1K_6/\left[\mathrm{H^+}\right]\right)\right\} \tag{23}$$

From a comparison of Equations (6) and (23) one obtains $k_2 = k_4K_5$ and $k_3 = k_5K_1K_6$. Equation (23) contains two terms, first term represents path independent of [H^+] and the second term represents path dependent on [H^+]. In comparison with the oxidation of [$Cr(NTA)(H_2O)_2$] [23] under the same conditions, the deprotonated complexes are significantly found to be more reactive than their conjugate acids. The rate of oxidation of this [$Cr(NTA)(H_2O)_2$] is more than [$Cr^{III}(NTA)(Ala)(H_2O)$]$^-$ This means that the stability of the ternary complex, [$Cr^{III}(NTA)(Ala)(H_2O)$]$^-$, is more than the binary one, [$Cr(NTA)(H_2O)_2$], toward oxidation. This may be due to the presence of the amino acid as a secondary ligand in the ternary complex, 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 [35]. 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 [35]. The relatively low value of ΔH^* for [$Cr^{III}(NTA)(Ala)(H_2O)$]$^-$ 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 4**. ΔH^* and ΔS^* for the oxidation of these complexes were calculated related to intramolecular electron transfer steps except for [$Cr^{III}(HIDA)_2(H_2O)$], 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 4**, and an excellent linear relationship

Table 4. Enthalpies and entropies of activation for the oxidation of chromium(III) complexes by periodate.

Complex	$10^3 k^{et}$ (s^{-1})	ΔH^* (KJ/mol)	$-\Delta S^*$ (J/Kmol)	Ref.	Figure 4 key
$[Cr^{III}(TOH)(H_2O)]$	2.95	76	38.7	29	1
$[Cr^{III}(NTA)(Asp)(H_2O)]^-$	3.93	64.6	76	13	2
$[Cr^{III}(Ud)(Asp)(H_2O)_3]^{2+}$	0.70	59.5	106.8	16	3
$[Cr^{III}(NTA)(Hist)(H_2O)]^-$	32.00	36.5	148	13	4
$[Cr^{III}(NTA)(Ala)(H_2O)]^-$	26.40	35.75	155.3	This work	5
$[Cr^{III}(Arg)_2(H_2O)_2]^+$	3.46	30	192	13	6
$[Cr^{III}(NTA)(H_2O)_2]$	62.00	14	220	23	7
$[Cr^{III}(HIDA)_2(H_2O)]$	10.90	12.3	240.7	25	8

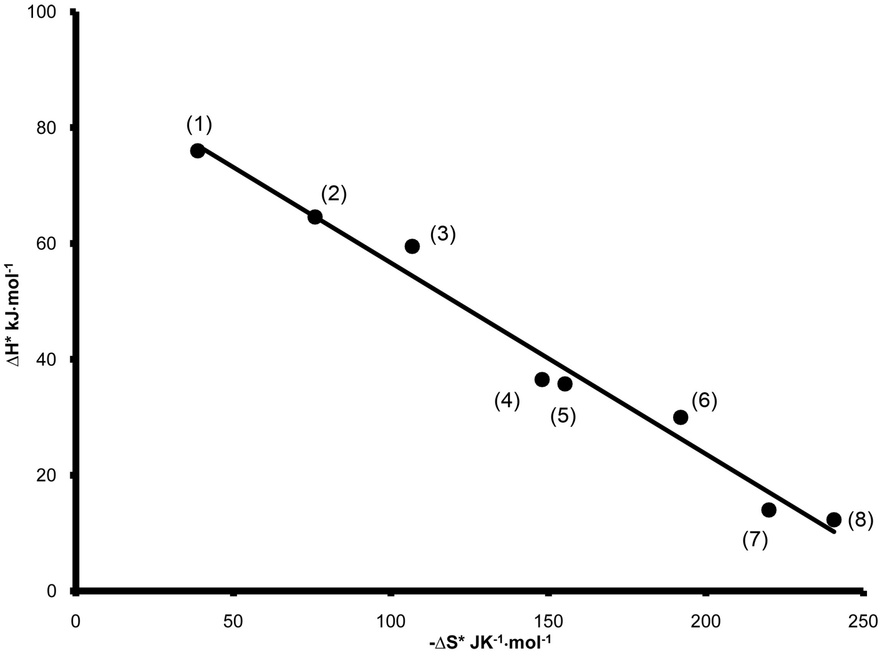

Figure 4. Enthalpies and entropies of activation of some chromium(III) complexes.

was obtained. Similar linear plots were found for a large number of redox reactions [36] [37] 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 [38] [39] [40].

4. Conclusion

Oxidation of $[\mathrm{Cr^{III}(NTA)(Ala)(H_2O)}]^-$ by periodate proceeds via an inner-sphere mechanism. Rate of oxidation increases with increasing pH. These reactions proceed through two-electron transfer process leading to the formation of chromium(VI). A common mechanism for the oxidation of ternary chromium(III) complex by periodate is proposed, and is supported by the excellent isokinetic relationship between ΔH^* and ΔS^* values for these reactions.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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