Kinetics of Oxidation of Novel Ternary Complexes of Chromium (III) Involving Alanine or Cysteine and 2-(Phenylamino)Acetohydrazide by Periodate

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Abstract—Kinetics of oxidation of both ternary complexes [Cr(cys)(HL)(H₂O)]^2+ and [Cr(ala)(HL)(H₂O)]^2+ (HL = 2-(phenylamino)acetohydrazide, cys = Cysteine and ala = alanine) by periodate have been studied spectrophotometrically in aqueous solution over a variety of pH and temperature ranges. The rate of the reaction increases with the increasing of periodate, temperature and pH. The reaction is independent on the complex concentration and decreases with ionic strength. The oxidation reaction [Cr(cys)(HL)(H₂O)]^2+ - periodate obeys the general rate law.

\[
d [Cr^{VI}] / dt = (k_{\text{obs}} + k_3 / [H^+]) [IO_2^-] [Cr(cys)(HL)(H₂O)]^2+.
\]

Where,

\[
k_{\text{obs}} = (k_4 + k_5 / [H^+]) [IO_2^-]
\]

While the oxidation of [Cr(ala)(HL)(H₂O)]^2+ by periodate, found obey the rate equation,

\[
d [Cr^{VI}] / dt = (k_6 + k_5 / [H^+]) [IO_3^-] [Cr(ala)(HL)(H₂O)]^2+.
\]

Where,

\[
k_{\text{obs}} = (k_6 + k_5 / [H^+]) [IO_3^-] [IO_3^-] [IO_3^-]
\]

An inner-sphere process accommodated through replacement of coordinate H₂O in the one species, by periodate. The enthalpy of activation ΔH^° and entropy of activation ΔS^° also are calculated.

Keywords—Cysteine; Alanine; Periodate; Hydrazides.

1. INTRODUCTION

In weakly and neutral acidic solutions Periodate is a two electron oxidant, its reactions with 1, 2-diols are often invoked in cyclic intermediates. [1] Previously, it was shown that in most of its reactions with transition metal complexes, Periodate acts as an inner-sphere oxidant. The kinetics of oxidation of a number of chromium (III) complexes by Periodate has been reported. In some of these reactions, the hydroxo form of the chromium (III) complex is the most involved in the rate determining step. In most of these reactions the hydroxo and the conjugate acid forms are the reactive species at the same time and the oxidation interpreted through the formation of intermediate precursor complex followed by an intra-molecular electron transfer step.[2-6] The slower step determines the reaction rate determining step. It is frequently proposed that substitution happens on the chromium (III) reactive species. This seems to be unlikely, even in the existence of the labilizing OH⁻ ligand, since chromium (III) complexes, usually, are known to be inert. The most likely process is one in which the coordination sphere of periodate is joined via coordination of the chromium (III) complex over the hydroxo ligand or by substitution on H₂IO₄⁻. In some oxidation reactions by Periodate the hydroxo form is not likely reactive species and the conjugate acid form are the reactive species in the pH range of study. The conjugate acid form are the reactive species in the oxidation of diaqua(nitrilotriacetato)-chromium(III) by periodate in aqueous solutions. [7]

Whole trivalent Cr is assumed to be a highly safe mineral while Hexavalent Cr is more soluble than trivalent Cr and at least five times as toxic. The genotoxicity of Cr⁴⁺ compounds is maybe based on an oxidative DNA damage. Chromium (V) is supposed to play a role in the genotoxic effects of chromium (III) complexes. The ease of oxidation of chromium (III) complexes near the physiological pH value is the reason for concern as chromium (V), and chromium (VI) may be readily formed in this pH range. [8] Chromium (V) is reported to be stabilized by some amino acids [2, 9]. Chromium (V) formation is reported in the most and almost all the oxidation reactions to be in fast steps and is not a rate determining step. [5, 6, 10].

Hydrazones have been demonstrated to own, among other, anticonvulsant, antimicrobial, anti-inflammatory, analgesic, antitubercular, antiplatelet and antitumoral activities. [11, 12]

In this work, the kinetics of oxidation reactions [Cr(cys)(HL)(H₂O)]^2+ - periodate and [Cr(ala)(HL)(H₂O)]^2+ - periodate were studied. Choice of this complexes is due to the Hydrazones biological importance [11] and its using as compounds for drug design, organocatalysis, and possible ligands for metal complexes. Cysteine and Alanine exist widely inside and outside of cells. It’s a probability to form binary or ternary complex with Cr⁶⁺ from natural food.

2. EXPERIMENTAL

2.1. Materials and methods

All chemicals used in this study were of reagent grade (BDH, Sigma and Aldrich) Stock solutions of sodium metaperiodate were prepared by weight and wrapped with...
aluminum foil and reserved in the dark. Solutions of periodate are known to undergo photochemical decomposition [13]. Buffer solutions were made from known concentrations of Na₂HPO₄ and citric acid or hydrochloric acid standard solutions and Potassium chloride [14]. NaN₃ was used in adjusting ionic strength in the different buffered solutions. Doubly distilled H₂O was used in all kinetic runs.

The formation of Cr⁶⁺ was followed at wavelength 356 nm using an Apel PD-303S spectrophotometer to measure the reaction rate. Pseudo-first-order conditions were maintained in all runs by the presence of an excess of periodate. The reaction mixture checked by acrylonitrile adding before the addition of periodate. Polymerization of acrylonitrile was not observed. The uv-visible absorption spectra of the product of this reaction was followed spectrophotometrically for a definite period of time using the doubly beam JASCO UV-530 spectrophotometer. Potentiometric measurements were performed with a Metrohm 702 SM titrim. The titrprocessor equipped with a 728 dosimat (Switzerland-Heriau). The titrprocessor and electrode were calibrated with standard buffer solution [15]. Calculations were performed using computer program MINIQUAD-75. The solution contains 5.0 ml 0.01 mol dm⁻³ complex, 5.0 ml 0.20 mol dm⁻³ NaNO₃, 5.0 ml 0.04 mol dm⁻³ HNO₃ and 25.0 ml deionized water, was titrated with 0.1 mol dm⁻³ NaOH at 25 °C. High performance liquid chromatography (HPLC) was performed with an Agilent 1100 series (Waldborn, Germany), quaternary pump(G1311A), Degasser (G1322A), Thermostated Autosamples (G1329A), variable wave length detector (G1314A); and column: Zorbax 300SB C₁₈ column (Agilent Technologies, USA). The pH of the reaction mixture was measured using a Chertsey Surrey, 7065 pH-meter.

2-(phenylamino)acetohydrazide abbreviated as HL were prepared by the reported method [16, 21]. Elemental anal. (%) for C₁₀H₁₁N₂O: Calcd: C, 58.17; H, 6.71; N, 25.00. Found: C, 58.30; H, 6.90; N, 25.00. IR band assignments of the prepared ligand HL νCH = 3304 cm⁻¹; νN₂H₂ 3342 cm⁻¹; νCN, 1260 cm⁻¹; aromatic νC-C 1601 cm⁻¹; ν CONH, 1650 cm⁻¹. The mass spectrum of HL revealed ion peak at m/e = 165.09 (88.60%).

The preparation of [Cr(cys)(HL)(H₂O)₂](NO₃)₂, was made by adding a mixture of Cr(NO₃)₃.6H₂O (0.4004 g, 1.0 mmol) and Cysteine (0.0761 g, 1.0 mmol) to 50 mL distilled water. After the complete dissolution. The resulting solution was heated under an air reflux condenser at 80 °C for 3 hours and the total volume kept as 50 mL. A violet colour appeared after 20 min. and increased gradually within the time. An equal moles of 2-(phenylamino)acetohydrazide (HL) (0.1651 g, 1.0 mmol) were added to the Cr³⁺ system complex solution and the resulting solution were heated under an air reflux condenser at 80 °C for 3 hours. The violet crystals of the complex separated by adding a solution of sodium bicarbonate 0.1 mol dm⁻³ drop by drop until the pH value of the system reached 7.0. The filtrate was washed several times with distilled water and dried in air at ambient temperature.

[Cr(ala)(HL)(H₂O)₃]NO₃, prepared by the same method as [Cr(cys)(HL)(H₂O)₃]NO₃ except that Alanine (0.0891 g, 1.0 mmol) was added instead of Cysteine. The pale brown crystals of the complex separated by adding 0.1 mol dm⁻³ sodium bicarbonate drop by drop until the pH value of the system reached 7.5.

2.2. OXIDATION PRODUCTS.

The products of the oxidation reactions revealed the producing of a relatively stable Cr⁶⁺. It is found that at the end of the reaction Cr⁶⁺ was formed by the sym-diphenylcarbazide test.

The HPLC retention time indicates how long it takes for a compound to come out of the HPLC column. Each peak in the chromatogram indicates the presence of a chemical in the sample. At the same experimental condition the retention time used as a way to determine the presence of these chemicals in other samples. Qualitative analysis involves running a standard that contains the target analytes to obtain the calibration standard retention times. After that run the samples of interest. The seen peaks present in the sample that correspond to peaks in our calibration standard determine the presence of these analytes. HPLC of the products of oxidation reactions revealed the dissociation of the Chromium ternary complexes after oxidation and the releasing of the ligands.

3. RESULTS AND DISCUSSION.

3.1. CHARACTERIZATION OF COMPLEXES.

Elemental analysis, IR, TGA and cyclic voltammetry were used on characterization of complexes. C₇H₈O₄N₃O₅ (Found: C, 24.77; H, 4.00; N, 15.95; S, 6.10; Calcd: C, 25.63; H, 4.50; N, 16.31; S, 6.22%) while the complex [Cr(cys)₂(NO₃)₃] (Found: C, 27.77; H, 4.90; N, 17.00; Calcd: C, 27.33; H, 4.80; N, 17.39%). In IR spectrum of complexes bands in the 3650-3300 cm⁻¹ region, were attributed to νOH of the coordinated water molecule. The νC=O Stretch and the in plane bending of the OH group associated with carboxylate functionality in the 1390 cm⁻¹ and 1206 cm⁻¹ region in cysteine IR spectrum and in the 1400 cm⁻¹ and 1210 cm⁻¹ region in alanine IR spectrum completely disappeared and a new carboxylate band νCOO⁻ appeared in the region 1380 to 1390 cm⁻¹ in the metal complexes IR spectrum, indicating that the carboxyl group of cysteine or alanine participate in the coordination with the metal ion through deprotonation [17]. The shifting of an infrared peaks which denotes the (-CONH) in HL to a lower wave number value in the spectrum of solid complexes indicating that the amide group participates in the coordination with Cr³⁺. The absence of an infrared peak between 450 cm⁻¹ and 490 cm⁻¹ in [Cr(cys)(HL)(H₂O)₃]³⁺ IR spectrum, which denotes the disulfide bond, indicates that Cr³⁺ didn’t oxidize cysteine to form cystine.

The thermogram of the complex [Cr(cys)(HL)(H₂O)₃](NO₃)₂ shows a weight loss of 11.27% over the temperature range of (50 – 200) °C corresponding to a loss of three molecules of coordinated water molecules (calc. 10.48%). While the complex [Cr(ala)(HL)(H₂O)₃](NO₃)₂ thermogram shows the weight loss of 10.10% being at 200°C corresponds to the loss of three coordinated water molecules (calc. 11.18%).

The electrochemical behaviour of Cysteine, alanine, 2-(phenylamino)acetohydrazide (HL), Cr³⁺, [Cr(ala)(HL)(H₂O)₃]²⁺ and [Cr(cys)(HL)(H₂O)₃]²⁺ was studied to identify the complexes formation and the easier on oxidation. The cyclic voltammogram (C.V) of (1×10⁻³ mol dm⁻³) [Cr(cys)(HL)(H₂O)₃]²⁺ was obtained at 25°C and pH = 2.50 over potential range -1.0 V to 1.5 V versus SCE with scanning
rate 0.025 V sec\(^{-1}\) and 2 mol dm\(^{-3}\) of NaNO\(_3\) as supporting electrolyte. A well-defined redox anodic electrochemical reaction at -0.33 V and 0.62 V revealed two oxidation reactions and four cathodic reactions at -0.73 V, -0.58 V, -0.48 V, 0.71 V corresponding to a reduction reaction. The cyclic voltammogram of [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) at the same conditions mentioned above, exhibited an anodic peak at -0.11 V and 0.77 V due to oxidation reactions and one cathodic peak at 0.42 V. The cyclic voltammogram of Cysteine gave anodic peak at -0.87 V and cathodic peaks at -0.82, 0.42 V. The cyclic voltammogram of alanine gave anodic peaks at -0.89 V and cathodic peaks at -0.83, -0.29, 0.44 V. C.V of 2-(phenylamino)acetohydrazide (HL) gave anodic peaks at -0.89, -0.21, 0.35 V and cathodic peaks at -1.21 V. The cyclic voltametric redox peak values of ligands are different from those of its complexes which gave an evidence of the complexes formation. The oxidation potential values shifted to those of its complexes which gave an evidence of the complexes formation. The oxidation process becomes more difficult in the complexes.

The stability constants of the complex [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) and [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) and its ligands were determined at T = 25°C and I = 0.4 mol dm\(^{-3}\) by potentiometric – pH plotting according the reported method of Irving and Rossotti [18]. The potentiometric titration curves of 2-(phenylamino)acetohydrazide and its complexes [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) and [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) were obtained by plotting pH versus added volume of alkali. The association constant for [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) = 9.95×10\(^{7}\) and the association constant for [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) = 1.86×10\(^{-3}\). The pK value for [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) = 6.00 and for [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) = 4.73.

3.2. Examination of oxidation products.

Identifying the reaction products may reflect the reaction mechanism and the oxidation products examined for this reason.

The calibration standards (alanine, IO\(_3\)\(^{-}\)) and the oxidation products of complexes [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) and [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) with periodate were checked individually by HPLC, using two different mobile phases. In the first, the product of oxidation of 1×10\(^{-3}\) mol dm\(^{-3}\) [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) with 1×10\(^{-3}\) mol dm\(^{-3}\) periodate revealed the presence of three peaks with high intensity at retention time 3.27, 3.92 and 4.29 min., Fig.5. The obtained peak at time 3.92 is identical with the retention time 3.89 min, shown in the chromatogram of KIO\(_3\) standard solution, under the same conditions Fig.6. While the product of oxidation of 1×10\(^{-3}\) mol dm\(^{-3}\) [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) with 1×10\(^{-3}\) mol dm\(^{-3}\) periodate revealed the presence of two peaks with high intensity at retention time 3.04 and 3.95 min., Fig. 7. The obtained peak at time 3.95 is identical with the retention time 3.89 min, shown in the chromatogram of KIO\(_3\) standard solution.

The above method used to check the presence of alanine in the oxidation products of [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) the HPLC analysis revealed the presence of two main peaks at 3.36 min and 4.29 min., Fig.3. The obtained peak at time 4.29 min is identical with the retention time 4.13 min, shown in the chromatogram of alanine standard solution, under the same conditions Fig.4. In the second system, the products of oxidation each complex was detected individually at UV, 223 nm on the diode array detector C\(_18\) column which was used for separation at a flow 0.5mL/min. The mobile phase composition was 50/50 Methanol/120 mM sodium phosphate, monobasic [20]. The above method used to check the presence of IO\(_3\)\(^{-}\) because it was expected that it will be one product of oxidation. The product of oxidation of 1×10\(^{-3}\) mol dm\(^{-3}\) [Cr(cys)(HL)(H\(_2\)O)]\(^{2+}\) with 1×10\(^{-3}\) mol dm\(^{-3}\) periodate revealed the presence of three peaks with high intensity at retention time 3.27, 3.92 and 4.29 min., Fig.5. The obtained peak at time 3.92 is identical with the retention time 3.89 min, shown in the chromatogram of KIO\(_3\) standard solution, under the same conditions Fig.6. While the product of oxidation of 1×10\(^{-3}\) mol dm\(^{-3}\) [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) with 1×10\(^{-3}\) mol dm\(^{-3}\) periodate revealed the presence of two peaks with high intensity at retention time 3.04 and 3.95 min., Fig.7. The obtained peak at time 3.95 is identical with the retention time 3.89 min, shown in the chromatogram of KIO\(_3\) standard solution.

The HPLC Chromatogram of complex [Cr(ala)(HL)(H\(_2\)O)]\(^{2+}\) oxidation products (10μL) injection using an eluent of isocratic mobile phase with the ratio of mobile phase A and B as 25:75, whereas mobile phase A is 2.5 mM Potassium dihydrogen phosphate with pH = 2.85 and B mobile phase is Acetonitrile and λ=254 nm.
Fig. 4. HPLC Chromatogram for alanine (5 μL) injection using an eluent of isocratic mobile phase with the ratio of mobile phase A and B as 25:75, whereas mobile phase A is 2.5 mM Potassium dihydrogen phosphate with pH=2.85 and B mobile phase is Acetonitrile and λ=254 nm.

Fig. 5. HPLC Chromatogram of complex [Cr(ala)(HL)(H$_2$O)$_3$]$^{2+}$ oxidation products (20μL) injection. Eluent (50/50 methanol/120 mM sodium phosphate, monobasic (pH=3.00) and λ=223 nm).

The oxidation of [Cr(cys)(HL)(H$_2$O)$_3$]$^{2+}$ and [Cr(ala)(HL)(H$_2$O)$_3$]$^{2+}$ with periodate were also followed by recording the UV-visible absorption spectra of the oxidation products between 320 and 700 nm as a function of time. A single peak appeared at 365-375 nm and increased with time due to the formation of Cr$^{VI}$ which have the same peak at the same pH this provides evidence that Cr$^{VI}$ is one of the oxidation products. Fig. 8 and Fig. 9.


The oxidation of [Cr(cys)(HL)(H$_2$O)$_3$]$^{2+}$ has been studied under condition of ionic strength range (0.2 - 0.6) mol.dm$^{-3}$, pH range (1.59 - 2.60) and temperature (20 - 40°C) over range of periodate and complex concentration; (1.0-4.5) ×10$^{-2}$ mol.dm$^{-3}$ and (2.0 - 6.0) ×10$^{-4}$ mol.dm$^{-3}$ respectively and the oxidation of [Cr(ala)(HL)(H$_2$O)$_3$]$^{2+}$ has been studied under the same conditions of ionic strength, temperature, periodate and complex concentrations but the pH range of study was (1.70-2.78).

Fig. 6. HPLC Chromatogram for IO$_3^-$ (10μL) injection using eluent (50/50 Methanol/120 mM sodium phosphate, monobasic (pH=3.00) and λ=223 nm).

Fig. 7. HPLC Chromatogram for IO$_3^-$ (10μL) injection using an eluent of isocratic mobile phase with the ratio of mobile phase A and B as 25:75, whereas mobile phase A is 2.5 mM Potassium dihydrogen phosphate with pH=2.85 and B mobile phase is Acetonitrile and λ=254 nm.

Fig. 8. Change in absorbance as a function of time. Curves (1 - 7) were recorded at 5, 10, 15, 20,25,30,35 mint, respectively from the time of initiation [Cr(cys)(HL)(H$_2$O)$_3$]$^{2+}$ = 1.0x10$^{-3}$ mol dm$^{-3}$, pH = 2.80 , I = 0.4 mol dm$^{-3}$ (NaNO$_3$), [IO$_3^-$] =2.0x10$^{-2}$ mol dm$^{-3}$ and T = 30°C Curve (8) spectrum of chromate ion (1.0x10$^{-3}$ mol dm$^{-3}$) at the same pH.
Kinetic measurements were carried out under pseudo first order conditions with periodate concentration ≥ 10 [Cr(III)]. Plots of ln(A∞ - At) versus time, where A∞ and At are absorbance values at infinity and time t respectively, are linear up to 85 % of reaction. Values of the pseudo-first-order rate constants, Kobs, at fixed periodate concentration, ionic strength and pH, are independent of the initial complex concentration as shown in Table 1, indicating first order dependence on complexes concentration, eq.(1,2).

\[
\begin{align*}
\text{Rate1} &= K_{obs1}[\text{Cr(cys})(\text{HL})(\text{H}_2\text{O})]^2 \quad (1) \\
\text{Rate2} &= K_{obs2}[\text{Cr(ala})(\text{HL})(\text{H}_2\text{O})]^2 \quad (2)
\end{align*}
\]

The variation of Kobs with [IO₄⁻] at various temperatures and pH values were found to be linear without intercept according to Eq. (3, 4). Plot of Kobs1, Kobs2 against [IO₄⁻] (Fig.10, 11).

\[
\begin{align*}
K_{obs1} &= k_1 [\text{IO}_4^-] \\
K_{obs2} &= k_2 [\text{IO}_4^-] \quad (3, 4)
\end{align*}
\]

The dependence of the reaction rate on pH has been investigated over the above mentioned pH ranges, complex [Cr(cys)(HL)(H₂O)]²⁺ or [Cr(ala)(HL)(H₂O)]²⁺ concentration, temperature and periodate concentration. Variation of (k₁ or k₂) with pH at different temperatures is listed in Tables (3, 4). From which the reaction rate increased gradually with increasing pH values. Plots of the slopes (k₁ or k₂) versus (1 / [H⁺]) is found to be linear with an intercept as shown in (Fig.12, 13). This behaviour can be described by Eq. (5, 6). For complex [Cr(cys)(HL)(H₂O)]²⁺, Eq.5

\[
k_1 = k_4 + k_5 \frac{1}{[H^+]} \quad (5)
\]

and for complex [Cr(ala)(HL)(H₂O)]²⁺, Eq.6

\[
k_2 = k_6 + k_7 \frac{1}{[H^+]} \quad (6)
\]

Where, k₁, k₂, k₃, k₄, k₅, k₆ are constants. From equation (5, 6) and substitution in equation (1, 2) the following equation can obtain the general rate low equations (7, 8);

\[
\begin{align*}
\text{Rate1} &= (k_1 + k_3 / [H^+]) [\text{IO}_4^-] [\text{Cr(cys)}(\text{HL})(\text{H}_2\text{O})]^2 \quad (7) \\
\text{Rate2} &= (k_5 + k_7 / [H^+]) [\text{IO}_4^-] [\text{Cr(ala)}(\text{HL})(\text{H}_2\text{O})]^2 \quad (8)
\end{align*}
\]

![Fig. 9. Change in absorbance as a function of time. Curves (1 - 8) were recorded at 5, 10, 15, 20, 25, 30, 35, 45 min, respectively from the time of initiation.](image)

![Fig. 10. Variation of Kobs1 with [IO₄⁻] at pH = 2.60, I = 0.4 mol dm⁻³ and [Cr(cys)(HL)(H₂O)]²⁺ = 4.0×10⁻³ mol dm⁻³.](image)

![Fig. 11. Variation of Kobs2 with [IO₄⁻] at pH = 2.25, I = 0.4 mol dm⁻³ and [Cr(ala)(HL)(H₂O)]²⁺ = 4.0×10⁻⁴ mol dm⁻³.](image)

| Table 1. Dependence of kobs1 on the initial of [Cr(cys)(HL)(H₂O)]²⁺ at [IO₄⁻] = 4.5 × 10⁻² mol dm⁻³, pH = 2.20, I = 0.4 mol dm⁻³ and temperature = 35±0.1 °C. |
|-----------------|-----------------|
| 10³[R] (Cr(cys)(HL)(H₂O))²⁺ mol dm⁻³ | 10³[kobs1 ±SD] (s⁻¹) |
| 2.0 | 42.40±1.61 |
| 3.0 | 42.10±1.06 |
| 4.0 | 42.20±0.95 |
| 5.0 | 42.40±1.02 |
| 6.0 | 42.10±1.16 |

| Table 2. Dependence of kobs2 on the initial of [Cr(ala)(HL)(H₂O)]²⁺ at [IO₄⁻] = 2.0 × 10⁻² mol dm⁻³, pH = 2.25, I = 0.4 mol dm⁻³ and temperature = 35±0.1 °C. |
|-----------------|-----------------|
| 10³[R] (Cr(ala)(HL)(H₂O))²⁺ mol dm⁻³ | 10³[kobs2 ±SD] (s⁻¹) |
| 2.0 | 16.80±0.33 |
| 3.0 | 16.80±0.45 |
| 4.0 | 16.80±0.57 |
| 5.0 | 16.80±0.71 |
| 6.0 | 16.80±0.82 |
Where;

\[ K_{obs1} = (k_4 + k_3/\left[H^+\right]) \left[IO_4^-\right] \]  
(9)

\[ K_{obs2} = (k_6 + k_5/\left[H^+\right]) \left[IO_4^-\right] \]  
(10)

The rate of complexes \([Cr(cys)(HL)(H_2O)_3]^{2+}\) or \([Cr(ala)(HL)(H_2O)_3]^{2+}\) oxidation reactions by periodate were decreasing by increasing the ionic strength of the solution as shown in Table 5, and this behavior can attributed to the fact that the reactions takes place between different charged species.

**TABLE 3.** Variation of \(k_1\) with pH of \([Cr(cys)(HL)(H_2O)_3]^{2+}\) at different temperatures.

<table>
<thead>
<tr>
<th>pH</th>
<th>(1/\left[H^+\right] (\text{mol}^{-1}\text{dm}^3))</th>
<th>10(^3) ([k_1\pm\text{SD}] (\text{mol}^{-1}\text{dm}^3\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 20°C</td>
<td>T = 25°C</td>
</tr>
<tr>
<td>1.59</td>
<td>38.90</td>
<td>3.58±0.18</td>
</tr>
<tr>
<td>1.85</td>
<td>70.79</td>
<td>3.61±0.12</td>
</tr>
<tr>
<td>2.20</td>
<td>158.49</td>
<td>3.94±0.12</td>
</tr>
<tr>
<td>2.60</td>
<td>398.11</td>
<td>5.14±0.23</td>
</tr>
</tbody>
</table>

**TABLE 4.** Variation of \(k_2\) with pH of \([Cr(ala)(HL)(H_2O)_3]^{2+}\) at different temperatures.

<table>
<thead>
<tr>
<th>pH</th>
<th>(1/\left[H^+\right] (\text{mol}^{-1}\text{dm}^3))</th>
<th>10(^3) ([k_2\pm\text{SD}] (\text{mol}^{-1}\text{dm}^3\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 20°C</td>
<td>T = 25°C</td>
</tr>
<tr>
<td>1.70</td>
<td>50.12</td>
<td>2.99±0.06</td>
</tr>
<tr>
<td>2.25</td>
<td>177.83</td>
<td>4.42±0.11</td>
</tr>
<tr>
<td>2.52</td>
<td>331.13</td>
<td>6.10±0.14</td>
</tr>
<tr>
<td>2.78</td>
<td>602.56</td>
<td>9.10±0.34</td>
</tr>
</tbody>
</table>

**TABLE 5.** Dependence of \(k_{obs1}\) on ionic strength at pH = 1.59, periodate = 4.0 × 10\(^{-2}\) mol dm\(^{-3}\) \([Cr(cys)(HL)(H_2O)_3]^{2+}\) = 4.0 × 10\(^{-4}\)mol dm\(^{-3}\) and temp. = 20 °C.

<table>
<thead>
<tr>
<th>(I (\text{mol dm}^{-3}))</th>
<th>10(^4) ([k_{obs1}\pm\text{SD}] (\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>13.20±0.27</td>
</tr>
<tr>
<td>0.3</td>
<td>12.60±0.15</td>
</tr>
<tr>
<td>0.4</td>
<td>12.20±0.23</td>
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<tr>
<td>0.5</td>
<td>12.00±0.19</td>
</tr>
<tr>
<td>0.6</td>
<td>11.70±0.17</td>
</tr>
</tbody>
</table>
TABLE 6. Dependence of $k_{obs}$ on ionic strength at pH = 1.70, periodate = $2.5 \times 10^{-2}$ mol dm$^{-3}$ [Cr(ala.)(HL)(H$_2$O)]$^{2+}$ = 4.0 $\times 10^{-4}$ mol dm$^{-3}$, and temp. = 40 °C.

<table>
<thead>
<tr>
<th>$I$ (mol dm$^{-3}$)</th>
<th>$10^3[k_{obs} \pm SD]$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>38.30 ± 0.51</td>
</tr>
<tr>
<td>0.3</td>
<td>20.80 ± 0.12</td>
</tr>
<tr>
<td>0.4</td>
<td>19.50 ± 0.44</td>
</tr>
<tr>
<td>0.5</td>
<td>14.90 ± 0.06</td>
</tr>
<tr>
<td>0.6</td>
<td>13.40 ± 0.11</td>
</tr>
</tbody>
</table>

From transition state theory equation, the thermodynamic activation parameters including enthalpy, $\Delta H^*$, and entropy, $\Delta S^*$, associated with constant $K_2$ are composite values and can be obtained by plotting $\ln K_i / T$ against $1 / T$ respectively as shown in (Fig.14, 15). The enthalpy of activation of [Cr(cys)(HL)(H$_2$O)]$^{2+}$, $\Delta H^*$, have been calculated as 49.31 kJ mol$^{-1}$. The corresponding entropy of activation, $\Delta S^*$, is equal to -1.12 K$^{-1}$ mol$^{-1}$ and the enthalpy of activation of [Cr(ala)(HL)(H$_2$O)]$^{2+}$, $\Delta H^*$, have been calculated as 48.38 kJ mol$^{-1}$. The corresponding entropy of activation, $\Delta S^*$, is equal to -148.94 JK$^{-1}$ mol$^{-1}$.

4.DISCUSION.

Periodate ion is well-known to be involved in complexes equilibrium in aqueous solution as shown in Eq. (11, 12, 13) [22]. Under the reaction conditions, the most likely periodate species are IO$_4^-$, H$_2$IO$_6^-$ and H$_3$IO$_7^-$. The enthalpy of activation of periodate = 2.5×10$^{-2}$ (11) and The corresponding entropy of activation, $\Delta S^*$, have been calculated as 48.38 kJ mol$^{-1}$. The corresponding entropy of activation, $\Delta S^*$, have been calculated as 49.31 kJ mol$^{-1}$. The oxidation reactions of [Cr(cys)(HL)(H$_2$O)]$^{2+}$ and [Cr(ala)(HL)(H$_2$O)]$^{2+}$ complexes also undergoes deprotonation–protonation equilibrium as shown in Eqs. (14, 15).

$[Cr(cys)(HL)(H_2O)]^{2+} \rightleftharpoons [Cr(cys)(HL)(H_2O)_2OH]^+ + H^+ \quad K_7$ (14)

$[Cr(ala)(HL)(H_2O)]^{2+} \rightleftharpoons [Cr(ala)(HL)(H_2O)_2OH]^+ + H^+ \quad K_8$ (15)

The reported values of $K_7$ and $K_8$ are 9.95×10$^{-7}$ and 1.86×10$^{-7}$ mol dm$^{-3}$, respectively, at 25.0 °C and $I = 0.4$ mol dm$^{-3}$. The oxidation reactions of [Cr(cys)(HL)(H$_2$O)]$^{2+}$ and [Cr(ala)(HL)(H$_2$O)]$^{2+}$ by Periodate are not likely proceed via the hydroxo form reactive species and the conjugate acid form are most likely reactive species in the pH range of study. The complexes deprotonated species is not involved in the rate determining step. Also the most likely periodate species present in the pH range covered in this study are H$_3$IO$_7^-$ and H$_2$IO$_6^-$. The mechanism of oxidation of [Cr(cys)(HL)(H$_2$O)]$^{2+}$ by Periodate may be represented by the reaction sequence in Eq. (16, 17, 18, 19,20,21) While the mechanism of oxidation of [Cr(ala)(HL)(H$_2$O)]$^{2+}$ by Periodate may be represented by the reaction sequence in Eq. (22, 23, 24, 25,26,27).

The reaction may go via one or two electron transfer, giving chromium (IV) or chromium (V), respectively, in the rate determining step leading to chromium (VI). Two electron transfer is the most likely pathway. This seems to be confirmed by the absence of polymerization with acrylonitrile.

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_9$ (16)

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{10}$ (17)

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{11}$ (18)

$[Cr(ala)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(ala)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{12}$ (19)

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{13}$ (20)

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{14}$ (21)

$[Cr(ala)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(ala)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{15}$ (22)

$[Cr(ala)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(ala)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{16}$ (23)

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{17}$ (24)

$[Cr(cys)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(cys)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{18}$ (25)

$[Cr(ala)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(ala)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{19}$ (26)

$[Cr(ala)(HL)(H_2O)]^{2+} + H_2IO_6^- \rightleftharpoons [Cr(ala)(HL)(H_2O)_2HIO_6]^+ + H_2O \quad K_{20}$ (27)
IO₃⁻ and Alanine in products confirmed using HPLC which support the dissociation of the complex [Cr(cys)(HL)(H₂O)]₃²⁺ or [Cr(alala)(HL)(H₂O)]₃²⁺ after oxidation.

From the above mechanisms, the rate of the reactions can be described by the following equations:

\[
d \frac{[Cr(VI)]}{dt} = k_{12} [Cr(cys)(HL)(H₂O)]²⁺ [H₂IO₆⁻] / (k_{12} + k_{10}) + k_{14} [Cr(alala)(HL)(H₂O)]²⁺ [H₂IO₆⁻] / (k_{14} + k_{13}) \]

Equation (30) gives:

\[
d \frac{[Cr(VI)]}{dt} = k_{12} k_{10} [Cr(cys)(HL)(H₂O)]²⁺ [H₂IO₆⁻] / (k_{12} + k_{10}) + k_{14} k_{13} [Cr(alala)(HL)(H₂O)]²⁺ [H₂IO₆⁻] / (k_{14} + k_{13}) \]

Substitution in Equation (30), (31) from equation 12 gives:

\[
d \frac{[Cr(VI)]}{dt} = k_{12} k_{10} [Cr(cys)(HL)(H₂O)]²⁺ [H₂IO₆⁻] / (k_{12} + k_{10}) + k_{14} k_{13} [Cr(alala)(HL)(H₂O)]²⁺ [H₂IO₆⁻] / (k_{14} + k_{13}) \]

Equation (32) is identical to the experimental rate law at Equation (7) and, equation (33) is identical to the experimental rate law at equation (8) therefore:

\[
k_{d} = k_{12} k_{10} / (k_{12} + k_{10}) \]

In conclusion it may be stated that the oxidation of both [Cr(cys)(HL)(H₂O)]₃²⁺ and [Cr(alala)(HL)(H₂O)]₃²⁺ by Periodate is likely proceed via the conjugate acid form and the hydroxo form reactive species are not the reactive species in the pH range of study. The oxidation of [Cr(alala)(HL)(H₂O)]₃²⁺ by Periodate is faster than that of [Cr(cys)(HL)(H₂O)]₃²⁺ as obvious from the values of Δν⁺ and voltammmogram oxidation potentials. The complex formation between Cr³⁺ and HL gave an attention to use the ligand in Cr³⁺ carcinogenic inhibition.

REFERENCES