

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

Ahmed A Abdel- Khalek*
Beni-Suef University, Faculty of Science
Chemistry Department
Beni-Suef City, Egypt.

Berry Abd-El Ghani Sabrah, Yasser Abdel Rhman
Fayoum University, Faculty of Science.
Chemistry Department
Fayoum City, Egypt.

Abstract— Kinetics of oxidation of both ternary complexes $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ (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 $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ - periodate obeys the general rate law.

$$d[\text{Cr}^{\text{VI}}] / dt = (k_4 + k_3 / [\text{H}^+]) [\text{IO}_4^-] [\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}.$$

Where,

$$k_{\text{obs.}} = (k_4 + k_3 / [\text{H}^+]) [\text{IO}_4^-]$$

While the oxidation of $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ by periodate, found obey the rate equation,

$$d[\text{Cr}^{\text{VI}}] / dt = (k_6 + k_5 / [\text{H}^+]) [\text{IO}_4^-] [\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}.$$

Where,

$$k_{\text{obs.}} = (k_6 + k_5 / [\text{H}^+]) [\text{IO}_4^-] \text{ and } [\text{IO}_4^-] \text{ is the periodate concentration}$$

An inner-sphere process accommodated through replacement of coordinate H_2O in the one species, by periodate. The enthalpy of activation ΔH^\ddagger and entropy of activation ΔS^\ddagger 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 H_4IO_6^- or H_5IO_6 . 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(nitritotriacetato)-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 Cr^{VI} 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 $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ - periodate and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ - 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 Cr^{III} 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 concentration of Na_2HPO_4 and citric acid or hydrochloric acid standard solutions and Potassium chloride [14]. NaNO_3 was used in adjusting ionic strength in the different buffered solutions. Doubly distilled H_2O was used in all kinetic runs.

The formation of Cr^{VI} 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 titrino. The titroprocessor equipped with a 728 dosimat (Switzerland-Heriau). The titroprocessor and electrode were calibrated with standard buffer solution [15]. Calculations were performed using computer program MINQUAD-75. The solution contains 5.0 ml 0.01 mol dm^{-3} complex, 5.0 ml 0.20 mol dm^{-3} NaNO_3 , 5.0 ml 0.04 mol dm^{-3} HNO_3 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 C_{18} 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 $\text{C}_8\text{H}_{11}\text{N}_3\text{O}$: Calcd: C, 58.17; H, 6.71; N, 25.44. Found: C, 58.30; H, 6.90; N, 25.00. IR band assignments of the prepared ligand HL ν_{NH} , 3304 cm^{-1} ; ν_{NH_2} , 3342 cm^{-1} ; ν_{CN} , 1260 cm^{-1} ; aromatic $\nu_{\text{C}=\text{C}}$, 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 $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3](\text{NO}_3)_2$, was made by adding a mixture of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4004 g, 1.0 mmol) and Cysteine (0.0761 g, 1.0 mmol) to 50 mL distilled water. After the complete dissolving. 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 $\text{Cr}^{\text{III}}[\text{cys}]$ 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.

$[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3](\text{NO}_3)_2$ prepared by the same method as $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3](\text{NO}_3)_2$ 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 Cr^{VI} . It is found that at the end of the reaction Cr^{VI} 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. $\text{C}_{11}\text{H}_{23}\text{CrN}_6\text{O}_{12}\text{S}$ (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 $\text{C}_{11}\text{H}_{23}\text{CrN}_6\text{O}_{12}$ (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 ν_{OH^-} of the coordinated water molecule. The $\nu_{\text{C}=\text{O}}$ 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 ν_{COO^-} appeared in the region 1380 to 1390 cm^{-1} in the metal complexes IR spectrum, indicating that the carboxylic 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 Cr^{III} . The absence of an infrared peak between 450 cm^{-1} and 490 cm^{-1} in $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ IR spectrum, which denotes the disulfide bond, indicates that Cr^{III} didn't oxidize cysteine to form cystine.

The thermogram of the complex $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3](\text{NO}_3)_2$ shows a weight loss of 11.27% over the temperature range of (50 – 200) °C corresponding to loss of three molecules of coordinated water molecules (calc. 10.48%); While the complex $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3](\text{NO}_3)_2$ 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), $\text{Cr}^{\text{III}}(\text{cys})$, $\text{Cr}^{\text{III}}(\text{ala})$, $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ was studied to identify the complexes formation and the easier on oxidation. The cyclic voltammogram (C.V) of (1×10^{-3} mol dm^{-3}) $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ 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 reactions. The cyclic voltammogram of $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ at the same conditions mentioned above, exhibited an anodic peaks 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 , -0.24 , 0.45 , -0.09 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 the more positive upon complexes formation means that the oxidation process becomes more difficult in the complexes.

The stability constants of the complex $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$, $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and its ligands were determined at $T = 25^\circ\text{C}$ and $I = 0.4 \text{ mol dm}^{-3}$ by potentiometric – pH plotting according the reported method of Irving and Rossotti [18]. The potentiometric titration curve of 2-(phenylamino)acetohydrazide and its complexes $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ were obtained by plotting pH versus added volume of alkali. The association constant for $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+} = 9.95 \times 10^{-7}$ and the association constant for $[\text{Cr}(\text{HL})(\text{ala})(\text{H}_2\text{O})_3]^{2+} = 1.86 \times 10^{-5}$. The pK value for $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+} = 6.00$ and for $[\text{Cr}(\text{HL})(\text{ala})(\text{H}_2\text{O})_3]^{2+} = 4.73$.

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 $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ with periodate were checked individually by HPLC, using two different mobile phases. In the first, the product of oxidation of $(1 \times 10^{-3}) \text{ mol.dm}^{-3}$ $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ with $1 \times 10^{-3} \text{ mol.dm}^{-3}$ periodate was analysed 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 $\text{pH} = 2.85$ and B mobile phase is Acetonitrile and $\lambda = 254 \text{ nm}$ [19].

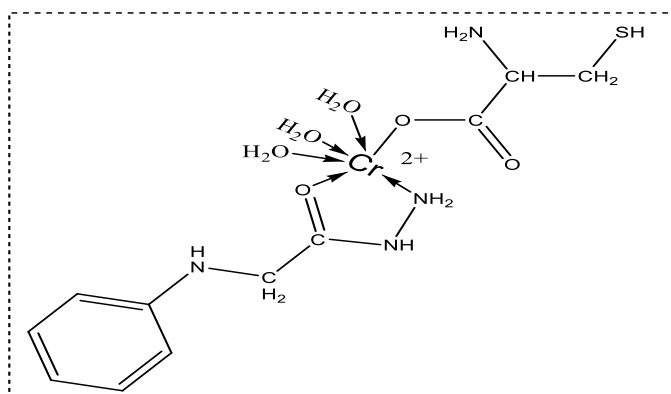


Fig.1. Suggested structures of $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$.

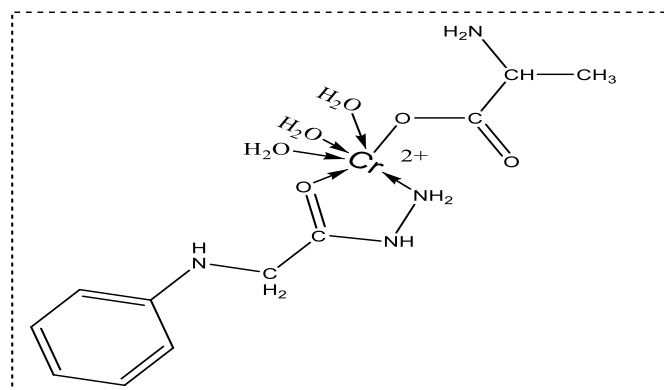


Fig.2. Suggested structures of $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$.

The above method used to check the presence of alanine in the oxidation products of $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ 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 of 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 0.5 mL/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 $1 \times 10^{-3} \text{ mol.dm}^{-3}$ $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ with $1 \times 10^{-3} \text{ mol.dm}^{-3}$ 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 $1 \times 10^{-3} \text{ mol.dm}^{-3}$ $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ with $1 \times 10^{-3} \text{ mol.dm}^{-3}$ periodate revealed 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.

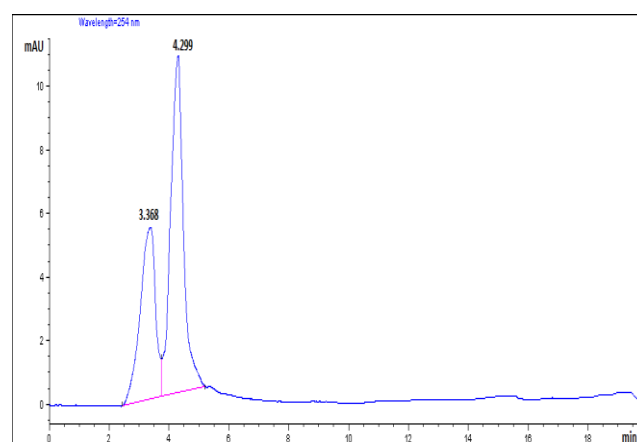


Fig.3. HPLC Chromatogram of complex $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ oxidation products ($10 \mu\text{L}$) injection using an eluent of isocratic mobile phase with the ratio of mobile phase A and B as 25:75, whereas mobile phase A is 2.5 mM Potassium dihydrogen phosphate with $\text{pH} = 2.85$, B mobile phase is Acetonitrile and $\lambda = 254 \text{ nm}$.

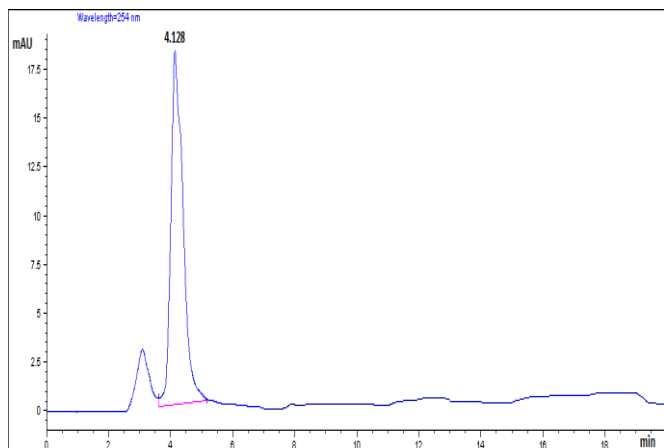


Fig.4. HPLC Chromatogram for alanine (5 μL) injection using an eluent of isocratic mobile phase with the ratio of mobile phase A and B as 25:75, whereas mobile phase A is 2.5 mM Potassium dihydrogen phosphate with $\text{pH}=2.85$ and B mobile phase is Acetonitrile and $\lambda=254$ nm).

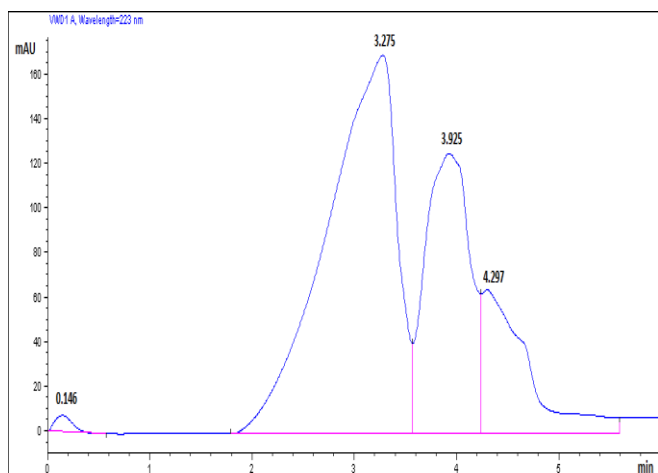


Fig.5. HPLC Chromatogram of complex $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ oxidation products (20 μL) injection. Eluent (50/50 methanol/120 mM sodium phosphate, monobasic ($\text{pH}=3.00$) and $\lambda=223$ nm).

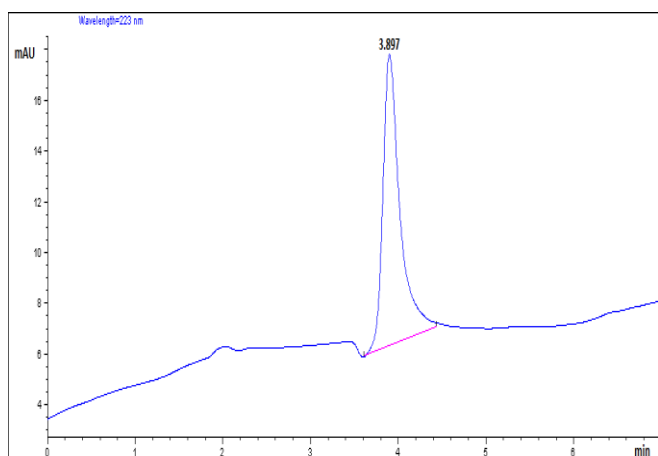


Fig.6. HPLC Chromatogram for IO_3^- (10 μL) injection using eluent (50/50 Methanol/120 mM sodium phosphate, monobasic ($\text{pH}=3.00$) and $\lambda=223$ nm).

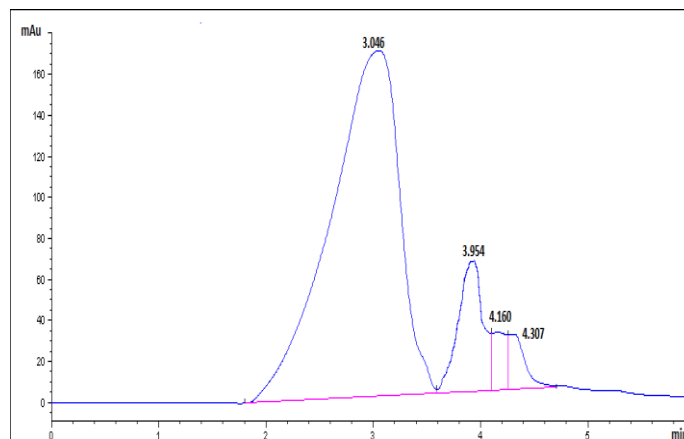


Fig.7. HPLC Chromatogram of complex $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ oxidation products (20 μL) injection. Eluent (50/50 methanol/120 mM sodium phosphate, monobasic ($\text{pH}=3.00$) and $\lambda=223$ nm).

The oxidation of $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ 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.

3.3. Kinetics of oxidation of $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ with periodate reaction in aqueous solution..

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

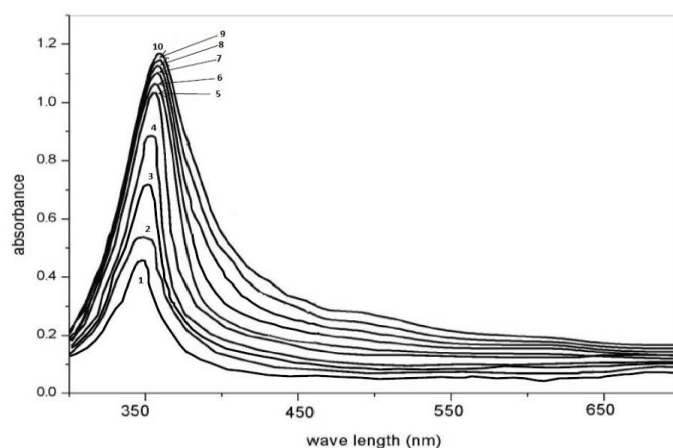


Fig.8. Change in absorbance as a function of time .curves (1 - 7) were recorded at 5, 10, 15, 20,25,30,35 mint, respectively from the time of initiation $[\text{Cr}(\text{cys})(\text{HL})(\text{H}_2\text{O})_3]^{2+} = 1.0 \times 10^{-3}$ $\text{mol}\cdot\text{dm}^{-3}$, $\text{pH} = 2.80$, $I = 0.4$ $\text{mol}\cdot\text{dm}^{-3}$ (NaNO_3), $[\text{IO}_4^-] = 2.0 \times 10^{-2}$ $\text{mol}\cdot\text{dm}^{-3}$ and $T = 30^\circ\text{C}$ Curve (8) spectrum of chromate ion (1.0×10^{-3} $\text{mol}\cdot\text{dm}^{-3}$) at the same pH.

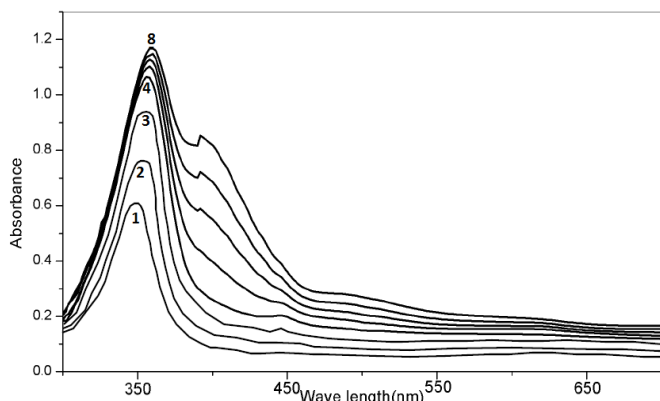


Fig.9. Change in absorbance as a function of time .curves (1 - 8) were recorded at 5, 10, 15, 20, 25,30,35,45 mint, respectively from the time of initiation $[Cr(ala)(HL)(H_2O)_3^{2+}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, pH = 2.60 , $I = 0.4 \text{ mol dm}^{-3} (\text{NaNO}_3)$, $[IO_4^-] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ and $T = 25^\circ\text{C}$.

Kinetic measurements were carried out under pseudo first order conditions with periodate concentration ≥ 10 $[Cr(III)]$. Plots of $\ln(A_\infty - A_t)$ versus time, where A_∞ and A_t are absorbance values at infinity and time t respectively, are linear up to 85 % of reaction. Values of the pseudo-first-order rate constants, K_{obs} , at fixed periodate concentration, ionic strength pH, and temperature, are independent of the initial complex concentration as shown in Table 1,2 indicating first order dependence on complexes concentration, eq.(1,2).

$$Rate1 = K_{obs1}[Cr(cys)(HL)(H_2O)_3^{2+}] \quad (1)$$

$$Rate2 = K_{obs2}[Cr(ala)(HL)(H_2O)_3^{2+}] \quad (2)$$

The variation of k_{obs} with $[IO_4^-]$ at various temperatures and pH values were found to be linear without intercept according to Eq. (3, 4). Plot of K_{obs1} , K_{obs2} against $[IO_4^-]$ (Fig.10, 11).

$$K_{obs1} = k_1 [IO_4^-] \quad (3)$$

$$K_{obs2} = k_2 [IO_4^-] \quad (4)$$

The dependence of the reaction rate on pH has been investigated over the above mentioned pH ranges, complex $[Cr(cys)(HL)(H_2O)_3^{2+}]$ or $[Cr(ala)(HL)(H_2O)_3^{2+}]$ concentration, temperature and periodate concentration. Variation of $(k_1$ or $k_2)$ with pH at different temperatures is listed in Tables (3, 4) .From which the reaction rate increased gradually with increasing pH values. Plotting of the slopes (k_1 or k_2) 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 $[Cr(cys)(HL)(H_2O)_3^{2+}]$, Eq.5

$$k_1 = k_4 + k_3 (1/[H^+]) \quad (5)$$

And for complex $[Cr(ala)(HL)(H_2O)_3^{2+}]$, Eq.6

$$k_2 = k_6 + k_5 (1/[H^+]) \quad (6)$$

Where, $k_1, k_2, k_3, k_4, k_5, k_6$ are constants. From equation (5, 6) and substitution in equation (1, 2) the following equation can obtain the general rate low equations (7, 8);

$$Rate1 = (k_4 + k_3 / [H^+]) [IO_4^-] [Cr(cys)(HL)(H_2O)_3^{2+}] \quad (7)$$

$$Rate2 = (k_6 + k_5 / [H^+]) [IO_4^-] [Cr(ala)(HL)(H_2O)_3^{2+}] \quad (8)$$

TABLE 1. Dependence of k_{obs1} on the initial of $[Cr(cys)(HL)(H_2O)_3^{2+}]$ at $[IO_4^-] = 4.5 \times 10^{-2} \text{ mol dm}^{-3}$, pH = 2.20, $I = 0.4 \text{ mol dm}^{-3}$ and temperature = $35 \pm 0.1^\circ\text{C}$.

$10^4 [Cr(cys)(HL)(H_2O)_3^{2+}] \text{ mol m}^{-3}$	$10^4 [k_{obs1} \pm SD] (\text{s}^{-1})$
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 k_{obs2} on the initial of $[Cr(ala)(HL)(H_2O)_3^{2+}]$ at $[IO_4^-] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, pH = 2.25, $I = 0.4 \text{ mol dm}^{-3}$ and temperature = $35 \pm 0.1^\circ\text{C}$.

$10^4 [Cr(ala)(HL)(H_2O)_3^{2+}] \text{ mol m}^{-3}$	$10^4 [k_{obs2} \pm SD] (\text{s}^{-1})$
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

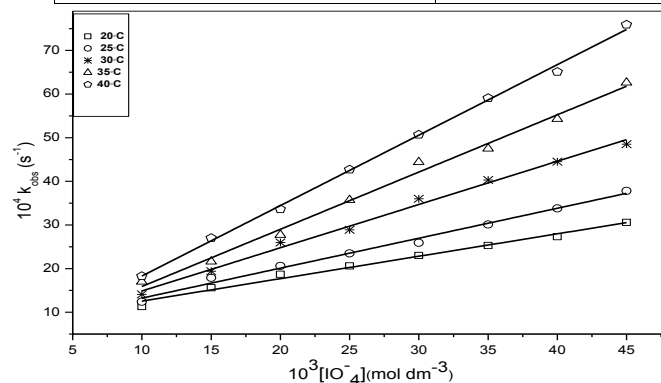


Fig.10. Variation of K_{obs1} with $[IO_4^-]$ at pH = 2.60, $I = 0.4 \text{ mol dm}^{-3}$ and $[Cr(cys)(HL)(H_2O)_3^{2+}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$.

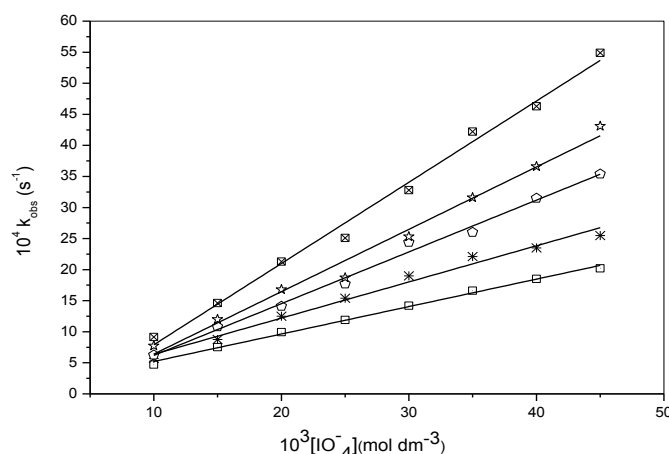


Fig.11. Variation of K_{obs2} with $[IO_4^-]$ at pH = 2.25, $I = 0.4 \text{ mol dm}^{-3}$ and $[Cr(ala)(HL)(H_2O)_3^{2+}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Where;

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

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

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, 6 and this behaviour can attributed to the fact that the reactions takes place between different charged species.

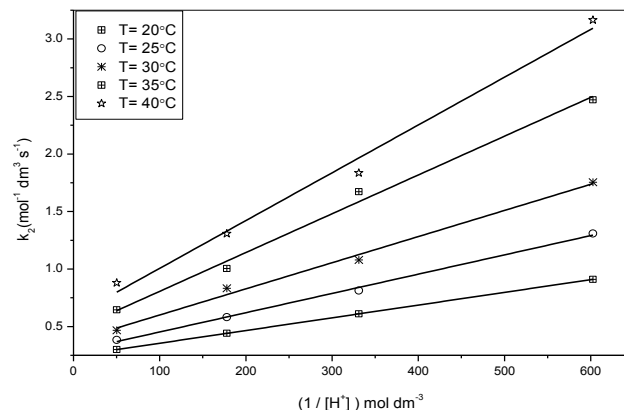


Fig.13. Variation of k_2 with pH at different temperature.

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

pH	1/ [H ⁺] (mol ⁻¹ dm ³)	10 ¹ [k ₁ ±SD] (mol ⁻¹ dm ³ s ⁻¹)				
		T = 20°C	T = 25°C	T = 30°C	T = 35°C	T = 40°C
1.59	38.90	3.58±0.18	4.20±0.10	6.16±0.18	8.28±0.21	9.39±0.38
1.85	70.79	3.61±0.12	4.66±0.17	6.72±0.19	8.97±0.35	10.56±0.59
2.20	158.49	3.94±0.12	5.21±0.29	7.54±0.23	10.47±0.30	12.42±0.37
2.60	398.11	5.14±0.23	6.86±0.25	9.91±0.31	13.11±0.43	16.15±0.29

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

pH	1/ [H ⁺] (mol ⁻¹ dm ³)	10 ¹ [k ₂ ±SD] (mol ⁻¹ dm ³ s ⁻¹)				
		T = 20°C	T = 25°C	T = 30°C	T = 35°C	T = 40°C
1.70	50.12	2.99±0.06	3.84±0.12	4.68±0.10	6.46±0.21	8.89±0.42
2.25	177.83	4.42±0.11	5.82±0.28	8.32±0.27	10.04±0.47	13.07±0.47
2.52	331.13	6.10±0.14	8.13±0.28	10.78±0.22	16.72±0.96	18.35±0.79
2.78	602.56	9.10±0.34	13.09±0.60	17.54±0.41	24.72±0.71	31.65±2.55

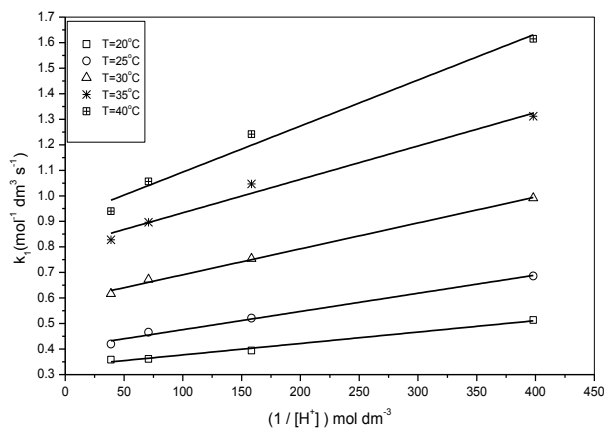


Fig.12. Variation of k_1 with pH at different temperature.

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.

I (mol dm ⁻³)	10 ⁴ [k _{obs1} ±SD] (s ⁻¹)
0.2	13.20±0.27
0.3	12.60±0.15
0.4	12.20±0.23
0.5	12.00±0.19
0.6	11.70±0.17

TABLE 6. Dependence of k_{obs2} on ionic strength at pH = 1.70, periodate = $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Cr(ala.)}(\text{HL})(\text{H}_2\text{O})_3]^{2+} = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, and temp. = 40°C .

$I \text{ (mol dm}^{-3}\text{)}$	$10^4[k_{obs2} \pm \text{SD}] \text{ (s}^{-1}\text{)}$
0.2	38.30 ± 0.51
0.3	20.80 ± 0.12
0.4	19.50 ± 0.44
0.5	14.90 ± 0.06
0.6	13.40 ± 0.11

From transition state theory equation, the thermodynamic activation parameters including enthalpy, ΔH^\ddagger , and entropy, ΔS^\ddagger , 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 $[\text{Cr(cys)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$, ΔH^\ddagger , have been calculated as $49.31 \text{ kJ mol}^{-1}$. The corresponding entropy of activation, ΔS^\ddagger , is equal to $-153.12 \text{ JK}^{-1} \text{ mol}^{-1}$ and The enthalpy of activation of $[\text{Cr(ala.)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$, ΔH^\ddagger , have been calculated as $48.38 \text{ kJ mol}^{-1}$. The corresponding entropy of activation, ΔS^\ddagger , is equal to $-148.94 \text{ JK}^{-1} \text{ mol}^{-1}$.

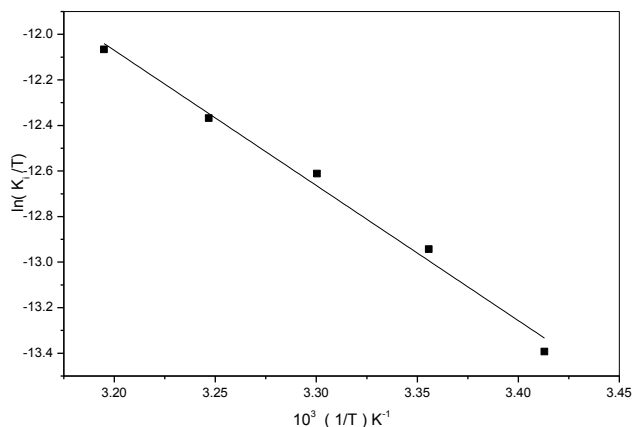


Fig.14. Plot of $(\ln K_i / T)$ against $(1/T)$ for complex $[\text{Cr(cys)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ over different temperatures.

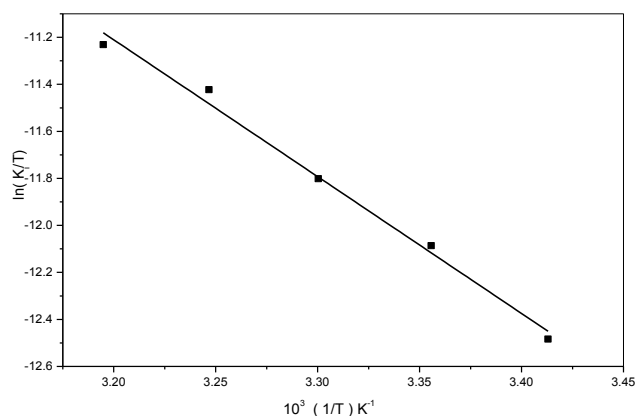
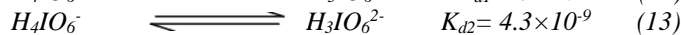
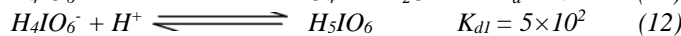
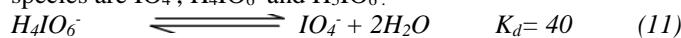


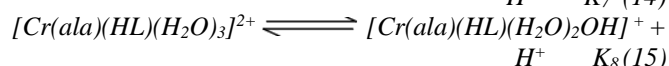
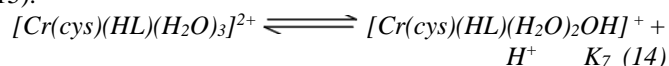
Fig.15. Plot of $(\ln K_i / T)$ against $(1/T)$ for complex $[\text{Cr(ala)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ over different temperatures.

4.DISCUSSION.

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_4IO_6^- and H_5IO_6 .

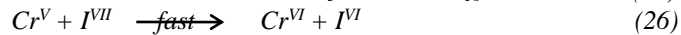
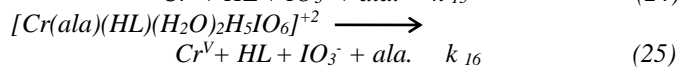
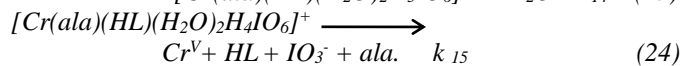
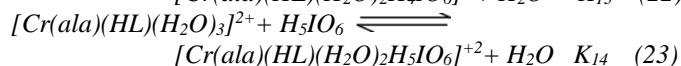
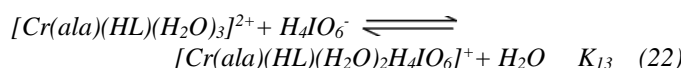
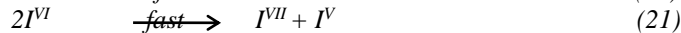
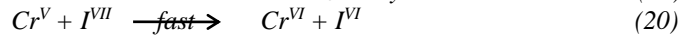
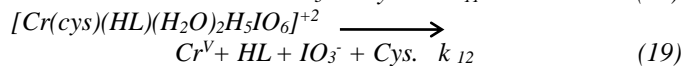
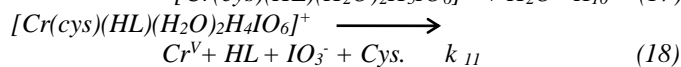
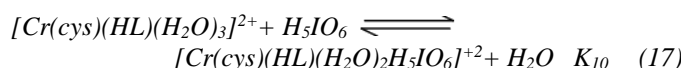
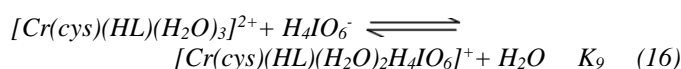


The $[\text{Cr(cys)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr(ala)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ complexes also undergoes deprotonation-protonation equilibrium as shown in Eqs. (14, 15).



The reported values of K_7 and K_8 are 9.95×10^{-7} and $1.86 \times 10^{-5} \text{ mol dm}^{-3}$, respectively, at 25.0°C and $I = 0.4 \text{ mol dm}^{-3}$. The oxidation reactions of $[\text{Cr(cys)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr(ala)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ 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_4IO_6^- and H_5IO_6 . The mechanism of oxidation of $[\text{Cr(cys)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ by periodate may be represented by the reaction sequence in Eq. (16, 17, 18, 19, 20, 21) While the mechanism of oxidation of $[\text{Cr(ala)}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ by periodate may be represented by the reaction sequence in Eq. (22, 23, 24, 25, 26, 27).

The reaction may go on 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.



IO_3^- and Alanine in products confirmed using HPLC which support the dissociation of the complex $[\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ or $[\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ after oxidation.

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

$$d[\text{Cr}^{\text{VI}}]/dt = k_{12} [\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_5\text{IO}_6^{2+}] + k_{11} [\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_4\text{IO}_6^+]. \quad (28)$$

$$d[\text{Cr}^{\text{VI}}]/dt = k_{16} [\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_5\text{IO}_6^{2+}] + k_{15} [\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_4\text{IO}_6^+]. \quad (29)$$

Using a steady state approximation for $[\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_5\text{IO}_6^{2+}]$, $[\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_4\text{IO}_6^+]$, $[\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_5\text{IO}_6^{2+}]$ and $[\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_2 \text{H}_4\text{IO}_6^+]$, and substitution in Equation (28,29) gives:

$$d[\text{Cr}^{\text{VI}}]/dt = k_{12}k_{10} \{ [\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_5\text{IO}_6] \} / (k_{12} + k_{10}) + k_{11}k_9 \{ [\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_4\text{IO}_6] \} / (k_{11} + k_9) \quad (30)$$

$$d[\text{Cr}^{\text{VI}}]/dt = k_{16}k_{14} \{ [\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_5\text{IO}_6] \} / (k_{16} + k_{14}) + k_{15}k_{13} \{ [\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_4\text{IO}_6] \} / (k_{15} + k_{13}) \quad (31)$$

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

$$d[\text{Cr}^{\text{VI}}]/dt = k_{12}k_{10} \{ [\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_5\text{IO}_6] \} / (k_{12} + k_{10}) + K_{d1} k_{11}k_9 \{ [\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_5\text{IO}_6] \} / (k_{11} + k_9) [\text{H}^+] \quad (32)$$

$$d[\text{Cr}^{\text{VI}}]/dt = k_{16}k_{14} \{ [\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_5\text{IO}_6] \} / (k_{16} + k_{14}) + K_{d1} k_{15}k_{13} \{ [\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3^{2+}] [\text{H}_5\text{IO}_6] \} / (k_{15} + k_{13}) [\text{H}^+] \quad (33)$$

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:

$$k_4 = k_{12}k_{10} / (k_{12} + k_{10}) \quad (34)$$

$$k_3 = K_{d1} k_{11}k_9 / (k_{11} + k_9) \quad (35)$$

$$k_6 = k_{16}k_{14} / (k_{16} + k_{14}) \quad (36)$$

$$k_5 = K_{d1} k_{15}k_{13} / (k_{15} + k_{13}) \quad (37)$$

In conclusion it may be stated that the oxidation of both $[\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ by Periodate are 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 $[\text{Cr}(\text{ala.})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ by periodate is faster than that of $[\text{Cr}(\text{cys.})(\text{HL})(\text{H}_2\text{O})_3]^{2+}$ as obvious from the values of ΔH^* and voltammogram oxidation potentials. The complex formation between Cr^{III} and HL gave an attention to use the ligand in Cr^{III} carcinogenic inhibition.

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