

Kinetics and Mechanism of Oxidation of Chromium (III) – [2-(Phenyl Amino) Acetohydrazide] by Periodate.

Ahmed A Abdel- Khalek, Berry Abd-El Ghani Sabrah, Yasser Abdel Rhman

Abstract— Oxidation of $[Cr(HL)(H_2O)_4]^{3+}$ (where HL = 2-(phenylamino)acetohydrazide ligand) by periodate was studied spectrophotometrically in aqueous solution over varying ranges of pH, ionic strength, temperature, complex concentration $(2.0 - 6.0) \times 10^{-4} \text{ mol dm}^{-3}$ and periodate $(1.0 - 4.5) \times 10^{-2} \text{ mol dm}^{-3}$. The reaction is first order with respect to $[H_5IO_6]$ and $[Cr^{III}]$. The rate of reaction increases with increasing of temperature and pH over the study range (1.59-2.62). The rate of the reaction is independent on the complex concentration and decreases with ionic strength. Oxidation of $[Cr(HL)(H_2O)_4]^{3+}$ follows the rate law, $d[Cr^{VI}]/dt = (k_2 + k_3/[H^+]) [H_5IO_6] [Cr(HL)(H_2O)_4]^{3+}$. Where, $k_{obs.} = (k_2 + k_3/[H^+]) [H_5IO_6]$. The thermodynamics activation parameters involving ΔH^* and ΔS^* have been calculated in excited state.

Keywords: Periodate, oxidation, acetohydrazide.

I. INTRODUCTION

The design and synthesis of hydrazides, hydrazones and hydrazine ligands for biomedical applications in the fields such as anticancer applications has become of great importance [1]. Hydrazones have been confirmed to own, among other, antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antitubercular, antiplatelet and antitumor activities [2], [3]. Trivalent Chromium is important in human nutrition as an essential microelement for normal carbohydrate, lipid and protein metabolism [4]. It has an increasing effect on insulin binding to a number of insulin receptors on the cell surface and improving sensitivity of pancreatic β -cells together with an overall increase of insulin-sensitivity [5]. Trivalent Cr is considered to be a highly safe mineral while Hexavalent Cr is toxic. Trivalent Cr propionate complex high repeated dosages do not induce DNA fragmentation in rat's peripheral lymphocytes [6]. Hexavalent Cr and Cr (V) intermediates, generated by the cellular reducing agents, are the DNA damaging agents [4].

The kinetics of oxidation of some trivalent Chromium complexes to Hexavalent Cr by periodate have been reported [7] - [11]. In almost all cases the Periodate oxidations are proceed via an inner-sphere mechanism, which is formed either through a bridging group [8] or by coordination of IO_4^- to the metal ion [10]. Periodate act as a two electron oxidant and the coordination sphere of it joined with chromium (III) complex via a hydroxo ligand of complex 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 [10]. Recently, the oxidation of chromium (III) complexes near the physiological pH value in biological systems came into consideration as chromium (V), and chromium (VI) may be readily formed in this pH range [4]. Chromium (V) is reported to be stabilized by some amino acids [12], [13]. 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 [14], [15], [16].

In this work, the kinetics of oxidation reactions $[Cr(HL)(H_2O)_4]^{3+}$ - periodate was studied. The stability of Cr^{III} complex towards oxidation also studied and compared with Cr^{III} species. Choice of this complexes is due to the hydrazide and Hydrazones biological importance [2], [3] and it's a probability to form binary complex with Cr^{III} from natural food.

II. MATERIAL AND METHODS

All chemicals used in this study were of reagent grade (Analar, BDH, Sigma and Aldrich). Stock solutions of sodium metaperiodate were prepared by weight, wrapped with aluminum foil and reserved in the dark as the periodate solutions are known to undergo photochemical decomposition [17]. Buffer solutions were made from known concentration of Na_2HPO_4 and citric acid or hydrochloric acid standard solutions and Potassium chloride [18]. The ionic strength of the buffered solutions was adjusted using $NaNO_3$. Doubly distilled H_2O was used in all kinetic runs.

Spectrophotometer, Apel PD-303S, was used to measure the reaction rate by following the Cr^{VI} absorbance at 356 nm. The pH of the reaction mixture was measured using a Chertsey Surrey, 7065 pH-meter. The uv-visible absorption spectra of the products of oxidation of complex by periodate was checked spectrophotometrically for a definite periods 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 (Switzer-land-Heriau). A standard buffer solution used to calibrate the electrode and titroprocessor [19]. MINQUAD-75 computer program used for Calculations. 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 $25^\circ C$.

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The electrochemical voltammogram of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ and $\text{Cr}(\text{NO}_3)_3$ was used to recognize the formation of the complex. The cyclic voltammogram of ($1 \times 10^{-3} \text{ mol dm}^{-3}$) $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ was obtained at 25°C and $\text{pH} = 2.50$ 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. High performance liquid chromatography (HPLC) was done by 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).

A. Preparation of 2-(phenylamino) acetohydrazide and its Cr^{III} complex.

The preparation of 2-(phenylamino) acetohydrazide which abbreviated as HL were performed by the reported method [20]. Elemental anal. (%) for $\text{C}_8\text{H}_{11}\text{N}_3\text{O}$: Calculated: C, 58.17; H, 6.71; N, 25.44. Found: C, 58.30; H, 6.90; N, 25.00. IR band assignments of the 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 shown an ion peak at $m/e = 165.09$ (88.60%). The preparation of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4](\text{NO}_3)_3$, was created by dissolving a mixture of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4004 g, 1.0 mmol) and 2-(phenylamino)acetohydrazide (HL) (0.1651 g, 1.0 mmol) in 50 mL distilled water. The resulting solution was heated under an air reflux condenser at 70°C for 3 hours and the total volume kept as 50 mL. A violet color appeared after 45 min. and increased gradually within the time. 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.

B. Kinetic procedures and oxidation products.

Pseudo-first-order conditions were kept in all runs by the presence of an excess (> 10-fold) of periodate. The ionic strength was maintained constant by the addition of NaNO_3 solution. The pH of the reaction mixture was found to be constant for the duration of the reaction run. All the reactants except periodate are thermostated at the wanted temperature for about 10 – 15 minutes to reach thermal equilibrium. The required amount of separately thermostated Sodium periodate solution is then added, and after rapid mixing, in the required time quickly transferred to an absorption cell and recording the absorbance is commenced.

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.

HPLC of the products of oxidation reactions shown the dissociation of the Chromium complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ once oxidation and liberating of the HL and IO_3^- . The oxidation product of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ with periodate was check by HPLC, using the mobile phases 50/50 Methanol/120 mM sodium phosphate, monobasic. The oxidation product was tested at 223 nm UV on the diode array detector C_{18} column and a separation flow rate of 0.5 mL/min . [21].

C. Stoichiometry

Periodate solution was added to a known excess of Cr^{III} complex and the absorbance of Cr^{VI} produced was measured at 356 nm after 24 hours from the beginning of the reaction. The quantity of Cr^{III} consumed was calculated using the molar absorptivity of Cr^{VI} at the employed pH.

III. RESULTS AND DISCUSSION

Elemental analysis, IR, TGA and cyclic voltammetry were used to check the formation of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot \text{C}_8\text{H}_{19}\text{CrN}_6\text{O}_{14}$ (Found: C, 20.70; H, 4.10; N, 17.00. Calcd: C, 20.22; H, 4.03; N, 17.68%). The IR spectrum of complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4](\text{NO}_3)_3$ exhibited a broad band in the ($3550\text{-}3100$) cm^{-1} region, was attributed to ν_{OH^-} of the water molecules. The absence of an infrared peak at 1730 cm^{-1} , which represents the stretching vibration of carbonyl group belongs to the amide group in 2-(phenylamino) acetohydrazide (HL) infrared spectrum and a new band appeared in the region at 1455 cm^{-1} due to the expected coordination of carbonyl with Cr^{III} . An observed shifting in infrared peak at 2979 cm^{-1} , which attributed to ν_{NH_2} to 2975 cm^{-1} in the IR spectrum of complex is due to the expected coordination of $-\text{NH}_2$ with Cr^{III} . The amount of water in the complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4](\text{NO}_3)_3$ was checked by TGA and it showed a weight loss of 14.64% over the temperature range of ($75 - 120$) $^\circ\text{C}$ corresponding to the loss of four coordinated water molecules (calc. 15.15 %). The complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ suggested structure shown in (Figure 1).

The electrochemical behavior of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ and 2-(phenylamino)acetohydrazide (HL) was studied to identify the complex formation and the stability of HL and its Cr^{III} complexes towards oxidation. The cyclic voltammogram (C.V) of ($1 \times 10^{-3} \text{ mol.dm}^{-3}$) $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ gave a clear redox anodic electrochemical reactions at -0.30 V and 0.60 V revealed a two oxidation reactions and one cathodic reaction at -0.47 V corresponding to a reduction reaction. The cyclic voltammogram of 2-(phenylamino)acetohydrazide (HL) at the same conditions mentioned above, revealed an anodic peaks at

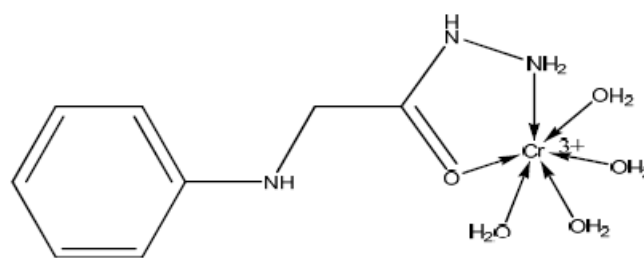


Figure .1-Suggested structure of complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$. -0.89 V , -0.35 V and -0.21 V due to an oxidation reactions and one cathodic peak at -1.21 V .

The cyclic voltammogram of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, gave an anodic peak at -0.79 V . The cyclic voltametric redox peak values of HL is different from those of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ which gave a confirmation of the complexes formation.

The oxidation potential values shifted to the more positive upon complex formation which means that the oxidation of complex became more difficult.

The stability constant of the complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ and its ligand HL was determined at $T = 25^\circ\text{C}$ and $I = 0.4 \text{ mol dm}^{-3}$ by potentiometric – pH plotting using the method of Irving and Rossotti of calculation [22]. The potentiometric titration curve of HL and its complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ were obtained and the association constant for

$$[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} = 5.2 \times 10^{-5} \text{ while the association constant for 2-(phenylamino) aceto-hydrazone (HL)} = 1.51 \times 10^{-4}.$$

The stoichiometry of the $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}/\text{H}_5\text{IO}_6$ reaction can be represented by Equation (1):



The ratio of I^{VII} initially present to Cr^{VI} produced was 1.50 ± 0.05 . The stoichiometry is reliable with the observation that IO_3^- does not oxidize the Cr^{III} -complex over the pH range where the kinetics were studied.

A. Analysis of an oxidation products.

The oxidation of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ with periodate was followed by recording the UV- visible absorption spectra of the oxidation products between 250 and 750 nm as a function of time. A peak appeared at 355 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 (Figure 2). The calibration standard of IO_3^- solution and the oxidation products of complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ with periodate were checked individually by HPLC. The HPLC of calibration standard of IO_3^- solution gave a sharp peak at time 3.897 min. (Figure 3), The HPLC chromatogram of the oxidation products of complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ (Figure 4), gave an identical peak with the retention time 3.899 min, which confirm that IO_3^- is a product of oxidation reaction.

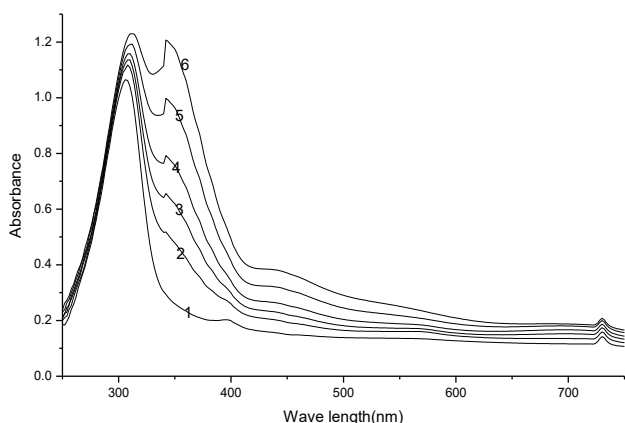


Figure 2. Change in absorbance as a function of time. Curves 1-6 were recorded at 1, 3, 6, 9, 12 and 15 min, respectively, from the time of initiation; $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_5\text{IO}_6] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.4 \text{ mol dm}^{-3} (\text{NaNO}_3)$, $\text{pH} = 3.0$ and $T = 25^\circ\text{C}$.

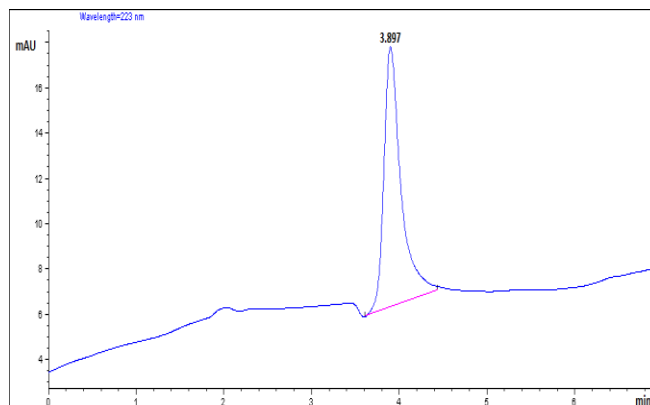


Figure 3. HPLC Chromatogram for IO_3^- (10 μL) injection using eluent (50/50 Methanol/120 mM sodium phosphate, monobasic (pH=3.00) and $\lambda=223 \text{ nm}$).

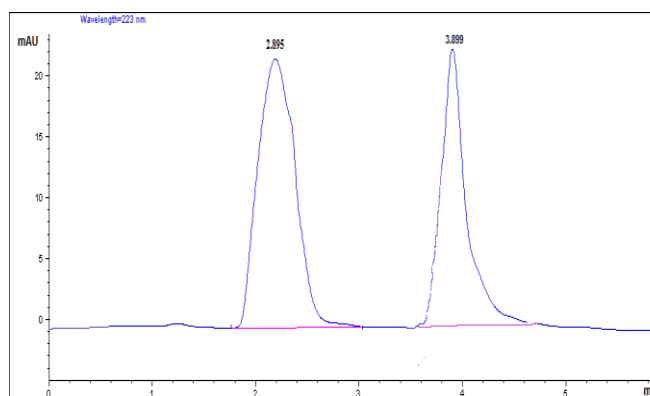


Figure 4. HPLC Chromatogram of complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ oxidation products (20 μL) injection. Eluent (50/50 methanol/120 mM sodium phosphate, monobasic (pH=3.00) and $\lambda=223 \text{ nm}$).

B. Kinetics of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} / \text{H}_5\text{IO}_6$ reaction in aqueous solution.

The oxidation reaction of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} / \text{H}_5\text{IO}_6$ has been studied under the condition of ionic strength range (0.2-0.6) mol.dm^{-3} , pH range (1.59-2.62) and temperature (20-40 $^\circ\text{C}$) over range of periodate and complex concentration; $(1.0-4.5) \times 10^{-2} \text{ mol.dm}^{-3}$ and $(2.0 - 6.0) \times 10^{-4} \text{ mol.dm}^{-3}$ respectively. The pseudo – first order rate constant (k_{obs}) were calculated from plots of $-\ln(A_t - A_\infty)$ with time where A_t and A_∞ are the absorbance at time t and time infinity, respectively. These plots were linear for about 80% from the beginning of the reaction. An error limits for the results were calculated using Microcal Origin.

Under a constant conditions of periodate conc. of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, ionic strength = 0.4 mol.dm^{-3} , $\text{pH} = 2.20$, $\text{temp.} = 25^\circ\text{C}$ and different concentrations of the complex over the range $(2-6) \times 10^{-4} \text{ mol.dm}^{-3}$. Values of $10^4 k_{\text{obs}}$, of $(9.49 \pm 1.16, 9.49 \pm 1.27, 9.49 \pm 1.45, 9.49 \pm 0.98$ and $9.49 \pm 1.40) \text{ S}^{-1}$ respectively showing that k_{obs} was unaffected when complex concentration varied, denoting that the reaction rate is first-order with respect to the complex concentration, Equation (2):

$$\text{Rate} = k_{\text{obs}} [\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}. \quad (2)$$

Oxidation reaction $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}/\text{H}_5\text{IO}_6$ k_{obs} values found dependent on $[\text{H}_5\text{IO}_6]$. The reaction studied at different concentration of H_5IO_6 (1.0 - 4.5) $\times 10^{-2}$ $\text{mol}\cdot\text{dm}^{-3}$ while the other constituents were kept constant. Plot of k_{obs} against $[\text{H}_5\text{IO}_6]$ at different temperatures were found to be linear without an intercept (Figure 5), according to Equation (3):

$$k_{\text{obs}} = k_1 [\text{H}_5\text{IO}_6] \quad (3)$$

The dependence of the reaction rate on pH has been studied over the pH range mentioned above and at constant $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} = 4.0 \times 10^{-4}$ $\text{mol}\cdot\text{dm}^{-3}$, $I = 0.4$ $\text{mol}\cdot\text{dm}^{-3}$ over a range of temp. (20 - 40°C) and different conc. of periodate of range (1.0 - 4.5) $\times 10^{-2}$ $\text{mol}\cdot\text{dm}^{-3}$. Plotting of the slopes (k_1) versus ($1 / [\text{H}^+]$) is found to be linear with an intercept as shown in (Figure 6), this behavior can be described by Equation (4):

$$k_1 = k_2 + k_3 (1/[\text{H}^+]) \quad (4)$$

Where, k_1 , k_2 , and k_3 are constants. The kinetics of the reaction are described by Equation (5):

$$d[\text{Cr}^{\text{VI}}]/dt = (k_2 + k_3/[\text{H}^+]) [\text{H}_5\text{IO}_6] [\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} \quad (5)$$

Thermodynamic activation parameters, including enthalpy and entropy of activation were calculated, using the Eyring equation, as $\Delta H^\ddagger = 1.67$ $\text{kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -204.08$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. ΔH^\ddagger is a composite value including the enthalpy of formation of precursor complex and the enthalpy of activation of an endothermic intramolecular electron transfer step. This is indicated by the positive value of ΔH^\ddagger .

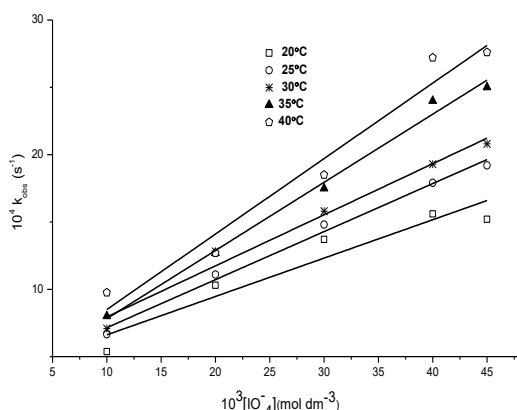


Figure 5. Variation of k_{obs} with H_5IO_6 at $\text{pH} = 2.42$, $I = 0.4$ $\text{mol}\cdot\text{dm}^{-3}$ and $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} = 4.0 \times 10^{-4}$ $\text{mol}\cdot\text{dm}^{-3}$.

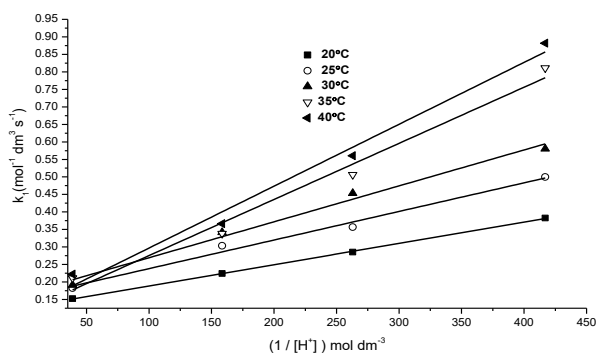


Figure 6. Variation of k_1 with $1/[\text{H}^+]$ at different temperatures $\{[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} = 4.0 \times 10^{-4}$ $\text{mol}\cdot\text{dm}^{-3}$, $I = 0.4$ $\text{mol}\cdot\text{dm}^{-3}\}$.

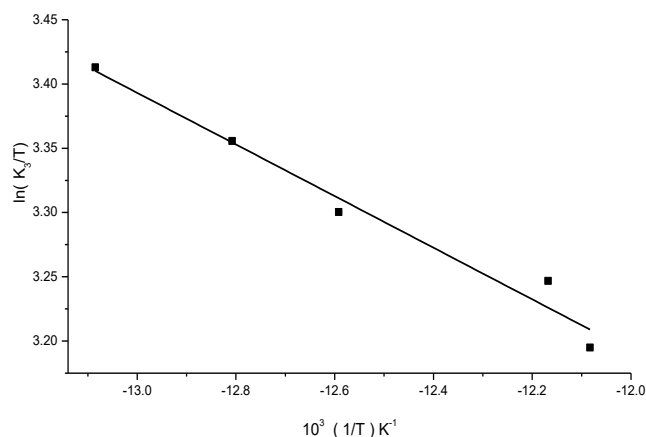


FIGURE 7. PLOT OF $(\ln k_3 / T)$ AGAINST $(1 / T)$ FOR COMPLEX $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ OVER DIFFERENT TEMPERATURES.

The enthalpy of activation, ΔH^\ddagger , and entropy of activation, can be obtained by plotting $\ln k_3 / T$ against $1 / T$ respectively as shown in (Figure 7). Under a constant conditions of periodate conc. of 3.0×10^{-2} $\text{mol}\cdot\text{dm}^{-3}$, $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} = 4.0 \times 10^{-4}$ $\text{mol}\cdot\text{dm}^{-3}$, $\text{pH} = 2.20$, temp. = 25°C and different concentrations of ionic strength over the range (0.2 - 0.6) $\text{mol}\cdot\text{dm}^{-3}$. Values of $10^4 k_{\text{obs}}$ of (9.77 ± 1.00 , 9.62 ± 0.24 , 9.49 ± 1.45 , 9.14 ± 1.90 and 8.95 ± 1.20) S^{-1} respectively showing that k_{obs} decreasing upon ionic strength increasing. This behavior is expected since the reaction takes place between two different charged species.

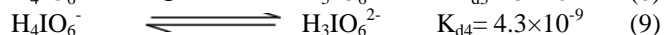
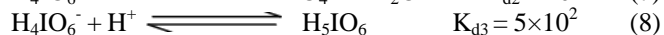
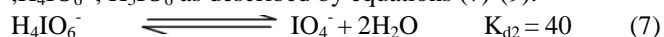
C. DISCUSSION.

The stability constant of the complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$, K_{d1} , was measured potentiometrically and had the value 5.2×10^{-5} at $T = 25^\circ\text{C}$ and $I = 0.4$ $\text{mol}\cdot\text{dm}^{-3}$. From the pH (1.59 - 2.62) and the K_{d1} value, it is clear that $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ may be the reactive species.



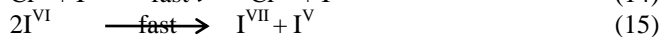
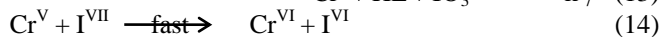
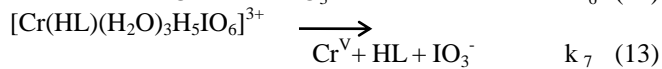
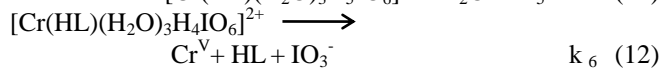
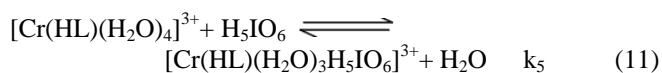
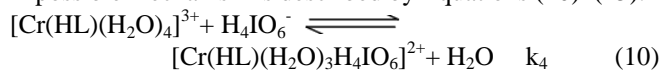
From the reported equilibrium constants of aqueous periodate solutions [23],

it may be concluded that, over the $[\text{H}^+]$ range used in this study, the periodate species likely to be present are IO_4^- , H_4IO_6^- , H_5IO_6 as described by equations (7)-(9).



K_{d1} was measured potentiometrically and had the value 5.2×10^{-5} at 25°C and $I = 0.20$ $\text{mol}\cdot\text{dm}^{-3}$. From the pH (1.59 - 2.62) and the K_{d1} value, it is clear that $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ may be the reactive species. The assignment of an inner-sphere mechanism for this reaction seems to be likely due to the fact that H_5IO_6 is able to act as a ligand in the coordination by copper(III) [24] and nickel(IV) [25], in which the coordinated H_2O is substituted by I^{VII} [26].

A possible mechanism is described by Equations (10)–(15):



IO_3^- in oxidation products confirmed using HPLC which support the dissociation of the complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ after oxidation.

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

$$d[\text{Cr}^{\text{VI}}]/dt = k_6 [\text{Cr}(\text{HL})(\text{H}_2\text{O})_3\text{H}_4\text{IO}_6]^{2+} + k_7 [\text{Cr}(\text{HL})(\text{H}_2\text{O})_3\text{H}_5\text{IO}_6]^{3+} \quad (16)$$

Using a steady state approximation for $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_3\text{H}_4\text{IO}_6]^{2+}$ and $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_3\text{H}_5\text{IO}_6]^{3+}$, and substitution in Equation (16) gives:

$$d[\text{Cr}^{\text{VI}}]/dt = k_4 k_6 \{ [\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} [\text{H}_5\text{IO}_6] \} / (k_6 + k_4) + k_7 k_5 \{ [\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} [\text{H}_4\text{IO}_6] \} / (k_7 + k_5) \quad (17)$$

Substitution in equation (17) from equation (8) gives:

$$d[\text{Cr}^{\text{VI}}]/dt = k_4 k_6 \{ [\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} [\text{H}_5\text{IO}_6] \} / (k_6 + k_4) + K_{d3} k_7 k_5 \{ [\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+} [\text{H}_5\text{IO}_6] \} / (k_7 + k_5) [\text{H}^+] \quad (18)$$

Equation (18) is identical to the experimental rate law Equation (5) therefore:

$$k_2 = k_4 k_6 / (k_6 + k_4) \quad (19)$$

$$k_3 = K_{d3} k_7 k_5 / (k_7 + k_5) \quad (20)$$

In conclusion it may be stated that the oxidation of $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ by periodate is likely proceed via an inner sphere mechanism. The complex conjugate acid form is the reactive species and the complex hydroxo form is not the reactive species in the pH range of study. The stability of binary complex $[\text{Cr}(\text{HL})(\text{H}_2\text{O})_4]^{3+}$ towards oxidation increased upon complex formation. The complex formation between Cr^{III} and HL gave an attention to use the ligand HL in Cr^{III} species stabilizing in body to prevent the carcinogenic Cr^{VI} formation.

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