MECHANISM OF ELECTRON TRANSFER FOR THE OXIDATION OF TERNARY COMPLEX OF CHROMIUM(III) INVOLVING GUANOSINE AND DL-ASPARTIC ACID WITH PERIODATE

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ABSTRACT

The oxidation of the ternary complex, $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ (Gu = guanosine and Asp = DL-aspartic acid) by periodate in aqueous solution to chromium(VI) has been studied spectrophotometrically over the 25–45°C range. The reaction is first order with respect to both $[IO_4^-]$ and [Cr(III)], and increases with pH over the 2.38–3.68 range. The experimental rate law is consistent with the derived mechanism and the reaction follows the rate law:

$$d[Cr(III)]/dt = (k_1K_5 + k_2K_6K_1/[H^+])[IO_4^-][Cr(III)]_T/\{1 + K_1/[H^+] + (K_5 + K_1K_6/[H^+])[IO_4^-]\},$$

where K_1, K_5 and K_6 are the deprotonation of $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ and pre-equilibrium formation constants for $[Cr(III)(Gu)(Asp)(H_2O)(OIO_3)]^+$ and $[Cr(III)(Gu)(Asp)(OH)OIO_3]$ precursor complexes, respectively. The reaction may follow a 2-step inner-sphere electron transfer mechanism *via* coordination of IO_4^- to chromium(III). Thermodynamic activation parameters have been calculated.

Keywords: ternary complex, periodate oxidation, inner-sphere mechanism, thermodynamic activation parameters.

AIMS AND BACKGROUND

Transition metal complexes are used as tools in molecular biology for probing nucleic acid structure and for the specific or nonspecific cleavage of nucleic acids[1,2]. Although interactions of DNA with a large number of metals ions have been investigated, the

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interaction of chromium(III) with DNA has apparently escaped attention, despite the fact that chromium(III) complexes draw particular attention due to their environmental toxicity and the carcinogenic nature of higher valent chromium[3]. The interest on chromium(III) complexes with nucleotides arises from the use of these complexes as enzymatic labels by substitution of the activator or inhibitor[4,5] and finding out the role of chromium(III) in transcription processes and RNA and DNA interactions[6].

Oxidations by periodate have been reported to play an important role in biological system[7,8]. They are used in the kinetics determination of glucose and fructose in invert sugar syrups[7]. Alpha-amino acids in proteins can be determined by measuring the ammonia produced through oxidation with periodate in alkaline medium[8]. Also, periodate has been used in the modification of human serum transferrin by conjugation to an oligosaccharide[9].

The biological oxidation of chromium from the trivalent to hexavalent states is an important environmental process because of the high mobility and toxicity of chromium(VI) (Ref. 10). The higher oxidation states of chromium are of interest due to the toxic and mutagenic nature of these oxidation states of chromium[10]. Oxidation of Cr(III) to Cr(V) and/or Cr(VI) in biological systems came into consideration as a possible reason of anti-diabetic activities of some Cr(III) complexes, as well as of long-term toxicities of such complexes[11]. The specific interactions of Cr(III) ions with cellular insulin receptors[12] are caused by intra- or extra-cellular oxidations of Cr(III) to Cr(V) and/or Cr(VI) compounds, which act as protein tyrosine phosphatase (PTP) inhibitors. The current perspective discusses chemical transformations of Cr(III) nutritional supplements in biological media, with implications both for beneficial and toxic actions of Cr(III) complexes, which are likely to arise from the same biochemical mechanisms, dependent on concentrations of the highly reactive Cr(IV/V/VI) species, formed in the reactions of Cr(III) with biological oxidants[13].

Oxidations of inorganic substrates[14,15] and transition metal complexes[16,17] by periodate are reported to proceed through inner-sphere mechanisms, either labile or inert complexes possessing at least one bridging ligand. The kinetics of oxidation of the chromium(III) complexes of uridine[18], 2-aminopyridine[19] and guanosine[20] by periodate were carried out. In all cases the electron transfer proceeds through an inner-sphere mechanism via coordination of IO_4^- to chromium(III). Binary and ternary chromium(III) complexes of nitrilotriacetate involving histidine and aspartate as secondary ligands[21,22] by periodate in acid medium were investigated in order to study the effect of secondary ligands on the stability of $[Cr(III)(NTA)(H_2O)_2]$ (Ref. 21) (NTA = nitrilotriacetate) towards oxidation.

Inner-sphere oxidation of the binary and ternary N-(2-acetamido)iminodiacetato-cobaltate(II) complexes[23,24] involving malonate[23] succinate and maleate[24] as secondary ligands by periodate has been investigated. In all cases, initial cobalt(III) products were formed, and these changed slowly to the final cobalt(III) products. It is proposed that the reaction follows an inner-sphere mechanism, which suggested relatively faster rates of ring closure compared to the oxidation step.

In this paper, the kinetics of oxidation of $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ (Gu = guanosine and Asp = DL-aspartic acid) are reported in order to study the effect of DL-aspartic acid as a secondary ligand on the stability of $[Cr(III)(G)(H_2O)_4]^{3+}$ (Ref. 20) towards oxidation.

EXPERIMENTAL

Materials and solutions. Chromium(III)-guanosine-aspartic acid was prepared by the reported method[25]. All chemicals used in this study were of reagent grade (Analar, BDH, Sigma). Buffer solutions were prepared from NaCl, and HCl of known concentration. KCl was used to adjust ionic strength in the different buffered solution. Doubly distilled H_2O was used in all kinetic runs. A stock solution of $NaIO_4$ (Aldrich) was prepared by accurate weighing and wrapped in aluminum foil to avoid photochemical decomposition[26].

Kinetic procedures. The UV-vis. absorption spectra of the products of oxidation of $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ by IO_4^- were monitored for a definite period of time using a JASCO UV-530 spectrophotometer. The oxidation rates were measured by monitoring the absorbance of Cr(VI) at 355 nm, on a Milton-Roy 601 spectrophotometer, where the absorption of the oxidation products is maximum at the reaction pH. The pH of the reaction mixture was measured using a Chertsey Surrey, 7065 pH-meter.

Pseudo-first order conditions were maintained in all runs by the presence of a large excess (>10-fold) of IO_4^-. The ionic strength was kept constant by the addition of $NaNO_3$ solution. The pH of the reaction mixture was found to be always constant during the reaction run.

RESULTS

Oxidation products. The UV-vis. absorption spectra of the oxidation products (Fig. 1) indicate that the chromium(III) peaks at 562 and 404 nm have disappeared and have been replaced by other peaks at 355 nm which correspond to chromium(VI). The presence of one isosbestic point at $\lambda = 503$ nm in the absorption spectra was taken as the criterion for the presence of 2 absorbing species in equilibrium.

The oxidation kinetics of $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ by periodate was studied over the 2.38–3.68 pH range, 0.2–0.6 M ionic strength and 25–45°C over a range of complex and periodate concentrations. Experiments were carried out varying the $[IO_4^-]$:[Cr(III) (Gu)(Asp)(H_2O)_2]^{2+}$ ratios, where the concentration of $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ was always at least twice that of $[IO_4^-]$. The study indicates that 2 mol of $[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+}$ were consumed for every 3 mol of IO_4^-, where the ratio of iodine(VII) to chromium(VI) initially present was 1.50 ± 0.1. The stoichiometry was also consistent with the observation that IO_3^- does not oxidise the chromium(III) complex over the pH range studied, so that the reaction can be represented stoichiometrically as:

$$2Cr(III) + 3I(VII) \rightarrow 2Cr(VI) + 3I(V) \tag{1}$$
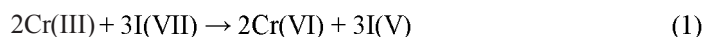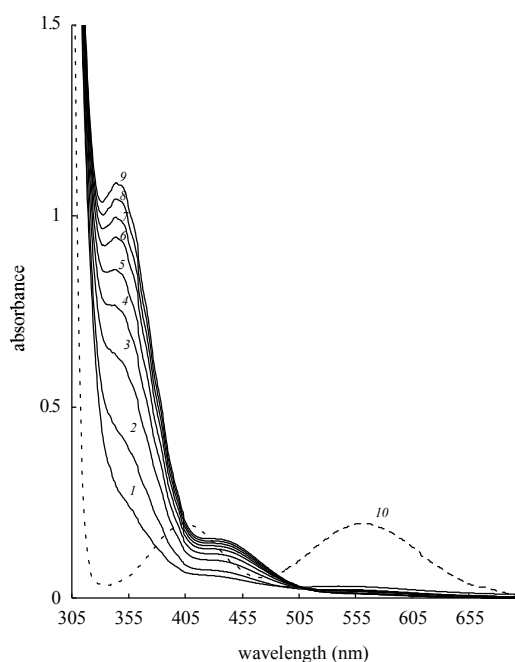
Fig. 1. Change in absorbance as a function of time. Curves (*1*)–(*9*) were recorded at 2, 5, 10, 15, 20, 25, 30, 35, and 40 min, respectively, from the time of initiation; [complex] = 1×10^{-3} mol dm^{-3}; [IO$_4^-$] = 0.02 mol dm^{-3}; I = 0.2 mol dm^{-3}; pH = 2.92; T = 35°C. Curve (*10*) (-----) spectrum of chromium(III)-complex (1.0×10^{-3} mol dm^{-3}) at the same pH

Plots of ln $(A_\infty - A_t)$ versus time were linear up to 85% of reaction where A_t and A_∞ are absorbance at time t and infinity, respectively. Pseudo-first order rate constants, k_{obs}, obtained from the slopes of these plots, are collected in Table 1. The results (Table 1) show that k_{obs} was unaffected when the concentration of the chromium(III)-complex was varied at constant periodate concentration, indicating first order dependence on complex concentration:

$$d[Cr(VI)]/dt = k_{obs}[Cr(III)]_T, \tag{2}$$

where $[Cr(III)]_T$ represents the total chromium(III) concentration present. At constant [H$^+$] and ionic strength, $1/k_{obs}$ varies linearly with $1/[IO_4^-]$ at different temperatures (Fig. 2), and the kinetics of the reaction are described by the following equation:

$$k_{obs} = a \, [IO_4^-]_T/1 + b \, [IO_4^-]_T \tag{3}$$

or

$$1/k_{obs} = 1/a \, [IO_4^-]_T + b/a \tag{4}$$

Table 1. Variation of initial rates with different concentrations of periodate and different temperatures
^{a}[Cr(III)(Gu)(Asp)(H$_2$O)$_2^{2+}$] = 2.5 × 10^{-4} mol dm^{-3}; pH = 2.92; I = 0.2 mol dm^{-3}

[IO$_4^-$]×10^2	k_{obs} ×10^3 (s^{-1})				
(mol dm^{-3})	25°C	30°C	35°C	40°C	45°C
5.0	3.46	3.58	3.83	5.44	7.22
4.5	2.90	3.14	3.28	4.94	6.72
4.0	2.53	2.92	3.17	4.36	5.61
3.5	2.41	2.64	3.06	3.83	5.11
3.0	2.33	2.56	2.81	3.53	4.50
2.5	2.11	2.28	2.44	3.28	4.14
2.0	1.67	2.30	2.08	2.44	3.44
1.5	1.37	1.48	1.67	2.00	2.60
1.0	1.02	1.50	1.22	1.54	1.91

^{a}[Cr(III)(Gu)(Asp)(H$_2$O)$_2^{2+}$] = 2.5 × 10^{-4} mol dm^{-3}; k_{obs} × 10^3 = 2.03, 2.24, 2.12 and 2.17 s^{-1} at [Cr(III)(Gu)(Asp)(H$_2$O)$_2^{2+}$] of 1.25, 3.75, 5.0 and 6.25 mol dm^{-3}, respectively at 35°C and [IO$_4^-$] = 0.02 mol dm^{-3}.
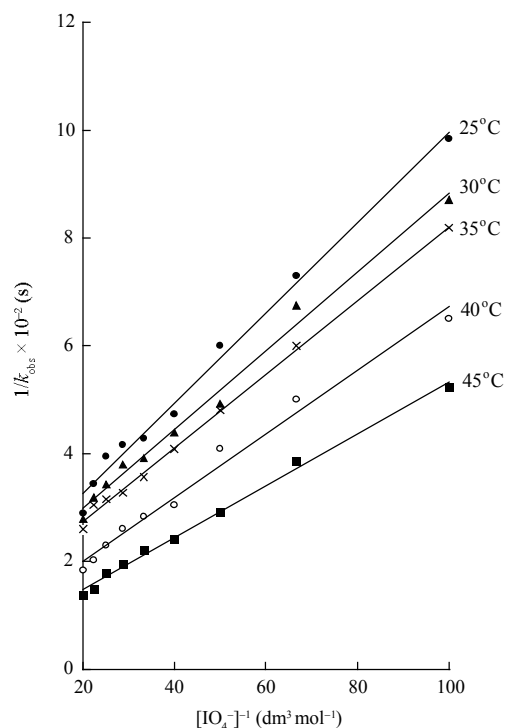
Fig. 2. Plot of 1/k_{obs} versus 1/[IO$_4^-$] at different temperatures

The values of a and b were obtained from the slopes and intercepts of the plots, respectively. Plots of 1/k_{obs} versus 1/[IO$_4^-$] at different pH (2.38–3.68) (Fig. 3) show that the reaction rate increased as the pH increased over the range studied (Table 2) and highlights the involvement of the deprotonated form of complex in the rate-

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determining step. Table 3 indicates that the reaction rate decreased with increasing the ionic strength. This phenomenon has been attributed to the fact that the reaction takes place between two oppositely charged species.

Table 2. Effect of pH on k_{obs} (s^{-1})
[Cr(III)(Gu)(Asp)(H$_2$O)$_2$$^{2+}$] = 2.5 × 10^{-4} mol dm^{-3}; I = 0.2 mol dm^{-3}; temperature 35°C

[IO$_4^-$]×10^2	k_{obs} ×10^3 (s^{-1})				
(mol dm^{-3})	pH 3.68	3.34	2.92	2.62	2.38
5.0	9.72	4.94	3.83	2.53	1.71
4.5	6.22	4.72	3.28	2.35	1.61
4.0	5.67	4.44	3.17	2.27	1.45
3.5	5.50	3.94	3.06	1.92	1.24
3.0	5.33	3.61	2.81	1.69	1.03
2.5	4.39	3.33	2.44	1.39	0.83
2.0	4.31	2.67	2.08	1.11	0.70
1.5	3.33	2.02	1.67	0.87	0.58
1.0	3.15	1.93	1.22	0.69	0.42

Table 3. Effect of ionic strength on the reaction rate
[Cr(III)(Gu)(Asp)(H$_2$O)$_2$$^{2+}$] = 2.5 × 10^{-4} mol dm^{-3}; [IO$_4^-$] = 2.0 × 10^{-2} mol dm^3; pH = 2.92; temperature 35 °C

I (mol dm^{-3})	k_{obs} × 10^4 (s^{-1})
0.2	2.08
0.3	1.87
0.4	1.46
0.5	1.12
0.6	0.76

DISCUSSION

In acid medium the chromium(III)-guanosine–aspartic acid complex is in equilibrium.

$$[Cr(III)(Gu)(Asp)(H_2O)_2]^{2+} \xrightleftharpoons{K_1} [Cr(III)(Gu)(Asp)(H_2O)(OH)]^+ + H^+ \qquad (5)$$

The observed [H$^+$] dependence suggests involvement of the deprotonated form of the chromium(III)-complex in the rate-determining step. There are two possibilities for the coordination of IO$_4^-$. First, the H$_2$O ligand in [Cr(III)(Gu)(Asp)(H$_2$O)$_2$]$^{2+}$ may be labile and hence substitution by IO$_4^-$ is likely[19–22]. Second, if the hydroxo form of the complex is the reactive species, the hydroxo ligand may bridge the two reactants[19,22].
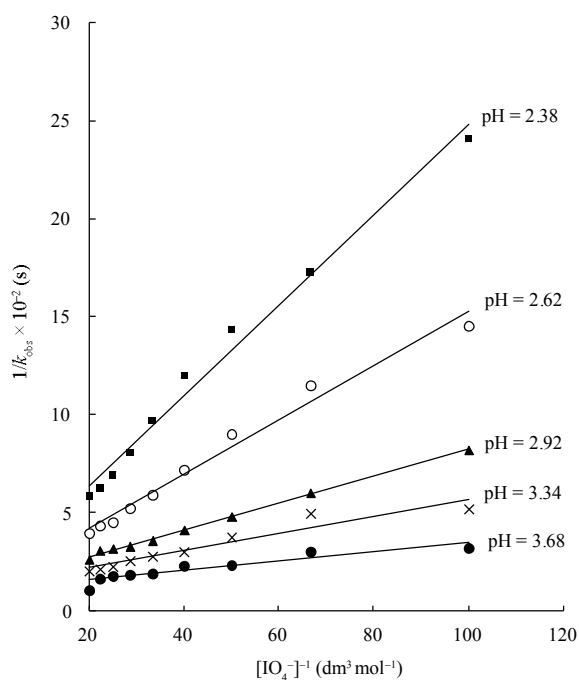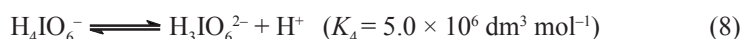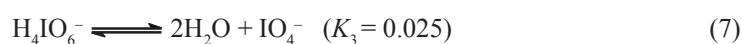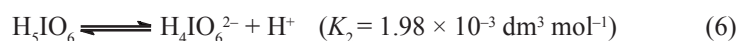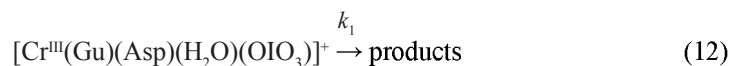
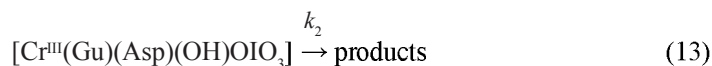**Fig. 3**. Plot of $1/k_{obs}$ versus $1/[IO_4^-]$ at different pH values

Also, it may be concluded that from the reported equilibrium constants of aqueous periodate solutions over the pH range used that the periodate species likely to be present[27] are IO_4^-, $H_4IO_6^-$ and $H_3IO_6^{2-}$, according to the following equilibria:

$$H_5IO_6 \rightleftharpoons H_4IO_6^{2-} + H^+ \quad (K_2 = 1.98 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}) \quad (6)$$

$$H_4IO_6^- \rightleftharpoons 2H_2O + IO_4^- \quad (K_3 = 0.025) \quad (7)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad (K_4 = 5.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}) \quad (8)$$

From the value of K_4 it follows that $H_3IO_6^{2-}$ is not the predominant species (I(VII) will be used to represent $H_4IO_6^-$).

The mechanistic pathway for the oxidation of chromium(III)-guanosine–aspartic acid complex by periodate over the studied pH range may be represented as follows:

$$[Cr^{III}(Gu)(Asp)(H_2O)_2]^{2+} \rightleftharpoons [Cr^{III}(Gu)(Asp)(H_2O)(OH)]^+ + H^+ \qquad K_1 \quad (9)$$

$$[Cr^{III}(Gu)(Asp)(H_2O)_2]^{2+} + [IO_4^-] \rightleftharpoons [Cr^{III}(Gu)(Asp)(H_2O)(OIO_3)]^+ + H_2O \qquad K_5 \quad (10)$$

$$[Cr^{III}(Gu)(Asp)(H_2O)(OH)]^+ + [IO_4^-] \rightleftharpoons [Cr^{III}(Gu)(Asp)(OH)OIO_3] + H_2O \qquad K_6 \quad (11)$$

$$[Cr^{III}(Gu)(Asp)(H_2O)(OIO_3)]^+ \xrightarrow{k_1} \text{products} \qquad (12)$$

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$$[\text{Cr}^{\text{III}}(\text{Gu})(\text{Asp})(\text{OH})\text{OIO}_3] \xrightarrow{k_2} \text{products} \qquad (13)$$

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

$$\text{d}[\text{Cr(III)}]/\text{d}t = (k_1 K_5 + k_2 K_6 K_1/[\text{H}^+])\ [\text{Cr(III)}(\text{Gu})(\text{Asp})(\text{H}_2\text{O})_2^{2+}]\ [\text{IO}_4^-] \qquad (14)$$

If we assume that $[\text{Cr(III)}]_\text{T}$ represents the total concentration of chromium(III) species, then:

$$[\text{Cr(III)}]_\text{T} = [\text{Cr(III)}(\text{Gu})(\text{Asp})(\text{H}_2\text{O})_2^{2+}](1 + K_1/[\text{H}^+] + (K_5[\text{IO}_4^-]+ (K_1 K_6/[\text{H}^+])[\text{IO}_4^-])) \quad (15)$$

Substituting for $[\text{Cr(III)}(\text{Gu})(\text{Asp})(\text{H}_2\text{O})_2^{2+}]$ from equation (15) into equation (14) gives:

$$\text{d}[\text{Cr(III)}]/\text{d}t = (k_1 K_5 + k_2 K_6 K_1/[\text{H}^+])[\text{IO}_4^-][\text{Cr(III)}]_\text{T}/(1 + K_1/[\text{H}^+] +$$
$$(K_5 + K_1 K_6/[\text{H}^+])[\text{IO}_4^-]) \qquad (16)$$

Hence,

$$k_\text{obs} = ((k_1 K_5\ [\text{H}^+] + k_2 K_1 K_6)\ [\text{IO}_4^-])/([\text{H}^+] + K_1 + (K_5[\text{H}^+] + K_1 K_6)[\text{IO}_4^-]) \qquad (17)$$

Since, the deprotonated form, $[\text{Cr(III)}(\text{Gu})(\text{Asp})(\text{H}_2\text{O})_3(\text{OH})]^{2+}$, is considered to be more reactive form than its conjugate acid, we can assume that $K_6 >> K_5$ and that equation (17) may be reduced to equation (18).

$$k_\text{obs} = k_2 K_1 K_6[\text{IO}_4^-]/([\text{H}^+] + K_1 + (K_5[\text{H}^+] + K_1 K_6)[\text{IO}_4^-]) \qquad (18)$$

Upon re-arrangement:

$$1/k_\text{obs} = 1/[\text{IO}_4^-]\{([\text{H}^+]/k_2 K_1 K_6) + (1/k_2 K_6)\} + \{(K_5[\text{H}^+]/k_2 K_1 K_6) + (1/k_2)\} \qquad (19)$$

At constant $[\text{H}^+]$, equation (19) is identical to the experimental rate law shown in equation (4) where,

$$a = k_2 K_1 K_6/K_1 + [\text{H}^+] \text{ and } b = (K_5[\text{H}^+] + K_1 K_6)/K_1 + [\text{H}^+].$$

Plot both of $1/a = K_1 + [\text{H}^+]/k_2 K_1 K_6$ and $b/a = (K_5[\text{H}^+] + K_1 K_6)/k_2 K_1 K_6$ versus $[\text{H}^+]$ (Figs 4 and 5) are linear confirming the proposed mechanism. The values of intercepts of Figs 4 and 5 are 1.38 mol dm^{-3} s and 114.75 s, respectively. The values of slopes of Figs 4 and 5 are 5.19×10^3 s and 1.29×10^4 mol^{-1} dm^3 s, respectively. The K_1 value was calculated by dividing the intercept by the slope of Fig. 4, as 2.66×10^{-4} mol dm^{-3} at 35°C. The intramolecular electron transfer rate constant, k_2, was calculated from the intercept of Fig. 5 as 8.72×10^{-3} s^{-1}. The value of K_5 was calculated by dividing the slope of Fig. 5 by that of Fig. 4 as 2.49 mol^{-1} dm^3. Substituting the value of k_2 gives K_6 from the intercept of Fig. 4 as 83.15 mol^{-1} dm^3. The calculated value of pK_1 (3.57) derived from the proposed mechanism is in a good agreement with the experimental pH used in our studies. This supports the validity of the suggested mechanism.
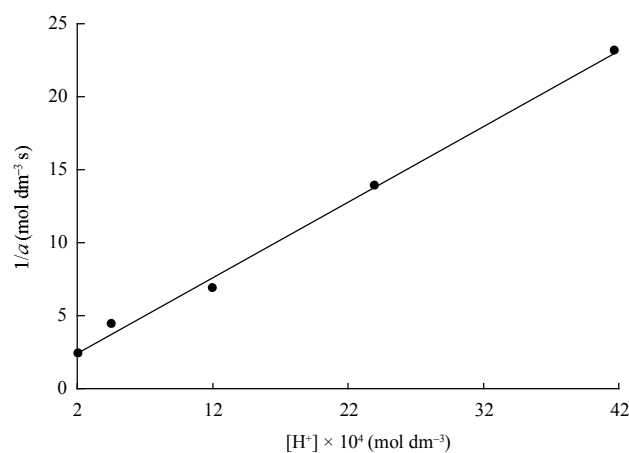
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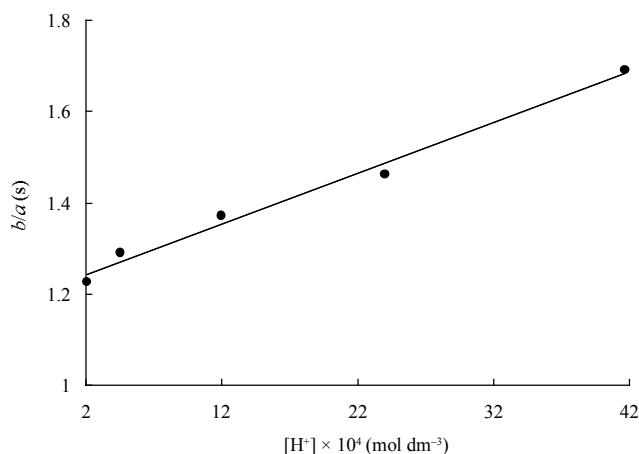**Fig. 4**. Plot of $1/a$ versus [H$^+$] at 35°C

Fig. 5. Plot of b/a versus [H$^+$] at 35°C

Thermodynamic activation parameters, ΔH^* and ΔS^*, associated with constant a in equation (3), were obtained from a least-squares fit to the transition state theory equation as 17.46 kJ mol^{-1} and -171.67 J K^{-1} mol^{-1}, respectively. ΔH^* is a composite value including the enthalpy of formation associated with the precursor complex [Cr(III)(Gu)(Asp)(H$_2$O)(OIO$_3$)]$^+$ and enthalpy of activation of the intramolecular electron-transfer step. The intramolecular electron-transfer step is endothermic as indicated by the positive ΔH^* value. The composite negative ΔS^* value was claimed to be largely the result of substantial mutual ordering of the solvated water molecules[28] of the equilibria and the intermolecular electron-transfer step.

From the above discussion, the following mechanism is proposed for the oxidation of [Cr(III)(Gu)(Asp)(H$_2$O)$_2$]$^{2+}$ by periodate which is supported by the observation that the ion is capable of acting as a ligand, as is apparent from its coordination to

copper(III) (Ref. 29) and nickel(IV) (Ref. 30). The oxidation of [Cr(III)(Gu)(Asp)$(H_2O)_2]^{2+}$ by periodate may proceed via one or 2-electron transfer giving chromium(IV) or chromium(V), respectively in the rate-determining step leading to chromium(VI). The fact that acrylonitrile was not polymerised seems to support 2-electron transfer process.

In comparison with oxidation of [Cr(III)(G)$(H_2O)_4]^{3+}$ (Ref. 20) under the same conditions deprotonated form of the complexes [Cr(III)(G)$(H_2O)_3$(OH)$]^{2+}$ and [Cr(III)(Gu)(Asp)(H_2O)(OH)$]^+$ are significantly more reactive than their conjugated acids. The value of the intramolecular electron transfer rate constant, k_2, for the oxidation of the [Cr(III)(G)$(H_2O)_4]^{3+}$ (2.73×10^{-2} s^{-1}) is higher than the value of k_2 (8.72×10^{-3} s^{-1}) for the oxidation of [Cr(III)(Gu)(Asp)$(H_2O)_2]^{2+}$, i.e. [Cr(III)(Gu)(Asp)$(H_2O)_2]^{2+}$ is more stable towards oxidation than [Cr(III)(G)$(H_2O)_4]^{3+}$. This may be due to the fact that DL-aspartic acid as a secondary ligand makes the ternary complex more stable towards oxidation by periodate than the binary one.

CONCLUSIONS

The oxidation of [Cr(III)(Gu)(Asp)$(H_2O)_2]^{2+}$ by periodate proceeds via an inner-sphere mechanism. The rate of oxidation increases with increasing of pH. This reaction proceed through 2-electrons transfer process leading to the formation of chromium(VI). Secondary ligand makes the ternary complex more stable towards oxidation. The intramolecular electron transfer step is endothermic as indicated by the positive ΔH^* value.

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