N-bromosuccinimide oxidation of a Ternary complex of Iminodiacetatochromium(III) involving DL-aspartic acid co-ligand

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Abstract

The kinetics of the oxidation of chromium(III)-complex, [Cr(IDA)(Asp)(H$_2$O)$_2$] (IDA = Iminodiacetic acid and Asp = DL-aspartic acid) to Cr(VI) have been carried out in the temperature range 20 – 40 ^{o}C. Reaction obeyed first order dependence with respect to [NBS] and [Cr(III)], and the rate of reaction increases with increasing of pH for the range 6.08 – 7.04. Experimentally, the mechanism of this reaction is found to be consistent with the rate law in which the hydroxo species, [Cr^{III}(IDA)(Asp)(H$_2$O)(OH)]$^-$ is considerably much more reactive than their conjugate acid. CTAB enhanced the reaction rate while SDS inhibits one. ΔH* and ΔS* have been calculated. It is proposed that electron transfer occurs through an inner-sphere mechanism.

Keywords: Ternary complex. *N*-bromosuccinimide, Oxidation, Inner-sphere, Micelles.

Introduction

Ternary complexes of iminodiacetic acid with some transition metal have great importance in biochemical studies[1,2]. It is used as antimicrobial agent[1] and in the protein purification technique known as immobilized metal-ion chromatography[2]. The oxidation of chromium(III) to chromium(VI) is biologically important due to its high mobility and the toxicity of chromium(VI)[3]. Oxidation of chromiumr(III) to chromium(V) and/or chromium(VI) in biological systems is most likely as a possible source of anti-diabetic activities of some chromium(III) complexes, and also of long-term toxicities of such complexes[4].

N-bromosuccinimide (NBS) were considered as a brominating and oxidant to the organic substrate. The oxidation process may be carried out in polar medium either through Br^{+5} ion or, by a free radical route including dissociation of NBS (homolytic) as reported in previous work[6,7]. Oxidation of Cr(III) complexes of EDDA[8], (EDDA = ethylenediaminediacetate), DPC[9] (DPC = dipicolinic acid), IDA[10] (IDA = iminodiacetic acid), 2-aminomethylpyridine[11] and inosine[12] by NBS has been studied. The mechanism of these reactions was proposed to behave through the replacement of coordinated water by NBS before the electron transfer.

The oxidation of the complex [Cr(Dpc)(Asp)(H$_2$O)$_2$][13] (Asp = aspartic acid) by NBS were kinetically examined. It was observed that aspartic acid as secondary ligand make the ternary [Cr(Dpc)(Asp)(H$_2$O)$_2$] complex considerably oxdisable via NBS than the binary [Cr(Dpc)$_2$(H$_2$O)$_2$]$^-$ complex[9]. The oxidation of the binary and ternary complexes of cobalt(II) including NTA, succinic acid, malonic acid and *N,N*-bis(salicylaldehyde-1,2-diaminoethane by NBS were studied kinetically[14-16]. It is noticed that oxidation process being outer-sphere and thus only final cobalt(III) was produced.

In this work ,we aim to study the kinetics of oxidation of the [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] complex by NBS to investigate the influence of aspartic acid as a secondary ligand on the stability of binary, [Cr^{III}(IDA)$_2$(H$_2$O)$_2$]$^{-10}$ complex towards oxidation.

Materials and Methods

Experimental Section: Preparation of ternary complexes, [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] and buffer solutions were prepared according to the schemes described in the literature[17]. To regulate the ionic strength of the buffered solutions we use NaNO$_3$. NBS was prepared and used as fresh solution. All other chemicals were purchased from Sigma-Aldrich. Kinetic measurements were done using doubly distilled H$_2$O.

Apparatus and procedure: UV-vis spectrophotometer model JASCO UV-530 was used to record the electronic spectra of the investigated complexes. The oxidation of complexes, [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] by NBS were followed spectrophotometrically. To prepare the reaction mixture we added the following: 0.2 M NaH$_2$PO$_4$ + 0.2 M Na$_2$HPO$_4$ (10 ml) + 2.0 M NaNO$_3$ (1.6 ml) + 0.01 M complex (1.0 ml) + 0.2 M NBS (4.0 ml) and complete it to 40 ml using deionized water and leave this mixture thermally equilibrated in automatic circulation thermostat, for 15 min. UV-vis spectrophotometer model Milton-Roy 601 at 360 nm was used to measure the rate

of oxidation by recording the absorbance of Cr(VI). The absorption measurements for the oxidation of reaction products are maximum at the reaction pH. Automatic circulation thermostat was used to regulate the temperature of solution. The average stabilizing accuracy was ±0.1°C. Large excess of NBS (>10-fold) was used in all measurements to get the pseudo-first order situation. NaNO$_3$ solution was utilized to make a constant ionic strength. It is noticed that during the course of the reaction the pH of the reaction is constant.

Oxidation Products: Figure-1 exhibits the measurements of the absorption spectra for oxidation reaction products of the complexes [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] via NBS using UV-vis spectrophotometer model JASCO UV-530. For the [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] 2 peaks at 545 and 395 nm are disappeared and a new one appeared at 371 nm. The absorption spectra and the molar absorptivity of the last reaction product were similar to chromate ion, confirming that the Cr(VI) is the main product.

Stoichiometry: The Cr(III) complex was added with known excess to a solution of NBS. The measurement of absorption spectra of Cr(VI) produced was performed at 371 nm after 24 hours the onset of the reaction.

Results and Discussion

The measurement of the oxidation reaction of [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] complex was carried out in the pH range 6.08 – 7.04, 0.1M ionic strength, [NBS] range (0.3 - 3.0) x 10^{-2} M and with temperature range 20 – 40°C (±0.1°C). Equation 1 exhibits the Stoichiometry of reaction with time which was determined as 1.9 ± 0.1 moles of NBS per mole of Cr(III).

$$Cr^{III} + 2\ NBS \rightarrow Cr(VI) + 2\ Br^- + \text{another product} \qquad (1)$$
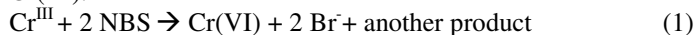
Table-1 shows Pseudo-first order rate constants, k_{obs}. Data obtained exhibits that k_{obs} does not have any effect when the we change the concentration of Cr(III) complex with constant [NBS], confirming that this reaction is first order and related to the concentration of Cr(III) complex. This behavior is represented by the following equation.

$$\text{Rate} = k_{obs}\ [Cr^{III}(IDA)(Asp)(H_2O)_2] \qquad (2)$$
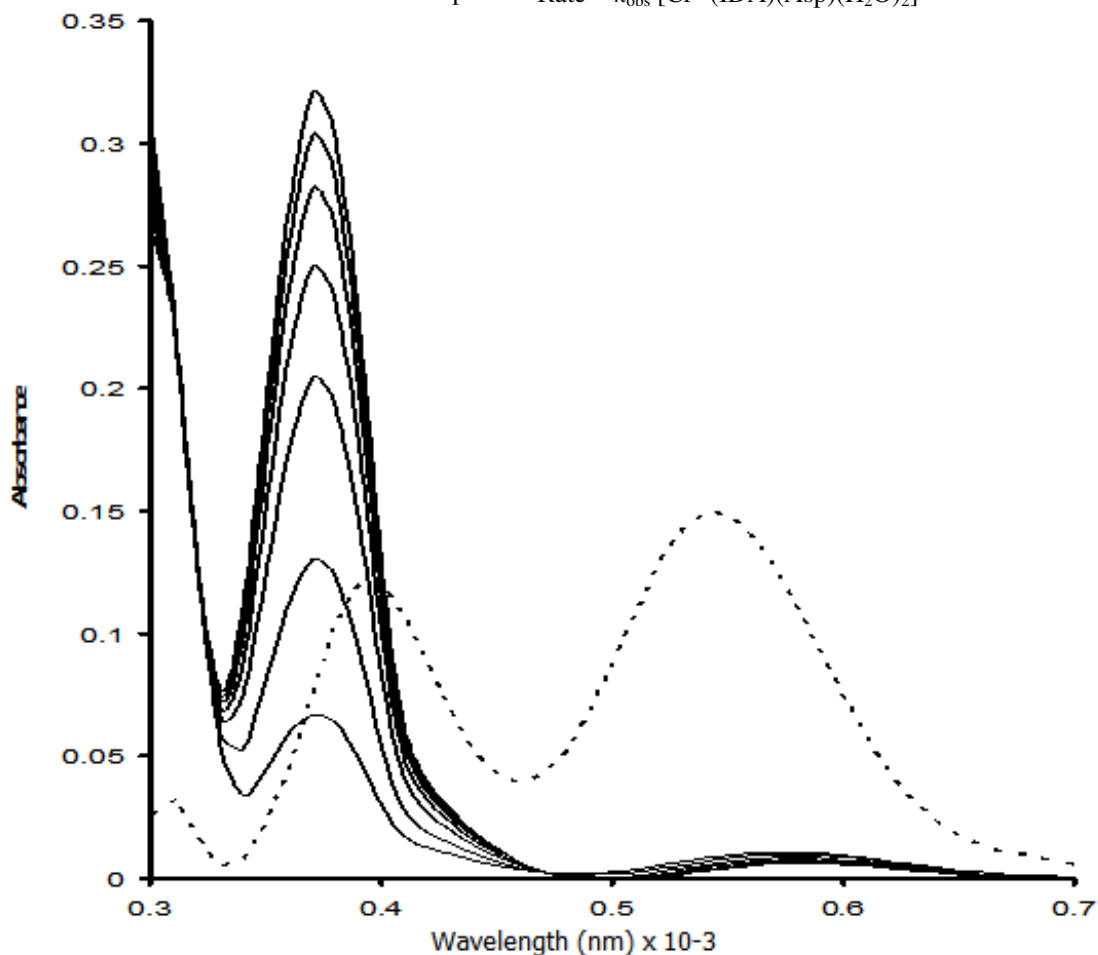
Figure-1
Study the change of absorbance with time in the reaction between [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] and NBS. Curve (……….),
spectrum of the complex at the same pH

Table-1
Dependence of k_{obs} on [NBS] at pH = 6.45, $[Cr^{III}(IDA)(Asp)(H_2O)_2]^a$ = 2.5 x 10^{-4} M , and I = 0.2 M. at various temperatures

10^2[NBS], (M)	$10^4 k_{obs}$ (s^{-1})				
	20 °C	25 °C	30 °C	35 °C	40 °C
0.3	0.20	0.50	1.08	1.40	2.03
0.5	0.67	2.17	1.95	2.07	3.05
1.0	1.30	1.77	3.32	3.63	5.50
1.5	2.82	3.29	4.30	5.72	8.50
2.0	3.62	4.13	6.23	7.67	10.33
2.5	4.37	5.52	8.53	10.18	13.89
3.0	5.22	6.53	9.88	11.67	------

$^a[Cr^{III}(IDA)(Asp)(H_2O)_2]$ = 2.5 x 10^{-4} M; $10^3 k_{obs}$ = 5.96, 6.26, 6.12 and 6.45 s^{-1} at $10^4[Cr^{III}(IDA) (Asp) (H_2O)_2]$ of 1.25, 3.75, 5.0 and 6.25 M, respectively at 30°C and [NBS] = 0.02 M.

Figure-2 indicates a linear relationship between k_{obs} and [NBS] at various temperatures. Equation 3 illustrates the kinetics of the reaction.

$$k_{obs} = k_A [\text{NBS}] \tag{3}$$
$$\text{Rate} = k_A [Cr^{III}(IDA)(Asp)(H_2O)_2][\text{NBS}] \tag{4}$$

The Variation of the k_{obs} with pH at constant temperature is summarized in table-2, which exhibits an increment in the reaction rate with raising the pH values. The Plot of k_{obs} against [NBS] at various pH is represented in figure-3. It is found that

the slopes are dependent on pH, (c.f. table-2). Plot of these slopes (k_A) versus 1/[H$^+$] are linear with slope (k_C) and an intercept (k_B) according to equation-5.

$$k_A = k_B + k_C /[\text{H}^+] \tag{5}$$

$$\text{Rate} = (k_B + k_C /[\text{H}^+])[Cr^{III}(IDA)_2 (H_2O)_2]^- [\text{NBS}]$$

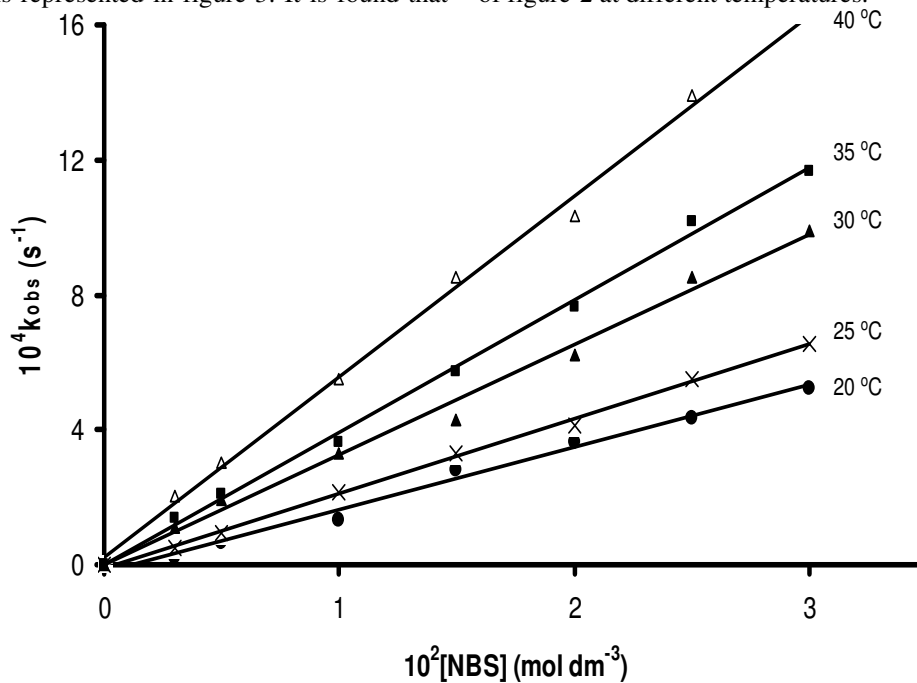Table-3 shows the values of k_A which calculated from the slopes of figure-2 at different temperatures.

Figure-2
Effect of temperature on k_{obs} versus [NBS]

Table-2
pH effect on k_{obs} at [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] = 2.5 x 10^{-4} M, I = 0.2 M , [NBS] = 2 x 10^{-2} M and T = 30 °C

10^2[NBS],(M)	$10^4 k_{obs}$ (s^{-1})			
	pH =7.04	pH = 6.74	pH = 6.45	pH = 6.08
0.3	2.52	1.23	1.08	0.25
0.5	3.22	2.88	1.95	0.33
1.0	6.37	3.97	3.32	0.80
1.5	11.50	6.95	4.30	0.93
2.0	14.98	9.68	6.23	1.30
2.5	19.50	12.40	8.53	2.22
3.0	20.38	15.82	9.88	2.50

Table-3
Variation of constant (k_A) with temperatures used

T(^{o}C)	10^3/T (K^{-1})	10^2 k_A (M^{-1}s^{-1})	-ln k_A /T(M^{-1}s^{-1}K^{-1})
20	3.41	10.43	1.12
25	3.35	12.65	1.3
30	3.30	19.68	1.78
35	3.24	23.46	1.98
40	3.194	31.55	2.29
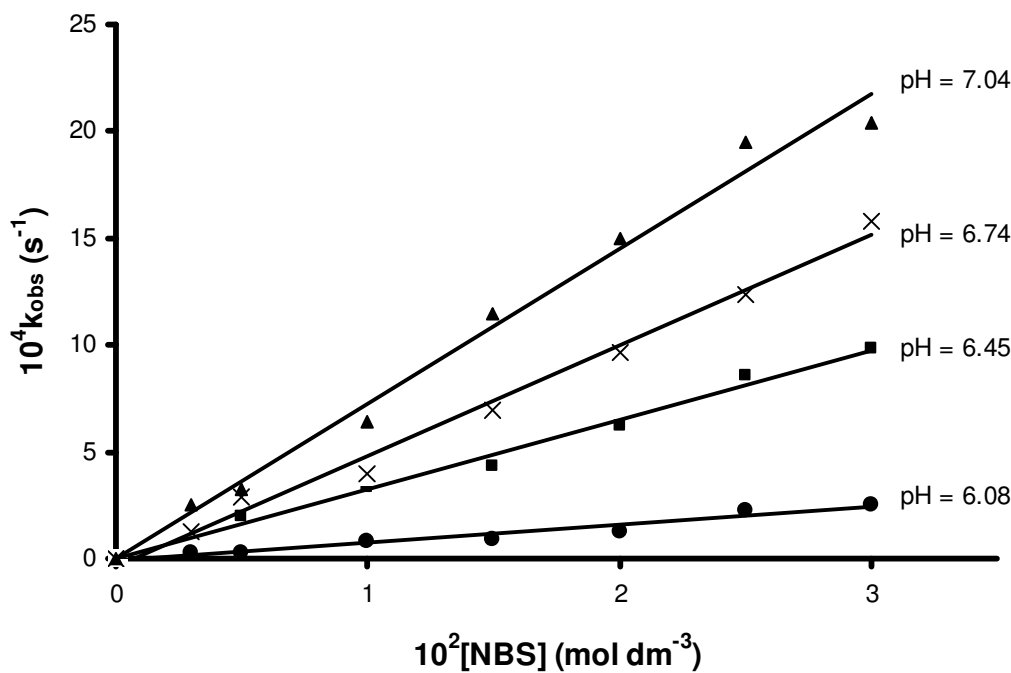
Figure-3
Effect of pH on k_{obs} versus [NBS]

The thermodynamic activation parameters, ΔH^* and ΔS^*, related to k_A, were achieved from the least-squares fit as 12.75 and -1.70, respectively. The values of $10^3 k_{obs}$ of 6.09, 6.31, 6.36 and 6.19 s^{-1} were achieved at I = 0.3, 0.4, 0.5 and 0.6 M, pH = 6.45, [NBS] = 0.02 M and T = 30 ^{o}C. Since, k_{obs} was unchanged by the ionic strength, this implied that this reaction was carried out between charged and uncharged moieties. Equation-7 illustrates the equilibrium that may be takes place in aqueous solution for the Cr(III) complex.

$[Cr^{III}(IDA)(Asp)(H_2O)_2] \rightleftharpoons [Cr^{III}(IDA)(Asp)(H_2O)(OH)]^- + H^+ K_1$ (7)
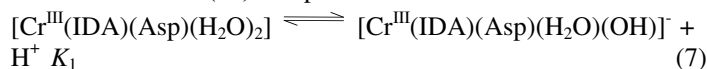
The value of K_1= 4.26 x 10^{-7}, at 30 ^{o}C was obtained potentiometrically. According to the results obtained from the pH range and the value of K_1 we can concluded that the complex $[Cr^{III}(IDA)(Asp)(H_2O)_2]$ is inert and due to the very low basicity of H_2O ligand which is coordinated to Cr(III),it is not expected to act as a bridging ligand[18]. Consequently, the $[Cr^{III}(IDA)(Asp)(H_2O)_2]$ complex appears to scarcity the preconditions for the oxidation via inner-sphere process. However, the oxidation via an inner-sphere process might be adjusted over substitution of the H_2O in the complex. The possible 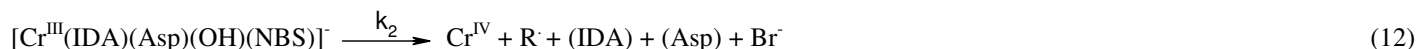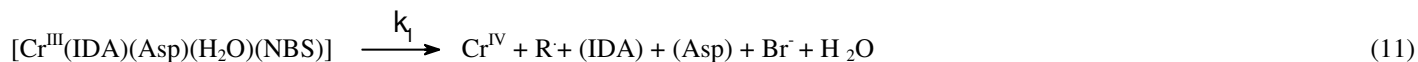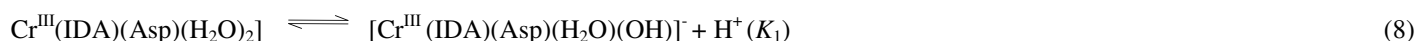mode of coordination for NBS is most likely through the H_2O ligand in $[Cr^{III}(IDA)(Asp)(H_2O)_2]$ Which may be labile and hence replacement by NBS is likely occurred[9, 19].Secondly when the hydroxo form of the complex is the reactive type, the OH ligand may bridge the two reactants[8]. The OH ligand acts in labialize a Cr-OH$_2$ bond, so ease the replacement of H_2O by NBS. The appearance of the H^+ ion in the rate law indicates the participation of the deprotonated complex $[Cr^{III}(IDA)(Asp)(H_2O)(OH)]^-$ in the rate determining step. Such behavior is probable because the reaction occurs between charged and uncharged forms.

According to these discussions, we can propose the mechanism given in Equation-(8) to (14)

On the other hand succinimide anion might pick H^+ from the solvent to produce succinimide, which is quite known product result from the oxidation of NBS. Succinimidyl radical may dimerize to bisuccinimidyl[20,21].

The formed bromide ion Br$^-$ was identified by the addition of AgNO$_3$ solution.
According to the above mechanism, this reaction rate is expressed as in Equation-(15) to (22).

$Cr^{III}(IDA)(Asp)(H_2O)_2] \rightleftharpoons [Cr^{III}(IDA)(Asp)(H_2O)(OH)]^- + H^+ (K_1)$ (8)

$[Cr^{III}(IDA)(Asp)(H_2O)_2] + NBS \rightleftharpoons [Cr^{III}(IDA)(Asp)(H_2O)(NBS)] + H_2O (K_2)$ (9)

$[Cr^{III}(IDA)(Asp)(H_2O)(OH)]^- + NBS \rightleftharpoons [Cr^{III}(IDA)(Asp)(OH)(NBS)]^- + H_2O (K_3)$ (10)

$[Cr^{III}(IDA)(Asp)(H_2O)(NBS)] \xrightarrow{k_1} Cr^{IV} + R^. + (IDA) + (Asp) + Br^- + H_2O$ (11)

$[Cr^{III}(IDA)(Asp)(OH)(NBS)]^- \xrightarrow{k_2} Cr^{IV} + R^. + (IDA) + (Asp) + Br^-$ (12)

$Cr^{IV} + R^. \xrightarrow{fast} Cr^V + R^-$ (13)

$Cr^V + NBS \xrightarrow{fast} Cr^{VI} + Br^- + R^.$ (14)

Where R$^.$ is the radical of succinimidyl, which considered being unstable relative to succinimide or NBS.

$d[Cr^{VI}]/dt = k_1[Cr^{III}(IDA)(Asp)(H_2O)(NBS)] + k_2[Cr^{III}(IDA)(Asp)(OH)(NBS)]^-$ (15)

Since $[Cr^{III}(IDA)(Asp)(H_2O)(NBS)] = K_2[Cr^{III}(IDA)(Asp)(H_2O)_2] [NBS]$ (16)

$[Cr^{III}(IDA)(Asp)(OH)(NBS)]^- = K_3[Cr^{III}(IDA)(Asp)(H_2O)(OH)]^- [NBS]$ (17)

Substitution equations (16) and (17) in equation(15) leads to:

$d[Cr^{VI}]/dt = k_1K_2[Cr^{III}(IDA)(Asp)(H_2O)_2][NBS] + k_2K_3[Cr^{III}(IDA)(Asp)(H_2O)(OH)]^-[NBS]$ (18)

Since $[Cr^{III}(IDA)(Asp)(H_2O)(OH)]^- = K_1[Cr^{III}(IDA)(Asp)(H_2O)_2]/[H^+]$ (19)

Substitution equation (19) in equation (18) then:

$d[Cr^{VI}]/dt = k_1K_2[Cr^{III}(IDA)(Asp)(H_2O)_2][NBS] + (k_2K_3K_1/[H^+])[Cr^{III}(IDA)(Asp)(H_2O)_2][NBS]$ (20)

On rearrangement: $d[Cr^{VI}]/dt = (k_1K_2 + k_2K_3K_1/[H^+]) [Cr^{III}(IDA)(Asp)(H_2O)_2][NBS]$ (21)

Hence: $k_{obs} = \{k_1 K_2 + k_2K_1K_3/[H^+]\} [NBS]$ (22)

Since the hydroxide ion ,OH$^-$ is an efficient bridging ligand than H$_2$O, the complex [Cr^{III}(IDA)(Asp)(OH)(NBS)]$^-$ has higher reactivity than the [Cr^{III}(IDA)(Asp)(H$_2$O)(NBS)] complex.

The previous equation (21) is in agreement with the rate law given in equation (6), since

$k_B = k_1K_2$ and $k_C = k_2K_1K_3 /[H^+]$

From the kinetics point of view the proposed oxidation mechanism of [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] complex by NBS might be an inner sphere mechanism and two evidences were corroborated by the following: (i) The mode of coordination of NBS to the central metal is most probably using the carbonyl group[22]. (ii) When pH < 6, no reaction was noticed, because at pH < 6, the OH$^-$ ions does not exist.

In comparison between the oxidation of the complexes [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$]   and   [Cr^{III}(IDA)$_2$(H$_2$O)$_2$]$^{-10}$ under similar reaction conditions, the two hydroxo complexes [Cr^{III}(IDA)(Asp)(OH)(NBS)]$^-$ and [Cr^{III}(IDA)(Asp)(OH)(NBS)]$^{2-}$ are considerably more reactive than the corresponding conjugate acids. The oxidation rate increases in the sequence [Cr^{III}(IDA)((H$_2$O)$_2$]$^-$ > [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$]. This might be explained on the basis that DL-aspartic acid, make the complex [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] more stable towards oxidation via NBS than the binary one. According to the crystal field theory, the crystal field stabilization energy (Δ_o) between t$^3_{2g}$ and e^o_g orbitals of chromium(III) in the ternary complex will increase due to the electrostatic field on the secondary ligand. Therefore, [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] losing three t$^3_{2g}$ electrons from the central chromium(III) ion during oxidation reaction becomes more difficult.

The influence of micelles (CTAB & SDS) towards oxidation reaction of [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] by NBS were carried at [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] = 2.5 x 10^{-4} M, [NBS] = 0.01 M , pH = 6.45 M , I = 0.20 M and T = 30.0 ^{o}C over the micelles concentration range (2.50 – 15.0) x 10^{-4} M. Table-4, shows that the increase in the rate of reaction when the concentration of CTAB increases. The role of CTAB micelles can be explained by electrostatic attraction between CTAB and [Cr^{III}(IDA)(Asp)(OH)(H$_2$O)]$^-$ and succinimidyl radical (R$^.$) which lead to the accumulation of these substrate micells phase and consequently the reaction is enhanced. These conclusions are in good conformity with our previous observations[23]. The effect of SDS anionic micelles on the oxidation rate (table-4), show a continuous decrease of the reaction rate, k_{obs}, with increasing [SDS]. The decreasing of rate of reaction in presence of SDS as anionic surfactants may be attributed to the SDS repel the negative charged [Cr^{III}(IDA)(Asp)(OH)(H$_2$O)]$^-$ to aqueous phase. Thus, decrease the concentration of reactant micellar phase (Stern layer) cannot participate in the reaction and consequently the reaction is retarded. The high negative ΔS^* for

investigated reactions were supposed to be largely the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated H$_2$O molecules[24]. From the positive values of ΔH^*, we concluded that the steps of intramolecular electron transfer are endothermic. Based on the values of ΔH^* and ΔS^* the factors controlling ΔH^* should be related to those controlling ΔS^*, because the contributions of ΔH^* and ΔS^* to the rate constant appear to compensate each other. The small enthalpy of activation, ΔH^*, could be elucidated in terms of forming more solvated complex. Thus, the state of solvation of the encounter complex would be significant in calculating ΔH^*[24].

Conclusion

Oxidation of [Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] by NBS proceeds via an inner-sphere mechanism. The rate of oxidation increases with increasing of pH. This reaction occurs via two step-one electron transfer process which lead to the formation of Cr(IV) followed

by a fast step leading to Cr(VI). CTAB enhanced the reaction rate while SDS inhibits one.

Table-4
Effect of micelles on the rate constant at
[Cr^{III}(IDA)(Asp)(H$_2$O)$_2$] = 2.50 x 10^{-4} M, [NBS] = 0.02 M, pH = 6.45, I = 0.20 M and T = 30.0^{o}C

10^4[Micelles], (M)	10^{4}k$_{obs}$ (s^{-1})	
	CTAB	SDS
0.00	6.23	6.23
2.50	7.42	5.07
5.00	8.50	4.33
7.50	9.18	3.48
10.00	10.62	2.76
12.50	11.38	2.14
15.00	12.16	1.83

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