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Inner-sphere oxidation of ternary iminodiacetato chromium (III) complex involving malonic by N-bromosuccinimide

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ABSTRACT

Preparation and characterization of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})]^-$ is performed. Conformation of the formation of the ternary complex has been done using IR spectrum, TGA, uv-visible spectroscopic and cyclic voltammetry measurements. The oxidation of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})]^-$ [IDA=iminodiacetate, Ma=malonic] by NBS have been studied kinetically in aqueous solution over 25-45 °C and a variety of pH ranges. The rate of oxidation obeys the equation $d[\text{Cr}^{\text{VI}}]/dt = \{[\text{Fe}^{\text{II}}](k_5 + k_6 K_1/[\text{H}^+]) + [\text{NBS}](k_7 K_2 + k_8 K_1 K_3/[\text{H}^+])\} [\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})]^-$. Catalysis is believed to be due to the oxidation of iron(II) to iron(III), which acts as the oxidizing agent. Thermodynamic activation parameters have been calculated. It is proposed that electron transfer proceeds through an inner-sphere mechanism via coordination of NBS to chromium(III). A common mechanism for this reaction is proposed and supported by an excellent isokinetic relationship between ΔH^* and ΔS^* values for some ternary chromium(III) complexes.

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INTRODUCTION

Ternary metal complexes might appear in biological fluids creating specific structure^[1-3], most frequently manifesting themselves as enzyme-metal ion-substrate complexes^[3-6]. This explains why ternary system has recently received increasing attention. Chromium (III) complexes with nucleotides are used as enzymatic labels by substitution of the activator or inhibitor^[7,8] and finding the role of chromium (III) in transcription processes and RNA and DNA interaction^[9]. The oxidation of chromium from +3 to +6 is an important environmental process because chromium (VI) is easily taken up by cells and is subsequently reduced to the trivalent form, the formation of chromium (III) or other intermediate oxidation states such as chromium (V) and (IV) is believed to play a role in the adverse biological

effects of chromium (VI) compounds^[10].

Iminodiacetic acid is the backbone of hydroxamic acid derivatives that could be used to treat cancer. Also it is useful in the prevention and treatment of TRX-mediated diseases, such as autoimmune, allergic and inflammatory diseases^[11]. Transition metal complexes of iminodiacetate have been widely adopted in biology and were gaining increasing use in biotechnology, particularly in the protein purification technique known as immobilized metal-ion^[12].

Succinimide and its derivatives are biologically and industrially useful compounds. Pharmaceutically, they are used as analgesics, nephrotoxic, anticonvulsant, ionic inhibitors of human leukocyte, etc. It has been reported that sulfonated derivatives of succinimide are more effective than aspirin and paracetamol. They are also used in industry as antifoaming agent, lubricating tackifiers,

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emulsion explosive, and corrosion inhibitors. N-bromosuccinimide (NBS) serves as an oxidizing agent in the synthesis of drugs and hormones.

N-bromosuccinimide (NBS) has been used widely as a brominating and oxidizing agent for organic compounds. It was reported that the oxidation process proceeds via bromonium ion $\text{Br}^{+[13]}$ in a polar medium or, alternatively by a free radical path involving the homolytic dissociation of NBS with reducing metal ions yields useful intermediates; The initiation is considered to be effected by one of both succinimidyl and bromine free radicals^[14,15].

Inner sphere oxidations of some Cr (III) binary complexes^[16-23] and ternary complexes^[16,24,25], involving some amino acids as secondary ligands, by NBS were studied. These reactions were found to proceed via a mechanism in which coordinated water was replaced by NBS prior to electron transfer step. Also, through bridging of NBS to the hydroxo conjugate species of the complex. Oxidation proceeds by homolytic fission of NBS follows by reaction of one or both of fragments (succinimidyl and bromine free radicals) with metal complex species^[16-25].

Here, preparation and kinetics of oxidation of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]$ are reported. Aim of this study is attributed to some considerations. Firstly, transition metal ternary complexes have been received particular focus and employed in mapping protein surfaces as probes for biological redox centers and in protein capture for both purification and study. Secondly, due to the probability of formation and oxidation of this complex in vivo, study the same system has been done as a model in vitro. Finally, to know effect of malonic ligand on stability of Cr (III) towards oxidation process.

EXPERIMENTAL

Materials and solutions

All reagent grade or analar chemicals were used. Freshly prepared solutions of NBS were used. Solutions of Na_2HPO_4 , NaH_2PO_4 and NaNO_3 were prepared by weighing. $\text{Na}_2\text{HPO}_4 / \text{NaH}_2\text{PO}_4$ buffers of known pH were used, and the ionic strength was adjusted with NaNO_3 solution. Doubly distilled H_2O was used in all kinetic runs.

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^[26]. Calculations were performed using computer program MINQUAD-75 loaded on an IBM-550 computer. The solution containing 5 mL 0.1M complex, 5 mL 0.8M NaNO_3 , 5 mL 0.05M HNO_3 and 25mL deionized water, was titrated with 0.01M NaOH at 30°C.

Cyclic voltammetry measurements are collected using potentiostat / Galvan state wenking PGS 95 with single-compartment voltammetric cell equipped with a platinum working electrode (area= 0.5 cm^2), a Pt wire counter electrode, and a SCE as reference electrode. The uv-vis absorption spectra of Cr^{III} complex and its oxidation product were recorded on Shimadzu UV-1601PC spectrophotometer equipped by automatic circulating water bath.

Ternary complex, $\text{Na} [\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]$. H_2O was prepared by heating an aqueous solution containing equal moles of chromium (III) nitrate, disodium iminodiacetate and malonic acid for 3 hours at 70°C. A deep pink crystal was separated, on cooling, from the concentrated solution. After washing with alcohol and drying the crystals, the elemental analysis data of the obtained complex are Found; C, 23.52; H, 3.50; N, 3.98%, Calcd: C, 23.21; H, 3.59; N, 3.87%

Kinetic procedures

Reaction rates were measured by monitoring the chromium (VI) absorbance at 370 nm on a Milton-Roy 601 spectrophotometer. All reactants, except NBS, were mixed and equilibrated at the required temperature for 15-20 min. The required amount of separately thermostated NBS stock solution was rapidly mixed, and then the recording of absorbance was started.

The pH of the reaction mixture was measured using a Chertsey Surrey, 7065 pH-meter. Pseudo-order conditions were maintained in all runs by the presence of a large excess (>10-fold) of [NBS] over that of Cr^{III} complex concentration. The error limits for results are calculated using Microcal™ Origin® (version 6.0).

Stoichiometry

Experiments were carried out by varying the [NBS]: $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]$ ratios, where the concentration of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]$ was always at least twice that of [NBS]. Concentration of Cr^{III} consumed was calculated using the molar absorptivity of Cr^{VI} .

RESULTS AND DISCUSSION

Formation and characterization of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$

Figure 1 represents a set of experimentally obtained potentiometric titration curves for Cr^{III} , Ma, IDA and HNO_3 at 25°C and ionic strength 0.1 mol dm^{-3} . The addition of Cr^{III} to the free ligands solution shifts the buffer region of the ligand to lower pH values. This indicates that the formation of the complex proceed via releasing of protons from such ligands. From curve 6 in figure 1, pK_a of ionization of a coordinated water molecule is found to be 5.7

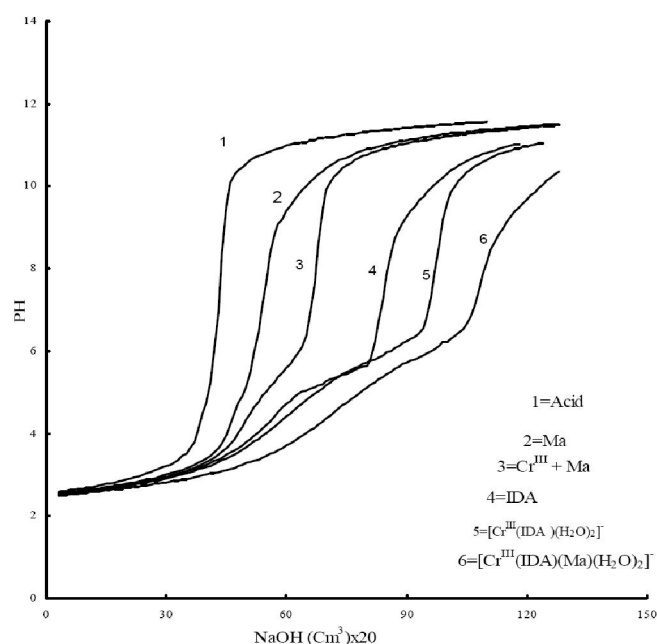


Figure 1 : Potentiometric titration curve for iminodiacetate chromium (III) - Malionic acid complex.

The spectrum of a solution containing $\text{Cr}(\text{III})$ exhibit absorption bands at about 396 nm and 546 nm with $\epsilon_{\text{max}} = 38.74$ and $\epsilon_{\text{max}} = 30.31 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. The solution containing IDA and $\text{Cr}(\text{III})$ (1:1 molar ration) undergoes a change in color and the spectrum of the reaction mixture exhibits a two absorption bands at 400 nm and 574nm with $\epsilon_{\text{max}} = 47.24$ and $33.77 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. However, the solution of the reaction mixture of IDA, Ma and $\text{Cr}(\text{III})$ (1:1:1 molar ration) gives maximum absorption bands at 398 nm and 548nm with $\epsilon_{\text{max}} = 165.3$ and $184.28 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. All measured solutions were of the same concentration ($7 \times 10^{-3} \text{ mol dm}^{-3}$) at $\text{pH} = 2.71$ Figure 2. Shift of the absorption bands to lower

wave length and increase values of the molar absorptivity of the IDA / Cr^{III} mixture than $\text{Cr}(\text{III})$ solution are presumably due to the formation of a binary complex $[\text{Cr}^{\text{III}}(\text{IDA})_2(\text{H}_2\text{O})_2]^-$. While the absorption bands of the reaction mixture solution containing IDA, Ma and $\text{Cr}(\text{III})$ are slightly shifted to lower wave lengths and larger increase of ϵ than the binary complex may confirm formation of the ternary complex $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$.

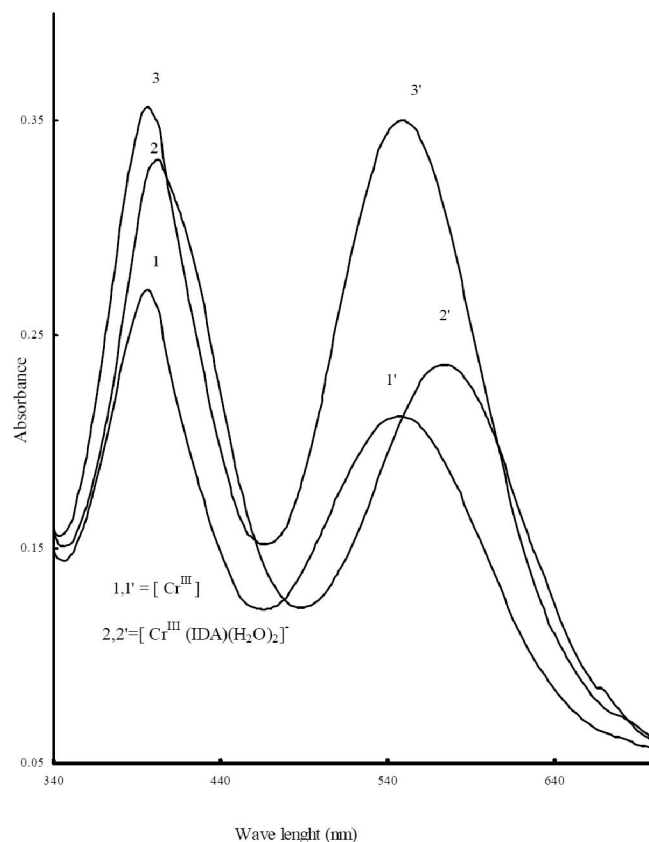
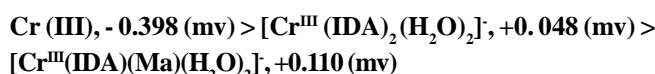


Figure 2 : Change in absorbance for each Cr^{III} , $[\text{Cr}^{\text{III}}(\text{IDA})(\text{H}_2\text{O})_2]^-$, $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$ at the same concentration (7.0×10^{-3}) and the same $\text{pH} = 2.71$

Figure 3 represents the cyclic voltammograms for the oxidation of $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cr}(\text{III})$ in the absence and presence of the complexed ligands ($2 \times 10^{-3} \text{ mol dm}^{-3}$) at $I = 0.12 \text{ mol dm}^{-3} \text{ NaNO}_3$, 25°C , and $\text{pH} = 2.71$. The reaction mixture of IDA with $\text{Cr}(\text{III})$ causes a slight shift of the (anodic) peaks to more (+ve) potential, indicating the formation of binary complex $[\text{Cr}^{\text{III}}(\text{IDA})_2(\text{H}_2\text{O})_2]^-$ in solution. Solution mixture of IDA, Ma, and $\text{Cr}(\text{III})$ makes amore shift peaks to more +ve Potential than $[\text{Cr}^{\text{III}}(\text{IDA})_2(\text{H}_2\text{O})_2]^-$ confirm the formation of ternary complex $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$. From a comparison of the values of the anodic Potentials of the

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three systems, it is clear that the stability of these systems follows the order;



To confirm the formula of the complex, IR spectrum and TGA are recorded. In the infrared spectrum, bands in the (3515-3363) Cm^{-1} region are attributed to γ (OH) of the water molecules. The OH of the carboxylic group disappeared and a new γ (COO^-) appeared in the region (1400-1300) Cm^{-1} , indicating that the carboxylic group of the ligands participates in the coordination with metal ion through deprotonation. Band at 3228 Cm^{-1} is attributed to γ NH. Bands at (2109-1656) Cm^{-1} region are attributed to γ C=O and γ C=C, respectively. The TGA curve of $\text{Na}[\text{Cr}^{\text{III}}\text{C}_8\text{H}_{19}\text{O}_{13}\text{N}_1]$ shows two-stage decomposition pattern. The weight loss [13.42 %] at 88.50 °C corresponds to the loss of one water molecules of crystallization [Calc. 13.11%], and the loss [9.94 %] at 135.80 °C corresponds to the loss of two coordinated water molecules [Calc. 10.06%].

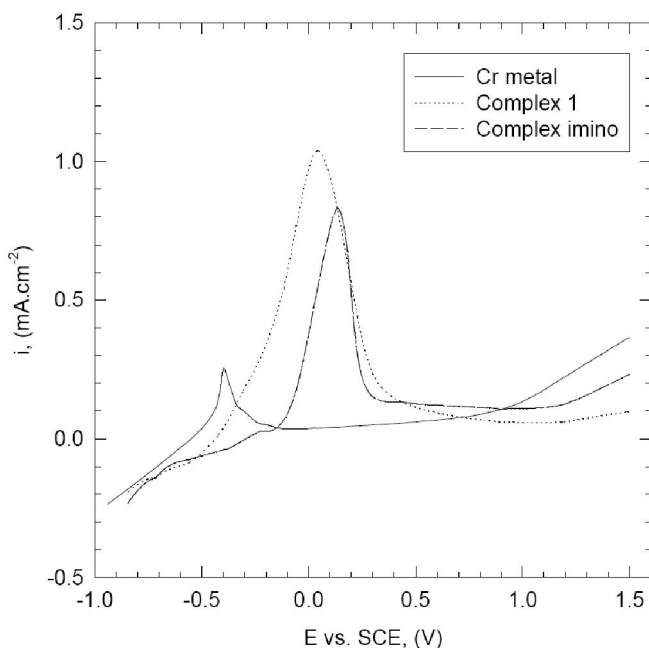


Figure 3 : Potentiodynamic polarization curves for the oxidation of Cr metal ion, complex1 $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^{-}$ and complex imino from solutions containing $3 \times 10^{-3} \text{ M}$ on Pt electrode at 300 K with scan rate of 25 mVs^{-1}

Oxidation products

During the oxidation, the deep pink aqueous solution of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^{-}$ changed gradually to yellow and original absorption maxima, at 345 and 385

nm, were replaced by a single peak at 370 nm with absorption coefficient $\epsilon_{370} = 193.43 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Figure 4), as the experimental value for Cr^{VI} at the same pH. Addition of AgNO_3 solution to the reaction mixture resulted in a yellowish white precipitate of AgBr , suggesting the presence of Br^- in the product. AgNO_3 solution had no effect on NBS under the experimental conditions.

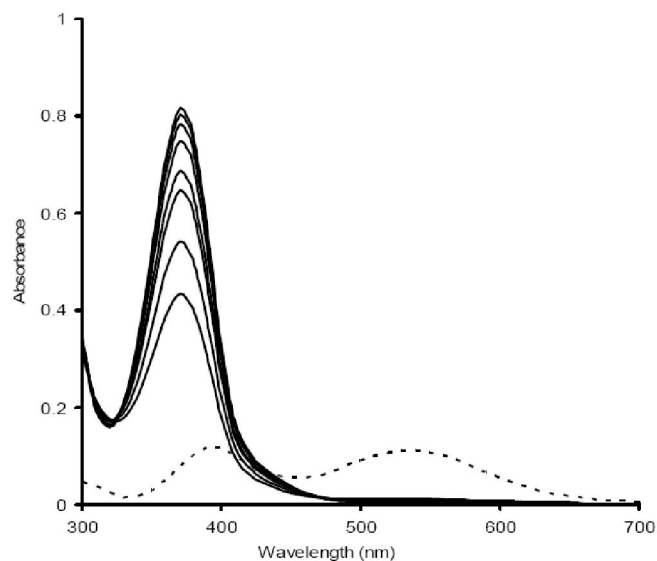


Figure 4 : Change in absorbance as a function of time in the reaction between $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^{-}$ and NBS.

Kinetics of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^{-}$ /NBS reaction in aqueous solution

Oxidation of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^{-}$ is studied over the (5.75 – 6.86) pH range, at 0.13 mol dm^{-3} ionic strength at 25-45 °C ($\pm 0.05^\circ\text{C}$) and the conc. of NBS $(0.5-5.0) \times 10^{-2} \text{ mol dm}^{-3}$. The over all stoichiometry of the reaction is (2.01 ± 0.1) moles of NBS per 2 moles of chromium (III) within the time of reaction. Hence the reaction is described by equation (1)



Plots of $\ln(A_\infty - A_t)$ versus time, were linear up to 85 % of reaction where A_t and A_∞ are the absorbance at time t and time 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} are unaffected when the concentration of the chromium (III) - complex are varied at constant NBS concentration, indicating first order dependence on complex concentration, equation (2).



Plots of k_{obs} against $[\text{NBS}]$ at different tempera-

TABLE 1 : Dependence of the reaction rate constant, k_{obs} on $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})]^{(\text{a})}$, $[\text{NBS}]$ and temperature at $\text{pH} = 6.05$ and $I = 0.13 \text{ mol dm}^{-3}$.

$10^2 [\text{NBS}]$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$			
	T = 25 °C	T = 35 °C	T = 40 °C	T = 45 °C
0.5	2.20±0.07	4.23±0.06	5.42±0.05	7.62±0.08
1.0	2.71±0.05	4.74±0.04	5.93±0.08	8.47±0.07
1.5	3.22±0.06	5.08±0.03	6.61±0.06	8.97±0.05
2.0	3.56±0.04	5.59±0.07	7.11±0.07	9.65±0.09
2.5	3.89±0.08	6.09±0.08	7.62±0.11	10.33±0.12
3.0	4.23±0.06	6.77±0.10	8.29±0.12	11.18±0.14
3.5	4.57±0.10	7.11±0.05	8.98±0.09	11.85±0.18
5.0	5.59±0.12	8.47±0.07	10.84±0.15	13.73±0.21

$[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$; $10^4 k_{\text{obs}} = 8.47 \pm 0.09$, 8.57 ± 0.07 , 8.30 ± 0.06 and $8.60 \pm 0.09 \text{ s}^{-1}$ at $10^4 [\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})]^{(\text{a})}$, of 2.0, 4.0, 5.0 and 8.0 mol dm^{-3} , respectively at 35 °C and $[\text{NBS}] = 0.02 \text{ mol dm}^{-3}$.

tures were found to be linear with intercept, figure 5. The dependence of k_{obs} on $[\text{NBS}]$, TABLE 1, is described by

$$k_{\text{obs}} = k_1 + k_2[\text{NBS}] \quad (3)$$

Values of k_1 and k_2 were calculated at different temperatures and are listed in TABLE 2. The thermodynamic activation parameters, associated with k_1 and k_2 , were calculated by using the transition state theory equation. The enthalpies of activation, ΔH_1^* and ΔH_2^* were obtained as 25.08 ± 0.11 and $22.12 \pm 0.02 \text{ kJ mol}^{-1}$, respectively.

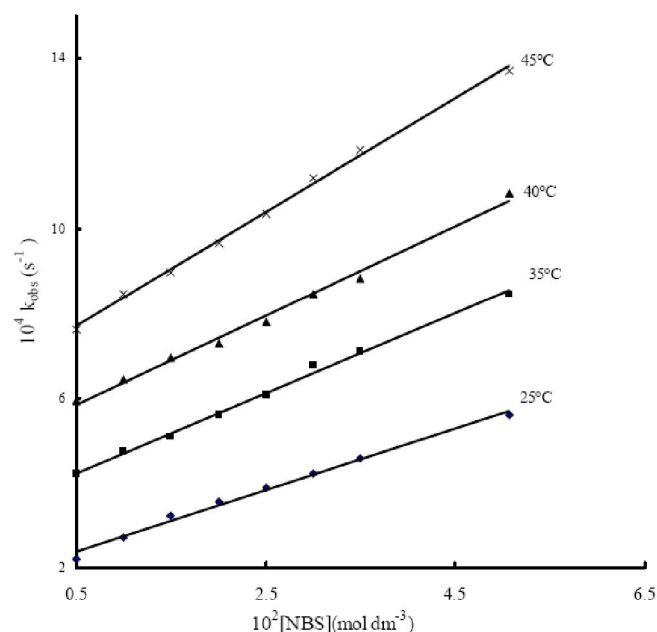


Figure 5 : Plot of k_{obs} versus $[\text{NBS}]$ at $\text{pH} = 6.05$ at different temperature

The corresponding entropies of activation, ΔS_1^* and ΔS_2^* were -200.83 ± 0.10 and $-210.11 \pm 0.18 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively. These activation parameters are composite values.

TABLE 2 : Variation of k_1 and k_2 with temperatures.

T (°C)	$10^4 k_1 (\text{s}^{-1})$	$10^3 k_2 (\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$
25	2.14±0.02	7.00±0.02
35	3.74±0.04	9.56±0.02
40	5.18±0.05	11.01±0.06
45	6.99±0.10	13.02±0.02

The kinetics of the reaction was studied over pH range of (5.75–6.86) at different temperatures. TABLE 3 lists the variation of k_2 with pH at different temperatures which indicate that the reaction rate increased gradually with increasing pH. Plots of k_2 versus $[\text{H}^+]^{-1}$ were linear, with Intercepts as shown in figure 6. This behavior can be described by equation (4).

$$k_2 = k_4 + k_3/[\text{H}^+] \quad (4)$$

Values of k_3 and k_4 were calculated at different temperatures, and were listed in TABLE 4. The enthalpies of activation, ΔH_3^* and ΔH_4^* , associated with k_3 and k_4 , were found to be 8.36 ± 0.02 and $6.32 \pm 0.28 \text{ kJ mol}^{-1}$, respectively. The corresponding entropies of activation, ΔS_3^* and ΔS_4^* , were calculated as -396.24 ± 0.18 and $-425.18 \pm 0.03 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively.

Furthermore, the reaction rate is unaffected by ionic strength since the rate determining reaction is taking place between charged and uncharged species. Thus values of $10^4 k_{\text{obs}}$ of $[6.78 \pm 0.05, 7.11 \pm 0.04, 7.11 \pm 0.06$ and $6.78 \pm 0.03] \text{ s}^{-1}$ are obtained at $I = 0.2, 0.3, 0.4$ and 0.5 mol dm^{-3} at $\text{pH} = 6.36$, temperature 35 °C and $[\text{NBS}] = 0.02 \text{ mol dm}^{-3}$.

From Equation (3) it is surprising to note that one reaction path is independent of NBS. It is also observe that k_{obs} value wasn't reproducible when different sources of reagent were used. This observation has

TABLE 3 : Variation of k_2 with pH at $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.13 \text{ mol dm}^{-3}$, different temperatures and $[\text{NBS}]$.

pH	$10^3 k_2, (\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$			
	T = 25 °C	T = 35 °C	T = 40 °C	T = 45 °C
5.75	6.02±0.02	8.29±0.07	9.60±0.07	11.61±0.02
6.05	7.00±0.02	9.56±0.02	11.00±0.06	13.02±0.02
6.36	8.68±0.04	10.00±0.08	12.00±0.02	13.90±0.06
6.86	13.55±0.02	14.84±0.05	16.61±0.07	20.30±0.10

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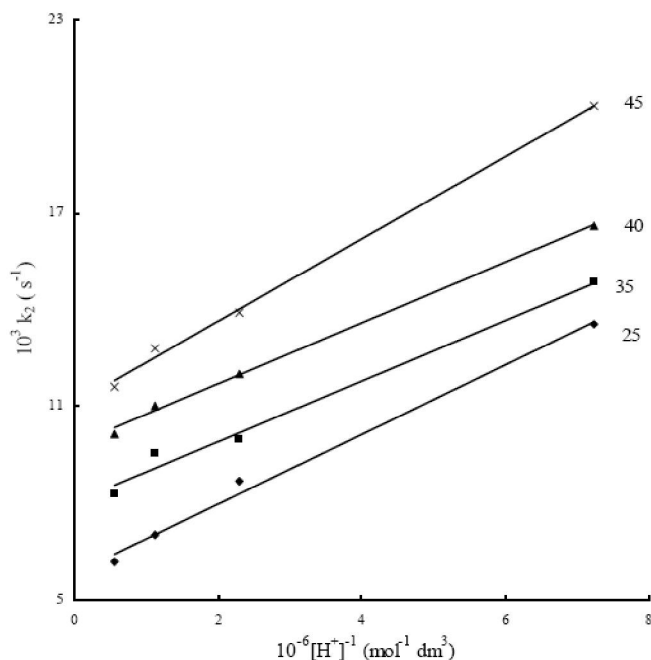


Figure 6 : Plot of k_2 versus $[H^+]^{-1}$ at different temperature.

TABLE 4 : Variation of k_3 and k_4 with temperatures at $[Cr^{III}(IDA)(Ma)(H_2O)_2] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.13 \text{ mol dm}^{-3}$, and different [NBS].

T (°C)	$10^9 k_3 (\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$	$10^3 k_4 (\text{s}^{-1})$
25	1.08 ± 0.06	5.83 ± 0.06
35	1.13 ± 0.07	8.05 ± 0.30
40	1.20 ± 0.08	9.54 ± 0.12
45	1.34 ± 0.02	10.64 ± 0.20

drawn our attention to the possibility of catalysis by trace amount of metal ions originating in the reagents and in the solvent, especially iron (II) and manganese (II)^[27].

The effect of iron (II) on the reaction rate was investigated over the $(3.0 - 10.0) \times 10^{-5} \text{ mol dm}^{-3}$ range at different NBS concentrations, $[Cr^{III}(IDA)(Ma)(H_2O)_2] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.13 \text{ mol dm}^{-3}$, $pH = 6.36$ and temperature 35°C . Plots of k_{obs} versus

TABLE 5 : Effect of $[Fe^{II}]$ on k_{obs} at $[Cr^{III}(IDA)(Ma)(H_2O)_2] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.13 \text{ mol dm}^{-3}$, $pH = 6.36$, $temp = 35^\circ \text{C}$ with different [NBS].

$10^2 [\text{NBS}]$ (mol dm^{-3})	$10^2 k_{\text{obs}} (\text{s}^{-1})$			
	$[Fe^{II}]$ (mol dm^{-3}) 3×10^{-5}	$[Fe^{II}]$ (mol dm^{-3}) 5×10^{-5}	$[Fe^{II}]$ (mol dm^{-3}) 7×10^{-5}	$[Fe^{II}]$ (mol dm^{-3}) 10×10^{-5}
5.0	7.22 ± 0.01	9.36 ± 0.02	11.33 ± 0.03	12.97 ± 0.06
4.0	5.26 ± 0.02	7.65 ± 0.02	9.69 ± 0.03	11.01 ± 0.07
3.0	3.45 ± 0.01	6.23 ± 0.03	8.36 ± 0.04	9.80 ± 0.05
2.0	2.36 ± 0.03	4.48 ± 0.04	6.39 ± 0.05	7.65 ± 0.10
1.0	1.26 ± 0.04	3.56 ± 0.05	4.85 ± 0.07	6.45 ± 0.30

[NBS] at different iron (II) concentration, show that the reaction is catalyzed by Fe^{II} , TABLE 5 and figure 7. It is apparent from TABLE 6, that k_2 is Fe^{II} independent. The dependence of k_1 on added $[Fe^{II}]$, figure 8, is in agreement with equation (5).

$$k_1 = k_0 + k_c [Fe^{II}] \quad (5)$$

From equations (2), (4), and (5), the experimental

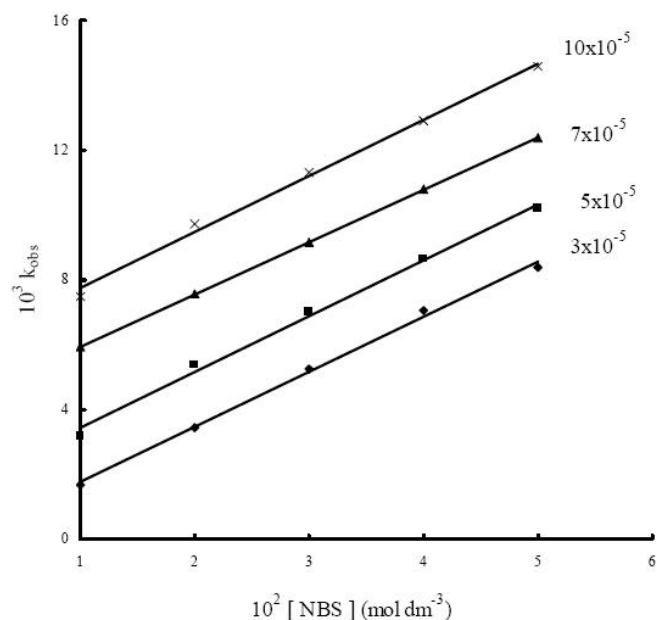


Figure 7 : Plot of k_{obs} versus [NBS] at different $[Fe(II)]$

TABLE 6 : Effect $[Fe^{II}]$ on k_1 and k_2 .

$10^5 [Fe^{II}] (\text{mol dm}^{-3})$	$10^2 k_1 (\text{s}^{-1})$	$10^2 k_2 (\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$
3.0	1.21 ± 0.02	1.10 ± 0.1
5.0	2.56 ± 0.04	1.13 ± 0.2
7.0	3.96 ± 0.05	1.12 ± 0.1
10.0	5.85 ± 0.04	1.15 ± 0.2

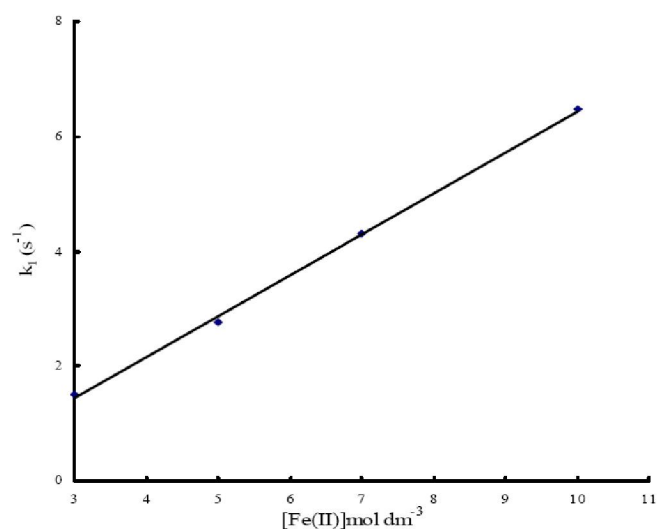


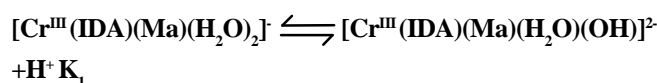
Figure 8 : Plot of k_1 versus $[Fe(II)]$.

rate law is represented by:

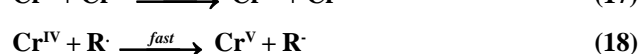
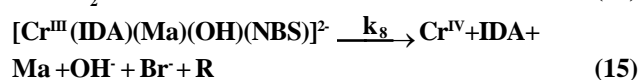
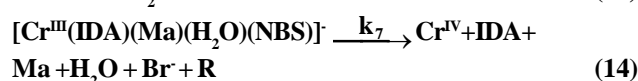
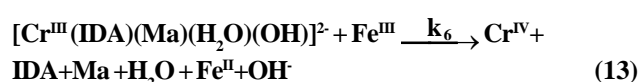
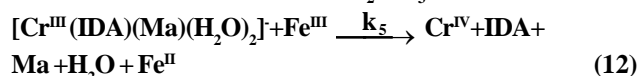
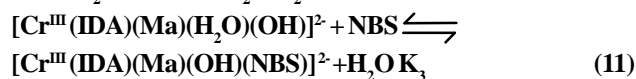
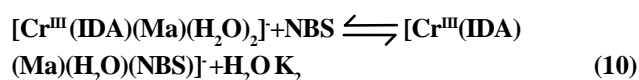
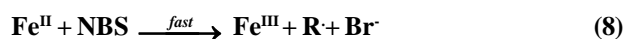
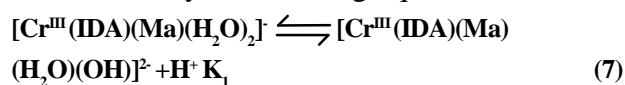
$$\frac{d[\text{Cr}^{\text{VI}}]/dt = \{[k_0 + k_c[\text{Fe}^{\text{II}}]] + [k_4 + (k_3/[\text{H}^+])][\text{NBS}]\}}{[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]_0} \quad (6)$$

DISCUSSION

NBS exists as protonated species HNBS^+ in highly acidic solution, but in our pH range the predominant species is NBS^[28,29]. Coordination of NBS to the metal ion is possible through the carbonyl group^[30]. In weakly acidic aqueous medium the following equilibrium is shown:



K_1 was measured potentiometrically, and has the value = 1.99×10^{-6} at 25 °C. From the pH range used (5.75 – 6.86) and the K_1 value, it is clear that the two species $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})(\text{OH})]^{2-}$ are predominated. An inner-sphere process may be accommodated through replacement of coordinated H_2O because coordinated H_2O ligand in $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$ may be labile and hence substitution by NBS is likely^[31,32]. The hydroxyl group acts in labilize a Cr-OH₂ bond, so facilitates the substitution of H_2O by NBS. The presence of $[\text{H}^+]$ dependence on the rate law suggests involvement of the deprotonated form of chromium (III) complex, $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})(\text{OH})]^{2-}$, in the rate determining step. Catalysis by iron (II) ions in several reactions is well established by the oxidation of iron (II) to iron (III), which acts as the oxidizing agent^[33,34]. In view of the above considerations, kinetics of oxidation of $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$ by NBS proceeds by one first-order pathway in each reactant. The mechanism could be described by the following Eqs.



It is known that the succinimidyl radical $\text{R} \cdot$ is not heavily resonance stabilized and hence is unstable with respect to succinimide or NBS^[35]. Succinimide anion R^- may well prefer to abstract a hydrogen ion from, for example, the solvent, to form succinimide. Thus the product may be succinimide, a well known product of organic NBS oxidation. Presence of Br^- as a product is indicated by the formation of AgBr which, increased gradually with time up on addition of AgNO_3 solution to the reaction mixture. From the above mechanism, the reaction rate is given by

$$\frac{d[\text{Cr}^{\text{VI}}]/dt = k_3[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2][\text{Fe}^{\text{III}}] + k_6[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})(\text{OH})]^{2-}[\text{Fe}^{\text{III}}] + k_7[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})(\text{NBS})] + k_8[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{OH})(\text{NBS})]^{2-}} \quad (20)$$

Substituting $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})(\text{OH})]^{2-}$, $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})(\text{NBS})]^-$ and $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{OH})(\text{NBS})]^{2-}$ from Eqs (7, 10 and 11) gives,

$$\frac{d[\text{Cr}^{\text{VI}}]/dt = \{[\text{Fe}^{\text{III}}](k_3 + k_6 K_1/[\text{H}^+]) + [\text{NBS}](k_7 K_2 + k_8 K_1 K_3/[\text{H}^+])\} [\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2] \quad (21)$$

And which is identical to the experimental rate law, equation (6)

$$k_{\text{obs}} = \{[\text{Fe}^{\text{III}}](k_3 + k_6 K_1/[\text{H}^+]) + [\text{NBS}](k_7 K_2 + k_8 K_1 K_3/[\text{H}^+])\} \quad (22)$$

At constant $[\text{H}^+]$, Eq (23) follows, in which A is a constant includes $k_6 K_1/[\text{H}^+]$:-

$$k_{\text{obs}} = \{[\text{Fe}^{\text{III}}](k_3 + A) + [\text{NBS}](k_7 K_2 + k_8 K_1 K_3/[\text{H}^+])\} \quad (23)$$

From equation (3), (5) and (23),

$$k_1 = [\text{Fe}^{\text{III}}](k_3 + A), k_2 = k_7 K_2 + k_8 K_1 K_3/[\text{H}^+] \text{ and } k_c = (k_3 + A)$$

The reason for the term k_0 , being independent of the iron (II) concentration in Equation (6), is not obvious. It probably arises from a catalytic pathway involving a metal ion such as copper(II) and manganese (II), being present as an impurities in the reagents used or in water^[27,36].

From the above mechanism, the kinetic data may

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be interpreted in terms of a mechanism involving rapid pre-equilibrium formation of Cr^{III} precursor complex followed by a slow intramolecular electron transfer may proceed through an inner-sphere mechanism via coordination of NBS to Cr (III). From Eq (4) and figure 6, it can be shown that $k_7K_2 = 6.39 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $k_8K_3 = 1.08 \times 10^{-9} \text{ s}^{-1}$ (using the value of $K_1 = 1.99 \times 10^{-6} \text{ mol dm}^{-3}$) at the temperature used. Also, from eq.(5) and figure 8, value of k_c at 35°C is $9.12 \times 10^{-2} \text{ s}^{-1}$.

In comparison, rate of oxidation of $[\text{Cr}(\text{IDA})_2(\text{H}_2\text{O})_2]^-$, by NBS, is faster than $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$ as evidenced from values of the intramolecular electron transfer rate constant for both two complexes, $k_{e,t} = 2.16 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$ and $1.36 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$ for $[\text{Cr}(\text{IDA})_2(\text{H}_2\text{O})_2]^-$ and $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$, respectively. This behaviour is consistent with cyclic voltammetric results, $E = +0.048$ (mv) and $E = +0.110$ (mv), respectively. Which indicates that the secondary malonic ligand stabilizes the complex towards oxidation. This can be explained using crystal field theory. Values of pK_a for iminodiacetic and malonic acids are 2.59 and 4.18, respectively, i.e. malonic is a conjugate base more stronger, with more electrostatic field, than iminodiacetate ligand, i.e. with more electrostatic field. Thus, the crystal field stabilization energy, Δ_o , between t_{2g}^3 and e_g^0 orbitals of Cr (III) in the ternary complex is increased due to malonic secondary ligand. Therefore, loss of the three t_{2g}^3 electron from the central Cr^{III} ion, in $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$, becomes more difficult.

The intramolecular electron transfer step is endothermic as indicated by the positive enthalpy of activation value and hence, the contributions of ΔH^* and ΔS^* to the rate constant seem to compensate each other. This suggests that the factors controlling ΔH^* must be closely related to those controlling ΔS^* ; therefore the solvation state of the activated complex would be important in determining ΔH^* ^[37]. Unusually small ΔH^* values and large negative activation entropies reasonably could reflect a non-adiabatic contribution to the electron transfer process. Then both ΔH^* and ΔS^* then may be expected to systematically increase as the orientation of the oxidant in the precursor complex is altered so as to enhance overlap between donor and acceptor redox orbitals and consequently the probability of adiabatic electron transfer^[38].

Enthalpies and entropies of activation for the

oxidation of some complexes of chromium (III), $[\text{Cr}^{\text{III}}(\text{EDDA})(\text{H}_2\text{O})_2]^+$, $[\text{Cr}^{\text{III}}(\text{en})_3]^{3+}$, $[\text{Cr}^{\text{III}}(\text{L})_2(\text{H}_2\text{O})]^{3+}$ and $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$ where [en = ethylene diamine, L = 2-amino methyl pyridine, EDDA = ethylene diamine diacetate] with NBS are tabulated in TABLE 7. A plot of ΔH^* versus ΔS^* for these complexes is shown in Figure 9.

TABLE 7 : Values of ΔH^* and ΔS^* for the oxidation of ternary chromium (III) complexes by NBS.

Complex	ΔH^* kJ mol ⁻¹	$-\Delta S^*$ JK ⁻¹ mol ⁻¹	Reference
$[\text{Cr}^{\text{III}}(\text{EDDA})(\text{H}_2\text{O})_2]^+$	13.37±0.2	258.6±5	18
$[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})_2]^-$	25.08±0.1	200.83±6	This work
$[\text{Cr}^{\text{III}}(\text{L})_2(\text{H}_2\text{O})]^{3+}$	65.02±0.3	114.4±3	21
$[\text{Cr}^{\text{III}}(\text{en})_3]^{3+}$	83.0±0.1	48.0±2	41

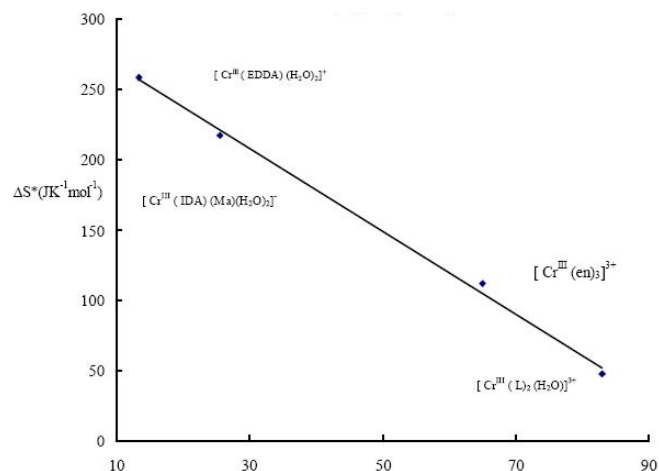


Figure 9 : Enthalpies and entropies of activation for the oxidation of some chromium (III) complexes by NBS

Similar linear plots were found for a large number of redox reactions^[38,39] and for each reaction series a common rate-determining step is proposed. An excellent linear relationship is seen. This isokinetic relationship lends support to a common mechanism for the oxidation of chromium(III) complexes; reported here, by NBS. This consists of NBS coordination to the chromium (III) complexes in a step preceding the rate-determining intramolecular electron transfer within the precursor complex. The electron transfer reactivities of these complexes with NBS are comparable, as the coordination of NBS with these complexes are identical. All of these suggest that the excellent correlation often observed between ΔH^* and ΔS^* mainly reflects the fact that both thermodynamic parameters are in reality two measures of the same thing, and that measuring a compensation temperature is just a rather indirect way of measuring the average temperature

at which the experiments were carried out.

Our suggestion that the NBS acts as an oxidant in a way such as to follow the radical reaction mechanism is in good agreement with the theoretical results^[40] which indicates that the N-Br BDE (Bond Dissociation Energy) of the Br radical formation is lower than that of the Br Or Br.

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