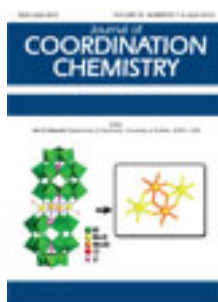


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Two-step one-electron transfer reaction of chromium(III) complex containing levodopa and uridine with *N*-bromosuccinimide

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$[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (LD = Levodopa; Urd = uridine) was prepared and characterized. The product of the oxidation reaction was examined using HPLC. Kinetics of the oxidation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with *N*-bromosuccinimide (NBS) in an aqueous solution was studied spectrophotometrically, with $1.0\text{--}5.0 \times 10^{-4} \text{ mol dm}^{-3}$ complex, $0.5\text{--}5.0 \times 10^{-2} \text{ mol dm}^{-3}$ NBS, $0.2\text{--}0.3 \text{ mol dm}^{-3}$ ionic strength (I), and $30\text{--}50^\circ\text{C}$. The reaction is first order with respect to $[\text{Cr}^{\text{III}}]$ and $[\text{NBS}]$, decreases as pH increases in the range 5.46–6.54 and increases with the addition of sodium dodecyl sulfate (SDS, $0.0\text{--}1.0 \times 10^{-3} \text{ mol dm}^{-3}$). Activation parameters including enthalpy, ΔH^* , and entropy, ΔS^* , were calculated. The experimental rate law is consistent with a mechanism in which the protonated species is more reactive than its conjugate base. It is assumed that the two-step one-electron transfer takes place *via* an inner-sphere mechanism. A mechanism for this reaction is proposed and supported by an excellent isokinetic relationship between ΔH^* and ΔS^* for some Cr^{III} complexes. Formation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ *in vivo* probably occurs with patients who administer the anti-Parkinson drug (Levodopa), since Cr^{III} is a natural food element. This work provides an opportunity to identify the nature of such interactions *in vivo* similar to that *in vitro*.

Keywords: Levodopa; Uridine; Chromium(III) complex; *N*-bromosuccinimide

1. Introduction

Chromium can exist in 11 valence states ranging from -4 to $+6$. Chromium in the trivalent (Cr^{III}) and hexavalent (Cr^{VI}) states have major environmental significance because of their stability in the natural environment [1]. Cr^{III} plays an important role in normal protein, fat, and carbohydrate metabolism as well as improving insulin sensitivity [2]. In contrast, Cr^{VI} is a highly toxic carcinogen due to its high water solubility and mobility as well as its easy reduction. Cr^{VI} compounds are easily taken up by cells and subsequently reduced to Cr^{IV} , Cr^{V} (intermediate oxidation states), and reactive oxygen species (ROS) which are believed to play a role in the adverse biological effect of Cr^{VI} compounds [3].

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Biological oxidation of chromium from the trivalent to hexavalent state is an important environmental process [2]. Oxidations of some binary [4–14] and ternary [5, 15–17] Cr^{III} complexes were studied, proceeding *via* an inner-sphere mechanism.

Levodopa is used in the treatment of Parkinson's disease, associated with the decrease of dopamine concentration in the brain. It must be medicated with drugs containing levodopa, as ad dopamine precursor, with the combination of decarboxylase enzyme such as carbidopa, which makes levodopa available for transport to the brain, and converted to dopamine in the basal ganglia [18–20].

Uridine, a nucleoside, is one of the four bases found in ribonucleic acid (RNA), which is involved in the synthesis of protein in the body. Uridine coordinating tendency is highly pH dependent [21], containing three potential metal ion binding sites, O(2), N(3), and O(4). Dissociation of a proton from N(3) occurs only at a high pH (≈ 9.0) leaving the other two as a viable alternate site for metal ion binding at biological pH. Among these two, O(4) is preferred as it possesses higher electron density than O(2) [22, 23].

N-bromosuccinimide is used as a halogenating agent and as an oxidant for a variety of substrates in both acidic and alkaline media [24–29].

Here, we prepare and characterize the ternary Cr^{III} complex of LD and Urd and study the kinetics and mechanism of its oxidation *in vitro* with NBS due to the probability for the formation of this ternary complex *in vivo* with patients who administer the anti-Parkinson drug (LD) since Cr^{III} is a natural food element. Finally, we study the effect of Urd as a secondary ligand on the stability of Cr^{III} toward oxidation.

2. Experimental

2.1. Instrumentation

A Jenway 6300 spectrophotometer equipped with temperature cell-holder connected to a thermostat-circulating water bath was used to measure the oxidation rates of [Cr^{III}(LD)(Urd)(H₂O)₄]²⁺ with [NBS].

A double beam JASCO UV-530 spectrophotometer equipped with a thermostated cell holder was used to measure the UV-Vis absorption spectra of the oxidation product of [Cr^{III}(LD)(Urd)(H₂O)₄]²⁺ by NBS.

Potentiometric measurements were performed on a Metrohm 702 SM titrino. The titroprocessor was equipped with a 728 dosimat (Switzerland-Hereaus). The titroprocessor and electrode were calibrated with standard buffer solution [30]. Calculations were performed using MINQUAD-75 loaded on an IBM-550 computer. The solution containing 5.0 mL of 0.01 mol dm⁻³ complex, 5.0 mL of 0.20 mol dm⁻³ NaNO₃, 5.0 mL of 0.04 mol dm⁻³ HNO₃, and 25.0 mL of deionized water was titrated with 0.1 mol dm⁻³ NaOH at 25°C.

Cyclic voltammetric measurements were performed on a potentiostat/Galvanostat (EG&G model 273A) with a single-compartment voltammetric cell equipped with a platinum working electrode (area = 0.5 cm²), a platinum wire counter electrode, and Ag/AgCl (3 mol dm⁻³ KCl) as reference electrode. M270 research electrochemistry software from EG&G Princeton Applied Research was used.

HPLC was performed with an Agilent (USA) series 1100 Quadra pump and Diode Array detector. C₁₈ 5 μm Eclipse XDB column (150 mm × 4.6 mm) was used. A Chertsey Surrey 7065 pH meter was used in pH measurements of the reaction mixture.

2.2. Chemicals and solutions

All chemicals used in this study were of analytical reagent grade (Analar, BDH, Sigma and Aldrich). Freshly prepared solutions of NBS were used. Buffer solutions were made from the known concentration of disodium mono hydrogen phosphate (Na₂HPO₄) and citric acid. The ionic strength of the buffered solutions was adjusted using NaNO₃. Doubly-distilled H₂O was used in all kinetic runs.

2.3. Preparation of [Cr^{III}(LD)(Urd)(H₂O)₄](NO₃)₂·3H₂O

A mixture of Cr(NO₃)₃·6H₂O (0.4004 g, 1.00 mmol) and LD (0.1972 g, 1.00 mmol) was dissolved in 75 mL distilled water followed by the addition of Urd (0.2442 g, 1.00 mmol); 20% excess of LD and Urd were added to ensure complete formation of the complex. Then, the total mixture was diluted to 100 mL. The resulting solution was warmed under an air reflux condenser at 60°C for 2 h; a brown color appeared after 10 min and deepened with time. After that, the reaction system was slowly cooled to room temperature and NaHCO₃ (1 × 10⁻³ mol dm⁻³) was added dropwise until the pH was adjusted to 8.60. A deep brown precipitate formed was separated from the concentrated solution by filtration. The precipitate was washed several times with distilled water and dried in air at ambient temperature. Elemental Anal. Calcd for Cr₁C₁₈H₃₆N₅O₂₃ (%): C, 29.09; H, 4.84; N, 9.42. Found (%): C, 28.64; H, 4.90; N, 9.4.

2.4. Kinetic studies

The reaction was studied under pseudo-first-order conditions keeping a large excess (10-fold) of NBS over complex in all runs. NaNO₃ solution was used to keep the ionic strength of the reaction constant. The pH of the reaction mixture was constant during the reaction runs. The reaction was initiated by mixing previously thermostated reactants, except NBS, with the required amount of separately thermostated NBS solution. The reaction was followed by monitoring the Cr^{VI} absorbance at 370 nm.

3. Results and discussion

3.1. Characterization of [Cr^{III}(LD)(Urd)(H₂O)₄](NO₃)₂·3H₂O

Confirmation of the complex formula was obtained from the IR spectrum, thermal gravimetric analysis (TGA), and UV-Vis absorption spectrum. In the IR spectrum, a broad band at 3619–2998 cm⁻¹ is due to νOH⁻ of the coordinated water and free OH⁻ in LD and Urd ligands. The νOH⁻ acid band in free LD completely disappears and a

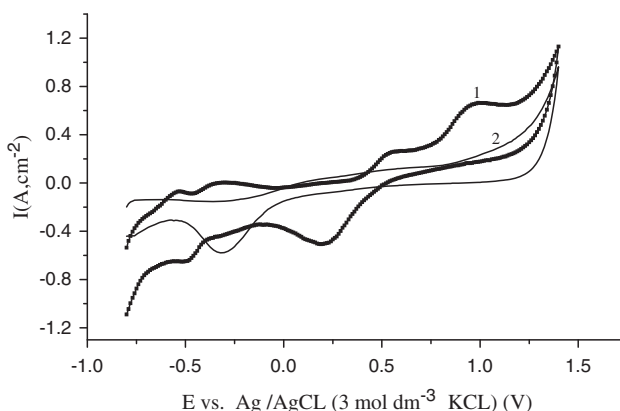


Figure 1. Cyclic voltammogram of $1 \times 10^{-3} \text{ mol dm}^{-3}$ for (1) $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ and (2) NaNO_3 as blank.

new carboxylate band (νCOO^-) appears at 1485 cm^{-1} , indicating that carboxylate of LD participates in coordination with Cr through deprotonation. The NH band located in Urd at 1678 cm^{-1} disappeared in the spectrum of the complex and a new band appeared at 1627 cm^{-1} . This may be attributed to the formation of an intramolecular hydrogen bond. The TGA curve of the complex shows two-stage decomposition. The first stage from 30°C to 62°C shows a weight loss (8.59%) corresponding to the loss of three crystal water molecules (Calcd 8.74%); the second stage from 62°C to 200°C (12.76% weight loss) corresponds to the loss of four coordinated water molecules (Calcd 11.66%). The UV-Vis absorption spectrum of $7.0 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ were recorded at $\text{pH} = 5.20$ and 25°C from 250 to 750 nm. The spectrum of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ exhibits absorptions at 575, 408, and 301 nm with $\epsilon_{\text{max}} = 78.8, 92.5, \text{ and } 106.7 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, respectively. The spectrum of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ gives a maximum absorption band at 311 nm with $\epsilon_{\text{max}} = 122.42 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The difference in the position of the absorption bands in the Cr^{III} ion and its ternary complex can be attributed to the difference in crystal field stabilization energy (Δ_0).

Another confirmation for the formation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ was done by cyclic voltammetry. The cyclic voltammogram of $1 \times 10^{-3} \text{ mol dm}^{-3}$ of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ was obtained using 0.1 mol dm^{-3} NaNO_3 as supporting electrolyte at $\text{pH} = 5.2$ and 25°C from -1.0 V to $+1.5 \text{ V}$ with a scan rate of 0.01 V sec^{-1} . A well-defined redox wave with oxidation potentials at $-0.536, -0.332, +0.542,$ and $+0.980 \text{ V}$ was obtained, indicating oxidation through four steps (figure 1). The cyclic voltammogram of $1 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under the same conditions shows one anodic peak at -0.784 V corresponding to an oxidation process. The difference in the oxidation potential identifies the formation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$. (Note: a blank of $1 \times 10^{-3} \text{ mol dm}^{-3}$ NaNO_3 gives only one cathodic peak at -0.315 V .)

The stability constant of the ternary complex, $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$, was determined potentiometrically by the method of Irving and Rossotti [31]. The titration curve was determined by plotting pH versus volume of the added alkali (figure 2). The stability constant is $\log K = 9.55$.

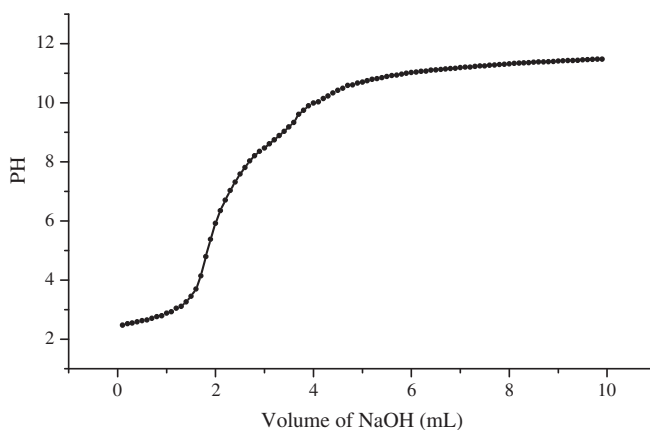


Figure 2. Potentiometric titration curve of $1 \times 10^{-3} \text{ mol dm}^{-3}$ for $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$.

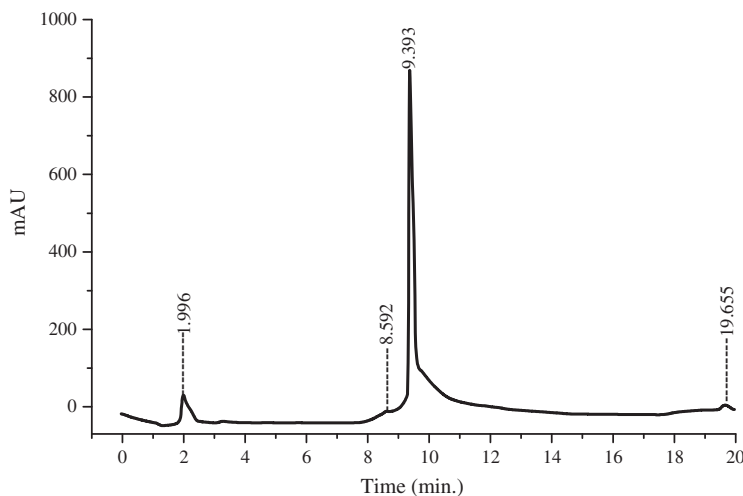


Figure 3. HPLC for the oxidation product of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with NBS using acetonitrile.

3.2. Examination of the oxidation products

Using HPLC in the reversed-phase partition mode, the product of the oxidation of $1 \times 10^{-4} \text{ mol dm}^{-3}$ of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ NBS at $\text{pH} = 5.87$ was analyzed. The mobile phase of acetonitrile and phosphate buffer ($\text{pH} 3.8$, using $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4/0.01 \text{ mol dm}^{-3}$ citric acid) was used [32]. The flow rate was 1 mL min^{-1} and the product was detected at 254 nm on the Diode-Array detector. HPLC results revealed the presence of two peaks of low intensity at retention times 8.592 and 1.996 min (figure 3). The qualitative HPLC profiles of $1 \times 10^{-4} \text{ mol dm}^{-3}$ each of LD and Urd standards were detected under the same conditions. The retention times were recorded at 8.50 and 2.109 min, respectively, indicating the existence of LD and Urd as oxidation products.

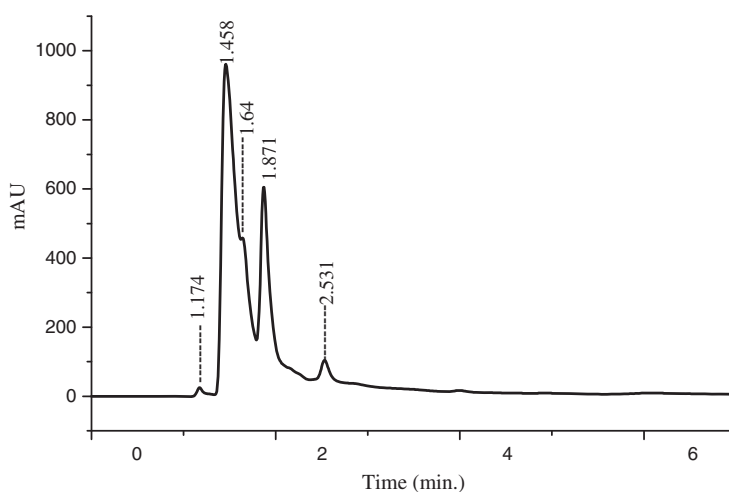


Figure 4. HPLC for the oxidation product of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with NBS using orthophosphoric buffer.

Utilizing a mobile-phase of methanol and $1 \times 10^{-5} \text{ mol dm}^{-3}$ orthophosphoric buffer solution (by ratio 5:95, V/V) [33], the HPLC chromatogram of $25 \mu\text{L}$ injection of oxidation product of $1 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ NBS at $\text{pH} = 5.87$ was obtained. The products were detected at 210 nm on the diode-array detector. A sharp broad peak with high intensity appeared at a retention time 1.458 min (figure 4) in good agreement with the sharp peak that appeared in the chromatogram of $25 \mu\text{L}$ injection of a succinimide standard at a retention time of 1.436 min. Thus, succinimide is one of the oxidation products.

The oxidation product of $1 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ of NBS at $\text{pH} = 5.87$, $I = 0.20 \text{ mol dm}^{-3}$, and 40°C was followed spectrophotometrically with time (figure 5). During oxidation, the deep brown solution of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ in water changed gradually to yellow and the original absorption maximum of the complex (at 311 nm) was replaced by another peak at 370 nm due to the formation of Cr^{VI} , which increased with time. Thus Cr^{VI} is the oxidation product.

The presence of Br^- as one of the oxidation products was demonstrated through the addition of AgNO_3 to the reaction mixture. A pale yellowish precipitate appeared and increased gradually with time due to the formation of AgBr , which indicates that Br^- is one of the oxidation products.

3.3. Kinetics of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}/\text{NBS}$ reaction in aqueous solution

Oxidation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ with NBS was studied under the conditions of $\text{pH} 5.46\text{--}6.54$, $I = 0.2\text{--}0.3 \text{ mol dm}^{-3}$ and $30\text{--}50^\circ\text{C}$ over a range of NBS and complex concentrations of $(0.5\text{--}5.0) \times 10^{-2}$ and $(1.0\text{--}5.0) \times 10^{-4} \text{ mol dm}^{-3}$, respectively. Plots of $\ln(A_\infty - A_t)$ versus time were linear for more than 85% from the beginning of the reaction, where A_t and A_∞ are absorbance at time t and time infinity, respectively.

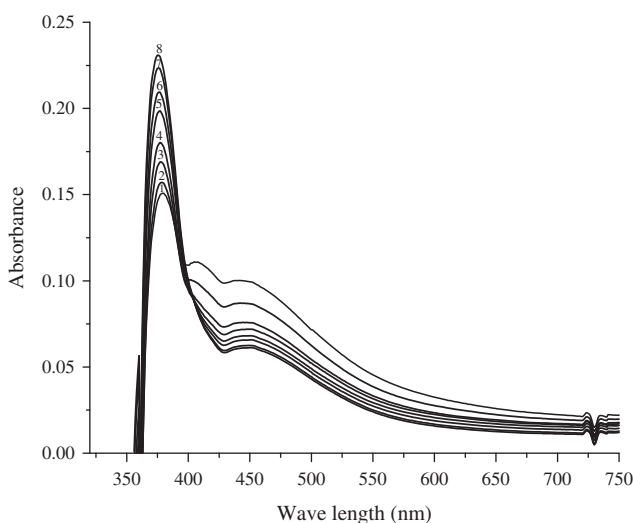


Figure 5. Change in absorbance as a function of time. Curves 1–8 were recorded at 1, 5, 10, 15, 20, 25, 30, and 35 min, respectively, from the time of initiation; $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NBS}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH} = 5.87$, $I = 0.20 \text{ mol dm}^{-3}$ and $T = 40^\circ\text{C}$.

Table 1. Dependence of k_{obs} on $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ ^a, $[\text{NBS}]$, and temperature at $\text{pH} = 5.87$, $I = 0.2 \text{ mol dm}^{-3}$.

$10^2 [\text{NBS}] (\text{mol dm}^{-3})$	$10^3 k_{\text{obs}} \text{ min}^{-1} \pm \text{SD}$				
	$T = 30^\circ\text{C}$	$T = 35^\circ\text{C}$	$T = 40^\circ\text{C}$	$T = 45^\circ\text{C}$	$T = 50^\circ\text{C}$
0.5	1.88 ± 0.01	1.94 ± 0.01	2.84 ± 0.01	5.04 ± 0.04	6.57 ± 0.02
1.5	5.23 ± 0.03	7.44 ± 0.02	10.50 ± 0.03	14.93 ± 0.01	20.75 ± 0.08
2.0	6.37 ± 0.04	9.23 ± 0.05	14.67 ± 0.05	20.68 ± 0.01	28.82 ± 0.01
2.5	8.52 ± 0.01	11.65 ± 0.02	17.13 ± 0.02	25.05 ± 0.01	35.63 ± 0.05
3.0	10.0 ± 0.06	13.77 ± 0.01	20.43 ± 0.06	31.51 ± 0.09	42.78 ± 0.01
3.5	11.92 ± 0.02	15.64 ± 0.03	23.76 ± 0.09	35.88 ± 0.08	49.35 ± 0.03
4.0	14.12 ± 0.01	18.74 ± 0.06	27.26 ± 0.02	39.89 ± 0.05	53.98 ± 0.09
5.0	16.93 ± 0.02	22.68 ± 0.04	34.47 ± 0.07	51.00 ± 0.01	70.56 ± 0.01

^a $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$; $10^3 k_{\text{obs}} = 17.01 \pm 0.01$, 17.45 ± 0.01 , 17.09 ± 0.08 , 17.48 ± 0.09 at 10^{-4} $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} = 2.0, 3.0, 4.0, 5.0 \text{ mol dm}^{-3}$, respectively, at $[\text{NBS}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, and $T = 40^\circ\text{C}$.

Pseudo-first-order rate constants (k_{obs}) were obtained from slopes of these plots. The error limits for the results were calculated using Microcal Origin program (version 5.0).

The effect of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ on reaction rate was studied from $(1.0\text{--}5.0) \times 10^{-4} \text{ mol dm}^{-3}$ at $[\text{NBS}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH} = 5.87$, $I = 0.20 \text{ mol dm}^{-3}$ and 40°C (table 1). The results in table 1 show that k_{obs} was unaffected when the complex concentration was varied, indicating that the reaction is first order with respect to $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$, thus

$$\text{Rate} = k_{\text{obs}}[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} \quad (1)$$

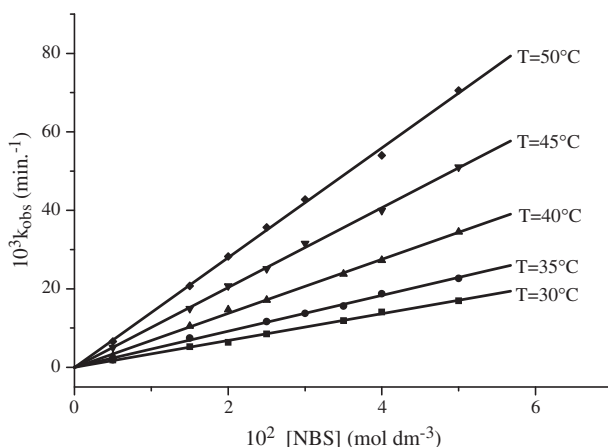


Figure 6. Variation of k_{obs} with NBS at $\text{pH} = 5.87$ and different temperatures.

At $\text{pH} = 5.87$ and $I = 0.20 \text{ mol dm}^{-3}$, the dependence of k_{obs} on NBS was examined over $[\text{NBS}]$ range of $0.5\text{--}5.0 \times 10^{-2} \text{ mol dm}^{-3}$ and a temperature range $30\text{--}50^\circ\text{C}$. Plots of k_{obs} versus $[\text{NBS}]$ at different temperatures were found to be linear without an intercept (figure 6). This behavior can be expressed by the following equation:

$$k_{\text{obs}} = k_1[\text{NBS}] \quad (2)$$

The dependence of the reaction rate on pH was investigated at different pH values from 5.46 to 6.54 at $30\text{--}50^\circ\text{C}$. Variation of k_1 with pH at different temperatures is listed in table 2. The reaction rate decreased gradually with increasing pH values. Plots of k_1 versus $[\text{H}^+]$ were linear with intercepts (figure 7). This can be expressed by the following equation:

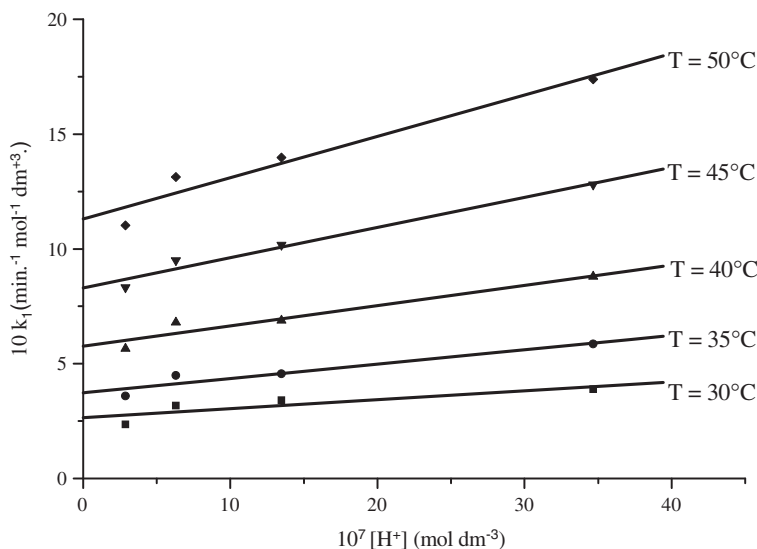
$$k_1 = k_3 + k_2[\text{H}^+] \quad (3)$$

Values of k_2 at different temperatures were calculated (table 3). Using a least-squares fit to the transition state theory equation, activation parameters including enthalpy, ΔH^* , and entropy, ΔS^* , associated with k_2 at different pH are composite values. These values were calculated from the plots of $\ln k_2/T$ against $1/T$ (figure 8). The calculated ΔH_2^* and ΔS_2^* are $59.5 \pm 0.04 \text{ kJ mol}^{-1}$ and $26.57 \pm 0.03 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

An effect of the anionic surfactant (SDS) on the kinetics of the reaction was studied. SDS was added to the reaction mixture at $\text{pH} = 5.87$ with varied concentration, $(0.0\text{--}1.0) \times 10^{-3} \text{ mol dm}^{-3}$, while the concentration of other reacting species was kept constant, $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, 40°C , and $[\text{NBS}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$. The obtained values of k_{obs} showed a continuous increase with the concentration of SDS used (table 4). However, k_{obs} was unaffected by ionic strength, which implied that the rate-determining reaction occurs between charged and uncharged species. Thus, values of $10^3 k_{\text{obs}}$ of 17.68 ± 0.06 , 17.89 ± 0.05 , 17.15 ± 0.06 , 17.35 ± 0.05 , and $17.60 \pm 0.06 \text{ min}^{-1}$ were obtained at $I = 0.22$, 0.24 , 0.26 , 0.28 , and 0.30 mol dm^{-3} , $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{pH} = 5.87$,

Table 2. Variation of k_1 with pH of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ at different temperatures.

pH	$10^7[\text{H}^+] \text{ mol dm}^{-3}$	$10 k_1 (\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}) \pm \text{SD}$				
		$T = 30^\circ\text{C}$	$T = 35^\circ\text{C}$	$T = 40^\circ\text{C}$	$T = 45^\circ\text{C}$	$T = 50^\circ\text{C}$
5.46	34.67	3.89 ± 0.01	5.86 ± 0.68	8.79 ± 0.49	12.79 ± 0.69	17.39 ± 1.59
5.87	13.48	3.41 ± 0.31	4.56 ± 0.41	6.88 ± 0.52	10.16 ± 0.63	13.98 ± 1.06
6.20	6.30	3.18 ± 0.30	4.49 ± 0.55	6.79 ± 0.89	9.49 ± 0.90	13.13 ± 1.00
6.54	2.88	2.36 ± 0.19	3.59 ± 0.78	5.65 ± 0.86	8.31 ± 1.03	11.03 ± 1.22

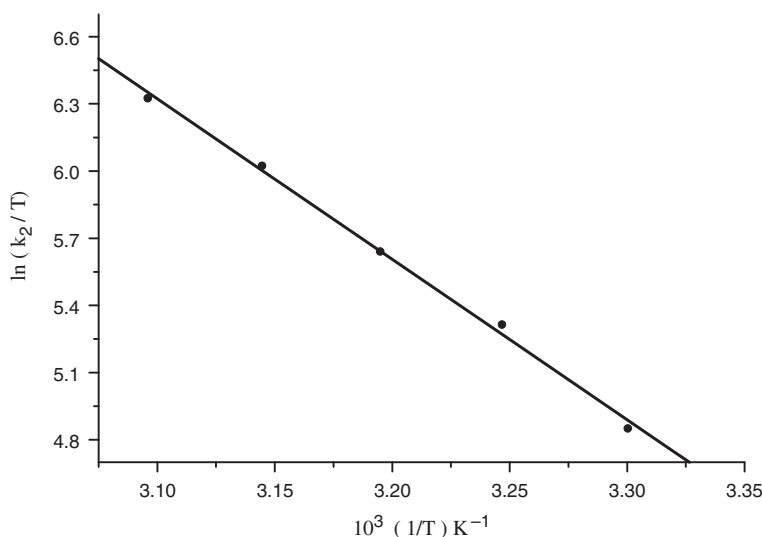
Figure 7. Variation of k_1 with $[\text{H}^+]$ at different temperatures.Table 3. Variation of k_2 with temperature.

$T (^\circ\text{C})$	$k_2 \times 10^4 (\text{mol}^{-2} \text{ dm}^6 \text{ min}^{-1}) \pm \text{SD}$
30	3.88 ± 0.39
35	6.26 ± 0.34
40	8.81 ± 0.42
45	13.12 ± 0.37
50	18.02 ± 0.77

$[\text{NBS}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ and 40°C . From equations (1)–(3), the experimental rate law can be represented by

$$\text{Rate} = \{k_3 + k_2[\text{H}^+]\}[\text{NBS}][\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{+2} \quad (4)$$

$$\text{where } k_{\text{obs}} = \{k_3 + k_2[\text{H}^+]\}[\text{NBS}] \quad (5)$$

Figure 8. Variation of $\ln(k_2/T)$ against $(1/T)$.Table 4. Variation of k_{obs} with [SDS] at pH=5.87, $[\text{NBS}] = 2.50 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, and $T = 40^\circ\text{C}$.

$10^3 [\text{SDS}] (\text{mol dm}^{-3})$	$10^3 k_{\text{obs}} \text{ min}^{-1} \pm \text{SD}$
0.00	17.13 ± 0.02
0.20	18.73 ± 0.13
0.40	21.34 ± 0.01
0.60	23.37 ± 0.04
0.80	25.42 ± 0.06
1.00	26.88 ± 0.88

4. Discussion

The ternary Cr^{III} complex can be formulated as $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, where LD is monodentate through carboxylate and Urd binds through O(4). An intramolecular hydrogen bond may be formed as a result of attraction between H of N(3) of Urd and oxygen of LD linked with Cr^{III} (figure 9). Then, H of N(3) of Urd is a link of a six-membered planar ring that may be playing a role in increasing the stability of the formed ternary complex. The value of the stability constant of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ supports this assignment ($K_{\text{st}} = 3.55 \times 10^9$).

The dependence on $[\text{H}^+]$ in the experimental rate law suggests involvement of a protonated form of the Cr^{III} complex in the rate-determining step and the following equilibrium can be suggested:



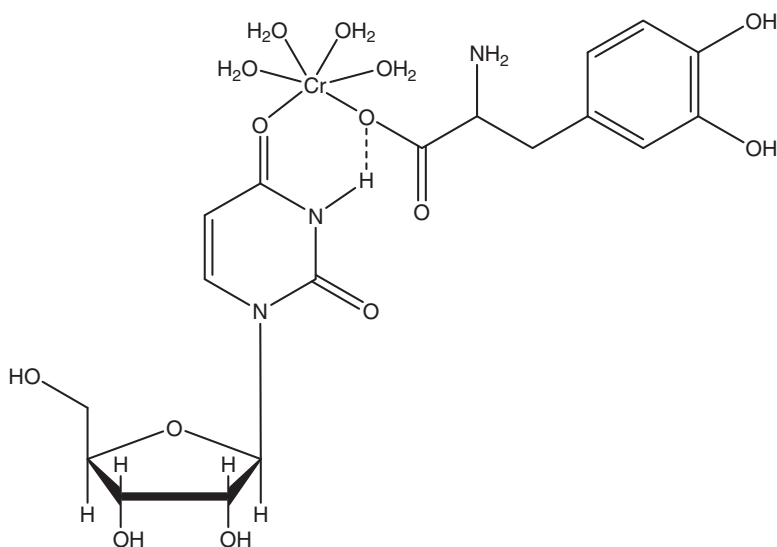
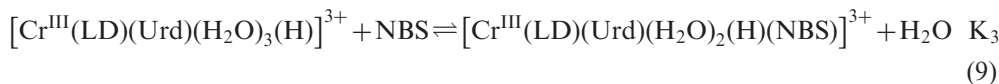
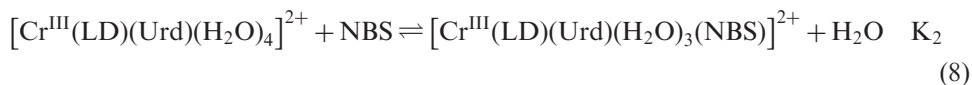
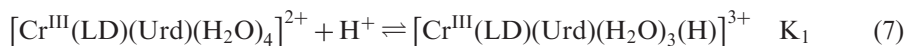


Figure 9. Suggested structure for $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$.

The protonated form may be the reactive species and the unprotonated complex is the predominant one and will be involved in the rate-determining step.

In the pH range 5.46–6.54 *N*-bromosuccinimide exists as NBS, whereas in highly acidic solutions, NBS exists as HNBS^+ [34, 35]. The oxidation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ by NBS probably involves an inner-sphere mechanism through the displacement of coordinated water in $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_3(\text{H})]^{2+}$ by NBS [36]. Water was not expected to serve as a bridging ligand due to its extremely low basicity [37]. Coordination of NBS is possible through the carbonyl group [38].

Thus, the oxidation of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ by NBS may proceed by two-step, one-electron transfer first-order reaction with the following mechanism:





where R^\bullet is the succinimidyl radical. It is unstable with respect to NBS or succinimide anion (R^-) since it does not have a resonance effect, so two succinimidyl radicals may dimerize to form bisuccinimidyl [39, 40]. R^- is the succinimide anion which prefers to abstract H^+ to form succinimide (RH), a known product of organic NBS oxidations. The oxidation may proceed *via* one or two-electron transfer process, giving Cr^{IV} or Cr^{V} in the rate-determining step. This may be followed by fast steps leading to Cr^{VI} . The cyclic voltammogram of $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$ exhibits four sequential oxidation peaks that promote one-electron transfer processes, where each oxidation peak corresponds to one step (figure 1). Furthermore, that acrylonitrile is polymerized supports the formation of the succinimidyl radical.

The suggested mechanism shows high compatibility with the data obtained from the examination of the oxidation products using HPLC, which supported the existence of LD, Urd, and succinimide as products. Furthermore, our suggestion that NBS is an oxidant by a free radical path involving homolytic dissociation of NBS with the reducing metal ions (Cr^{III}) yielding R^\bullet and Br^\bullet as intermediates is in good agreement with the theoretical results which calculated the bond dissociation energies (BDEs), involving the formation of Br^\bullet , Br^+ , and Br^- of the N–Br bond. The N–Br BDE for Br^\bullet formation is lower than that of Br^+ or Br^- [41].

When SDS was added to the reaction mixture, it dispersed as monomers until its concentration reached the critical micelle concentration. Micelles consist of hydrophobic groups (their tails) and hydrophilic groups (their heads). Hydrophobic tails of SDS remain inside the micelle due to unfavorable interactions. The polar sulfate heads of SDS, due to favorable interactions with water, form a hydrophilic outer layer that protects the hydrophobic core of the micelle. According to the Stern modification of the diffuse double layer, all the molecules migrate from the bulk solution to the micelles. The observed rate acceleration is due to preferential partitioning of the positively charged Cr^{III} complex by electrostatic attraction and the neutral substrate, NBS, in the micellar surface (i.e., Stern layer) through ion–dipole interaction [42, 43]. Thus, SDS allows the reaction to proceed in both aqueous and micellar inter-phase. So, the observed rate acceleration is due to the favored reaction in the micellar phase where both the Cr^{III} complex and NBS are preferentially accumulated.

From the above mechanism, the rate of the reaction can be described by equation (15):

$$\begin{aligned} d[\text{Cr}^{\text{VI}}]/dt = & k_4[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_3(\text{NBS})]^{2+} \\ & + k_5[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_2(\text{H})(\text{NBS})]^{3+} \end{aligned} \quad (15)$$

since

$$[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_3(\text{H})]^{3+} = K_1[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}[\text{H}^+] \quad (16)$$

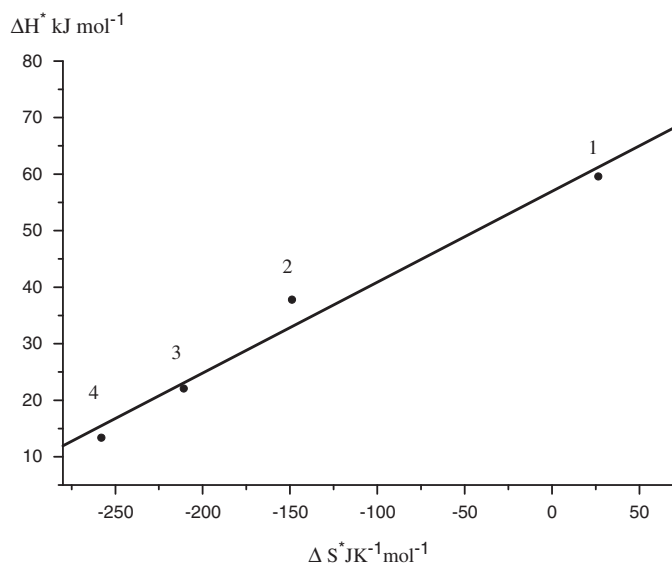
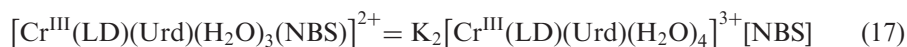


Figure 10. Enthalpies and entropies of activation for the oxidation of (1) $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}$, (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, (3) $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})^-]$, and (4) $[\text{Cr}^{\text{III}}(\text{EDDA})(\text{H}_2\text{O})^+]$.

and



From equations (15)–(18), one gets

$$\begin{aligned} d[\text{Cr}^{\text{VI}}]/dt &= k_4K_2[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}[\text{NBS}] \\ &+ k_5K_3K_1[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+}[\text{H}^+][\text{NBS}] \end{aligned} \quad (19)$$

Then

$$d[\text{Cr}^{\text{VI}}]/dt = \{k_4K_2 + k_5K_1K_3[\text{H}^+]\}[\text{NBS}][\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{2+} \quad (20)$$

$$\text{where } k_{\text{obs.}} = \{k_4K_2 + k_5K_1K_3[\text{H}^+]\} \quad (21)$$

This is identical to the experimental rate law equation (4). From equations (5) and (21):

$$k_3 = k_4K_2, \quad k_2 = k_5K_1K_3 \quad (22)$$

The small positive value of ΔS_2^* can be attributed to the moderate restriction of solvent molecules around the relatively large size of the activated complex in the transition state. As solvent water molecules are more restricted around reactants due to its relatively small size, the net ΔS^* will be positive. ΔH_2^* associated with k_2 is a

composite value involving the enthalpy of the formation of the precursor complex, $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_2(\text{H})(\text{NBS})]^{3+}$, and the enthalpy of activation of the intramolecular electron transfer step. The obtained positive value of ΔH_2^* means that the intermolecular electron-transfer step is endothermic.

Oxidation reactions of the following Cr^{III} -complexes: $[\text{Cr}(\text{H}_2\text{O})_6^{+3}]$ [44], $[\text{Cr}^{\text{III}}(\text{EDDA})(\text{H}_2\text{O})^+]$ [8], $[\text{Cr}^{\text{III}}(\text{IDA})(\text{Ma})(\text{H}_2\text{O})^-]$ [17], and $[\text{Cr}^{\text{III}}(\text{LD})(\text{Urd})(\text{H}_2\text{O})_4]^{+2}$ (where EDDA = ethylenediaminediacetate, IDA = iminodiacetate, Ma = malonic) with NBS appear in a linear dependence of ΔH^* on ΔS^* values for these reactions (figure 10). This iso-kinetic relationship is due to the parallel changes in ΔH^* and ΔS^* values of these reactions and a common mechanism for such closely related reactions can be proposed in which NBS coordinates to the Cr^{III} complexes in a step preceding the rate-determining intramolecular electron transfer within the precursor complex. Similar linear plots were found for a large number of redox reactions, and a common rate-determining step for each reaction series was proposed [7, 17, 44, 45].

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