Two step one-electron transfer reaction of chromium(III) complex containing carbidopa and inosine with N-bromosuccinimide

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Oxidation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4]^{2+}\) (where CD = carbidopa, Ino = inosine) with N-bromosuccinimide (NBS) was studied kinetically in aqueous media over varying ranges of concentrations of complex \((1.0-5.0) \times 10^{-4}\) mol dm\(^{-3}\) and NBS \((0.5-5.0) \times 10^{-2}\) mol dm\(^{-3}\), pH, ionic strength and temperature. The reaction is first order with respect to \([\text{Cr}^{III}]\) and \([\text{NBS}]\). The rate of reaction increases with increasing \(pH\) over the studied range (6.76-7.84). The anionic surfactant, sodium dodecyl sulphate is found to increase the rate of the oxidation in the range \((0.0-1.0) \times 10^{-3}\) mol dm\(^{-3}\). Thermodynamic activation parameters have also been calculated. The rate of oxidation obeys the equation \(d[\text{Cr}^{VI}]/dt = \{k_1 + k_2(1/[\text{H}^+])\}[\text{NBS}][[\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4]^{2+}\]. The experimental rate law is consistent with the proposed mechanism in which the protonated and deprotonated species are involved in the rate determining step. It is proposed that a two step one-electron transfer takes place via an inner sphere mechanism.

Keywords: Kinetics, Reaction mechanisms, Carbidopa, Inosine, Chromium, Electron transfer

Chromium is probably one of the most controversial transition metal ions in terms of its nutritional value and toxicity\(^1\). \(\text{Cr}^{III}\) has generally been considered as one of the least toxic transition metals due to its poor bioavailability\(^2\). Most nutritionists regard \(\text{Cr}^{III}\) as an essential micronutrient, acting as an insulin activator\(^3,4\). On the other hand, the genotoxicity and carcinogenicity of \(\text{Cr}^{VI}\) are well known, which is due to its ability to enter the cells through the anion channel, leading to rapid intracellular accumulation\(^5\).

In presence of cellular reductants such as ascorbate and glutathione, the accumulated \(\text{Cr}^{VI}\) is converted to \(\text{Cr}^{III}\). During the reduction of \(\text{Cr}^{VI}\) to \(\text{Cr}^{III}\), intermediates such as \(\text{Cr}^{V}\) and \(\text{Cr}^{IV}\) are formed due to reduction either by sequential single-electron transfers, progressively reducing \(\text{Cr}^{VI}\) to \(\text{Cr}^{V}\) and then \(\text{Cr}^{III}\), or by a two-electron transfer to \(\text{Cr}^{IV}\), then by single-electron transfers to \(\text{Cr}^{III}\) (Refs 6 & 7). It is believed that the interaction between the generated \(\text{Cr}^{IV}\) and \(\text{Cr}^{V}\) with DNA is responsible for carcinogenesis. For instance, \(\text{Cr}^{IV}\) and \(\text{Cr}^{V}\) generated by ascorbate reduction have been shown to react with hydrogen peroxide to produce hydroxyl radicals (OH\(^{-}\)), which causes breaking of the DNA strand\(^8\).

N-Bromosuccinimide (NBS) is a well known N-halogen compound, and has been used as a brominating agent as well as oxidant for some transition metal complexes\(^9-21\) and a wide variety of organic compounds\(^22\). Oxidations of some binary\(^9-17\) and ternary\(^17-21\) \(\text{Cr}^{III}\) complexes by NBS have been studied. A mechanism in which coordinated water is replaced prior to electron transfer by NBS has been suggested for these reactions with the oxidation proceeding through hemolytic fission of NBS followed by reaction of one or both fragments (succinimidyl and bromine free radicals) with the metal species.

We report herein preparation and characterization of the mixed ligand \(\text{Cr}^{III}\) complex with carbidopa (CD) and inosine (Ino), \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4](\text{NO}_3)_2\cdot\text{H}_2\text{O}\). The kinetics and mechanism of its oxidation with NBS due to formation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4]^{2+}\) has been proposed. Finally, the effect of CD on stability of the binary complex\(^17\) \([\text{Cr}^{III}(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) towards oxidation has also been studied.
Materials and Methods

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

A Jenway 6300 spectrophotometer, equipped with a temperature cell holder and connected to a thermo-circulating water bath, was used to measure the oxidation rates by monitoring the absorbance of Cr²⁺.

The UV-visible absorption spectra of the oxidation product of [Cr(III)(CD)(Ino)(H₂O)₃]²⁺ by NBS was followed spectrophotometrically for a definite period of time using the double beam Jasco UV-530 spectrophotometer. pH of the reaction mixture was measured using a Chertsey Surrey, 7065 pH-meter.

Potentiometric measurements were performed with a Metrohm 702 SM Titriino potentiometer. The titroprocessor was equipped with a 728 dosimat (Switzerland-Heriau). The titroprocessor and electrode were calibrated with standard buffer solutions. Calculations were performed using the computer program MINIQUAD-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 deionized water, was titrated with 0.1 mol dm⁻³ NaOH at 25 °C.

Cyclic voltammetry measurements were operated 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 was used as the counter electrode and Ag/AgCL (3 mol dm⁻³ KCL) as the reference electrode. M 270 research electrochemistry software from EG & G Princeton Applied Research was used for the calculations.

HPLC chromatography was performed using Agilent (USA) series 1100 Qudra pump and diode array detector. The compounds were separated on C₁₈ (5 μm) Eclipse XDB column (150 mm × 4.6 mm).

Preparation of [Cr(III)(CD)(Ino)(H₂O)₃]²⁺(NO₃)₂·H₂O

A mixture of Cr(NO₃)₃·6H₂O (0.4004 g, 1.0 mmol) and CD (0.2261 g, 1.0 mmol) was dissolved in 75 mL distilled water followed by addition of Ino (0.2682 g, 1.0 mmol). Then, 20 % excess of CD and Ino were added to ensure completely formation of the complex, keeping the total volume as 100 mL. The resulting solution was heated under an air reflux condenser at 60 °C when a pale brown color appeared after 15 min, which increased gradually within the time. After 3 hours, the reaction system was slowly cooled to room temperature and NaHCO₃ (1 × 10⁻³ mol dm⁻³) was added drop by drop until the pH value of the system was adjusted to about 8.70. A pale brown precipitate separated from the concentrated solution by filtration. The filtrate was washed several times with distilled water and dried in air at ambient temperature. Anal. (%) for Cr₇C₂₀H₁₈N₈O₁₈: Calcd: C, 37.76; H, 5.50; N, 17.62. Found: C, 37.25; H, 4.95; N, 18.10.

Kinetic studies

The reaction was studied under pseudo-first order conditions, with a large excess (10-fold) of NBS over complex in all runs. NaN₃ solution was used to keep the ionic strength of reaction constant. The pH of the reaction mixture was found to be constant during the reaction runs. The reaction was initiated by mixing the previously thermostated solutions of the reactants (except NBS) with the required amount of separately thermostated NBS solution.

Results and Discussion

Characterization of [Cr(III)(CD)(Ino)(H₂O)₃]²⁺(NO₃)₂·H₂O

IR, TGA and cyclic voltammetric data were used to confirm formation of [Cr(III)(CD)(Ino)(H₂O)₃]²⁺(NO₃)₂·H₂O. The IR spectrum shows symmetrical and asymmetrical bands (νCOO-Cr) at 1383 and 1486 cm⁻¹, respectively. The νOH acid band in the free CD ligand disappeared, indicating the participation of the carboxylic group of the CD ligand in the coordination with the Cr³⁺ ion through deprotonation. A broad band appeared in the 3650–2998 cm⁻¹ region of the spectrum, which may be attributed to νOH⁻ of the free OH⁻ of the CD, Ino ligands and OH⁻ of the coordinated waters. The band due to NH- group of Ino was washed several times with distilled water and dried in air at ambient temperature. Anal. (%) for Cr₇C₂₀H₁₈N₈O₁₈: Calcd: C, 37.25; H, 4.95; N, 18.10.

IR and TGA data of the complex agree with the formula [Cr(III)(CD)(Ino)(H₂O)₃]²⁺(NO₃)₂·H₂O.
Further investigation on the formation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) was carried out by UV-visible spectral analysis of \(5.0 \times 10^{-3}\) mol dm\(^{-3}\) \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) and \([\text{Cr}(\text{NO}_3)_3]^{3-}\) recorded at pH 5.2 and temperature 25 °C over 250 – 750 nm. The spectrum of \([\text{Cr}(\text{NO}_3)_3]^{3-}\) exhibited maximum absorption bands (\(\lambda_{\text{max}}\)) at 575, 408, 301 nm with molar absorptivity (\(e_{\text{max}}\)) = 109, 129.8, 149 mol\(^{-1}\) dm\(^{3}\) cm\(^{-1}\), respectively. On the other hand, the spectrum of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) exhibited \(\lambda_{\text{max}}\) at 347 nm with \(e_{\text{max}}\) = 296 mol\(^{-1}\) dm\(^{3}\) cm\(^{-1}\). The difference in the position of the absorption bands in the Cr\(^{III}\) metal ion and its ternary complex may be attributed to the difference in the quantity of absorbed energy, the crystal field stabilization energy (\(\Delta_0\)), required to excite electrons from the \(t_2g\) to the \(e_g\) orbitals of Cr\(^{III}\) metal ion in each species.

The electrochemical behavior of the two compounds was used to identify the formation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\). The cyclic voltammogram of \((1 \times 10^{-3}\) mol dm\(^{-3}\) \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) was obtained at 25 °C and pH = 4.2 over a potential range from –1.0 V to +1.5 V with scanning rate 0.025 V s\(^{-1}\) and 10 mol dm\(^{-3}\) of NaNO\(_3\) as supporting electrolyte. A well defined redox wave was obtained with anodic peaks at -0.640 V, -0.41 V, +0.64 V and +1.003 V, indicating an oxidation reaction through four sequential steps and one cathodic peak at –0.486 V as a result of the reduction reaction. The cyclic voltammogram of \((1 \times 10^{-3}\) mol dm\(^{-3}\) \(\text{Cr(NO}_3)_3\)), under the same conditions, exhibited an anodic peak at –0.784 V due to one oxidation step and a cathodic peak at potential -0.669 V as a result of one reduction step. (Note: A NaNO\(_3\) blank gives only a cathodic peak at potential –0.315 V). The difference in potential values of oxidation and reduction between \(\text{Cr(NO}_3)_3\) and \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) confirm the formation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\).

The stability constant of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) was estimated at \(T = 25^\circ\) C by potentiometric-pH measurements using Irving and Rossotti method of calculation\(^{24}\). The titration curves for CD, Ino and their Cr\(^{III}\)-complexes were obtained by plotting pH versus added volume of alkali. The \(pK\) value is 8.44.

Oxidation products

The oxidation product of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) with NBS was analyzed by HPLC, reversed-phase partition mode using three different mobile phase systems. In the first, the oxidation product was detected at 254 nm on the diode array detector. C\(_{18}\) column was used for the separation at a flow rate of 1.0 mL/min. The mobile phase consisted of trifluoroacetic acid (0.1 % v/v in deionized water, pH 2.2) and methanol gradient. The obtained profile showed a peak at retention time 4.10 min, which is identical with the retention time 4.18 min shown in the profile of Ino standard, under the same conditions. In the second system, sulfuric acid/acetone/nitrite was used as a mobile phase\(^{25}\). The product of oxidation was detected at 254 nm with flow rate 1.0 mL/min. A peak was obtained at 5.152 min, similar to the retention time shown in the chromatogram of C\(_{18}\) standard (5.163 min) under the same conditions. In the third, the chromatograms of the product of oxidation and succinimide standard were detected with methanol /orthophosphoric buffer solution (5.95 v/v) as the mobile phase on UV-visible detector\(^{26}\). A sharp broad peak appeared at 1.462 min. in the profile of the oxidation product and at 1.436 min. in chromatogram of succinimide standard. Thus, HPLC analysis indicates that CD, Ino and succinimide are the products in the oxidation process.

The oxidation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4]^{2+}\) with NBS was also followed by recording the UV-visible absorption spectra of the oxidation product between 350 and 750 nm as a function of time. A single peak appeared at 374 nm and increased with time due to the formation of Cr\(^{VI}\). The peak of Cr\(^{VI}\) is different from that of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_3]^{2+}\) complex, at 347 nm. This indicates that Cr\(^{VI}\) is the main product in the oxidation reaction.

On addition of AgNO\(_3\) solution to the reaction mixture a pale yellowish precipitate appeared, which increased gradually within the reaction time due to formation of AgBr, indicating Br\(^-\) anion as one of the oxidation products.

Kinetics of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4]^{2+}/\text{NBS}\) reaction in aqueous solution

Kinetics of oxidation of \([\text{Cr}^{III}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_4]^{2+}\) by NBS was studied over a \(pH\) range of 6.76 – 7.84, ionic strength (0.2 – 0.3) mol dm\(^{-3}\); temperature 30 – 50 °C, complex (1.0 – 5.0) \(\times 10^{-4}\) mol dm\(^{-3}\) and NBS (0.5 – 5.0) \(\times 10^{-2}\) mol dm\(^{-3}\), respectively. The pseudo-first order rate constants (\(k_{\text{obs}}\)) were determined from plots of \(\ln(A_e-A_t)\) against time where \(A_t\) and \(A_e\) are the absorbance at time \(t\) and time infinity, respectively. These plots are linear for about 85 % of the time from the beginning of the reaction. The error limits for results were calculated using Microcal Origin (ver. 5.0).
Under constant conditions of \( \text{pH} = 7.13 \), \([\text{NBS}] = 2.5 \times 10^{-2} \) mol dm\(^{-3}\), \( I = 0.20 \) mol dm\(^{-3}\) and \( T = 40 \) °C, effects of concentration of the complex on the rate of oxidation was studied. There was no variation in the values of \( 10^{3}k_{\text{obs}} \) of 13.77 ± 0.06, 13.50 ± 0.03, 13.47 ± 0.04, 13.55 ± 0.06 and 13.61 ± 0.02 min\(^{-1}\) obtained at \([\text{Cr}^{III}(\text{CD})(\text{Ino})_{2}H_{2}O]^{2+} = 1.0, 2.0, 3.0, 4.0 \) and \( 5.0 \times 10^{-4} \) mol dm\(^{-3}\), respectively indicating that the reaction rate is first-order with respect to the complex concentration, Eq. (1).

\[
\text{Rate} = k_{\text{obs}}[\text{Cr}^{III}(\text{CD})(\text{Ino})(H_{2}O)]^{2+} \quad \ldots(1)
\]

Dependence of \( k_{\text{obs}} \) on [NBS] was studied at different concentrations of NBS \((0.5 – 5.0) \times 10^{-2} \) mol dm\(^{-3}\) while the other constituents were kept constant. Plots of \( k_{\text{obs}} \) against [NBS] at different temperatures were found to be linear without intercept (Fig. 1) according to Eq. (2).

\[
k_{\text{obs}} = k_{1}[\text{NBS}] \quad \ldots(2)
\]

Effects of \([H^{+}]\) on the rate of oxidation reaction was investigated over the \( \text{pH} \) range of 6.76 – 7.84, NBS = \((0.5 – 5.0) \times 10^{-2} \) mol dm\(^{-3}\) and \( T = (30 – 50) \) °C while the complex concentration and ionic strength were kept constant at \( 1 \times 10^{-3} \) and 0.20 mol dm\(^{-3}\), respectively. Plots of the slopes \( (k_{1}) \) versus 1/[\(H^{+}\]) were found to be linear with intercept on the y-axis (Fig. 2). This behavior can be described by Eq. (3),

\[
k_{1} = k_{2} + k_{3}(1/[H^{+}]) \quad \ldots(3)
\]

where, \( k_{1}, k_{2} \) and \( k_{3} \) are constants.

Values of \( k_{2} \) and \( k_{3} \) calculated from slopes and intercepts of Fig. 2, respectively at different temperatures are tabulated in Table 1. From transition state theory equation, the thermodynamic activation parameters including enthalpy, \( \Delta H^{*} \), and entropy, \( \Delta S^{*} \), associated with constant \( k_{2} \) and \( k_{3} \) are composite values and can be obtained by plotting \( \ln k_{2}/T \) and \( \ln k_{3}/T \) against \( 1/T \) respectively. The enthalpies of activation, \( \Delta H^{*}_{2} \) and \( \Delta H^{*}_{3} \) were calculated as 22.508 and 42.89 kJ mol\(^{-1}\), respectively. The corresponding entropies of activation, \( \Delta S^{*}_{2} \) and \( \Delta S^{*}_{3} \) were found to be –339.87 and –129.01 J K\(^{-1}\) mol\(^{-1}\), respectively.

The rate of the reaction was unaffected by ionic strength, where the \( k_{\text{obs}} \) values were \((13.77\pm0.06, 13.24\pm0.09, 13.84\pm0.01, 13.55\pm0.09, 13.08\pm0.01) \times 10^{-3} \) min\(^{-1}\) at \( I = 0.2, 0.22, 0.24, 0.26, 0.28 \) and \( 0.30 \) mol dm\(^{-3}\), respectively when the other factors were kept constant at \( \text{pH} = 7.13 \), \([\text{NBS}] = 2.5 \times 10^{-2} \) mol dm\(^{-3}\) and \( T = 40 \) °C. This behavior was expected since the reaction is taking place between charged and uncharged species.

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( 10^{3}k_{2} ) (min(^{-1}) ± SD)</th>
<th>( 10^{3}k_{3} ) (min(^{-1}) mol(^{-1}) dm(^{3}) ± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>7.34 ± 0.31</td>
<td>2.18 ± 0.24</td>
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<tr>
<td>35</td>
<td>8.63 ± 0.29</td>
<td>3.04 ± 0.23</td>
</tr>
<tr>
<td>40</td>
<td>10.39 ± 0.21</td>
<td>3.91 ± 0.16</td>
</tr>
<tr>
<td>45</td>
<td>11.70 ± 0.57</td>
<td>5.42 ± 0.44</td>
</tr>
<tr>
<td>50</td>
<td>13.60 ± 0.11</td>
<td>6.61 ± 0.08</td>
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Table 1—Variation of \( k_{2} \) and \( k_{3} \) with temperature. \([\text{Cr}^{III}(\text{CD})(\text{Ino})(H_{2}O)]^{2+} = 1.0 \times 10^{-4} \) mol dm\(^{-3}\); \( I = 0.20 \) mol dm\(^{-3}\); \( \text{pH} = 6.76-7.84; \).
In order to study the effect of an anionic surfactant on kinetics of oxidation of [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2]\textsuperscript{2+} by NBS, the reaction was studied in presence of varying concentrations of SDS (0.0–1.0 × 10\textsuperscript{-3} mol dm\textsuperscript{-3}), keeping other parameters constant. Calculated values of $k_{obs}$ listed in Table 2 show that $k_{obs}$ increases with increase in SDS, concentration. This behavior can be attributed to the presence of SDS, which allows the reaction to proceed in both aqueous and micellar interphases. Hence, the observed rate of acceleration is due to the favoured reaction in micellar phase where both Cr\textsuperscript{III} complex and NBS are preferentially accumulated.

From Eqs (1)-(3) the experimental rate law can be represent by Eq. (4),

$$\text{Rate} = \frac{k_3 + k_2}{[\text{H}^+]} \times [\text{NBS}] [\text{[Cr}^{\text{III}}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_2]^{2+}]$$ \hspace{0.5cm} (4)

where $k_{obs} = k_3 + k_2 (1/ [\text{H}^+])[\text{NBS}]$ \hspace{0.5cm} (5)

**Mechanism**

The ternary Cr\textsuperscript{III} complex can be formulated as [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2][NO_3]_2·H_2O, where CD functions as monodentate ligand through the carboxylic group and Ino acts as a secondary ligand through O(6) (Ino contains two potential metal ion binding sites, i.e., N(5) and O(6)). The dissociation of a proton from N(5) occurs only at a high pH (≥9.0) leaving the other site as viable alternate site for metal ion binding. An intramolecular hydrogen bond may be formed as a result of interaction between H atom of N(5) in Ino with oxygen atom of CD linked with Cr\textsuperscript{III} - metal ion (I). Then, H atom of N(5) in Ino is a link of a six-membered planar ring that may have a role in increasing the stability of the formed complex. The potentiometrically calculated value of the stability constant of [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2]\textsuperscript{2+} ($K_{31} = 2.76 \times 10^{10}$) supports this assignment.

In neutral and slightly basic solution, [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2]\textsuperscript{2+} may participate in the equilibrium shown in Eq. (6):

$$[\text{Cr}^{\text{III}}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_2]^{2+} \Leftrightarrow [\text{Cr}^{\text{III}}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_2(\text{OH})]^{+} + \text{H}^+ \hspace{0.5cm} K_1 \hspace{0.5cm} (6)$$

In the studied pH range, the protonated complex and its conjugated base prevail. The [H\textsuperscript{+}] dependence in the experimental rate law suggests involvement of the protonated complex, [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2]\textsuperscript{2+}, and its conjugated base, [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2(OH)]\textsuperscript{+}, in the rate determining step.

| Table 2—Variation of $k_{obs}$ with [SDS]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2]\textsuperscript{2+} | NBS | [SDS] (mol dm\textsuperscript{-3}) | $k_{obs}$ (min\textsuperscript{-1}) | SD)
| 1.00 | 0.00 | 1.0 × 10\textsuperscript{-3} | 13.77 ± 0.06 |
| 0.20 | 0.00 | 1.0 × 10\textsuperscript{-3} | 15.12 ± 0.01 |
| 0.40 | 0.00 | 1.0 × 10\textsuperscript{-3} | 16.53 ± 0.07 |
| 0.60 | 0.00 | 1.0 × 10\textsuperscript{-3} | 18.13 ± 0.09 |
| 0.80 | 0.00 | 1.0 × 10\textsuperscript{-3} | 19.49 ± 0.01 |
| 1.00 | 0.00 | 1.0 × 10\textsuperscript{-3} | 21.02 ± 0.09 |

Considering the coordination of NBS with Cr\textsuperscript{III} metal ion in the studied pH range, NBS exists without protonation while in highly acidic solutions NBS exists as the protonated species, i.e., HNBS\textsuperscript{+}. Also, the coordinated H_2O may be labile due to its low basissity to act as a bridge. Therefore, if the hydroxo form of the complex is the reactive species, the hydroxol group, which forms a labile (Cr\textsuperscript{III}-OH\textsuperscript{2-}) bond, facilitates the substitution of H_2O by i.e., HNBS\textsuperscript{+}. Finally, coordination of NBS is possible through its carbonyl group.

There is a probability of one- or two-electron transfer during the oxidation reaction giving Cr\textsuperscript{IV} or Cr\textsuperscript{V}, respectively in the rate determining step followed by a fast step leading to Cr\textsuperscript{VI}. The fact that acrylonitrile was polymerized when added to the reaction mixture as a separate experiment seem to supports formation of the succinimidyl radical via one-electron transfer in the rate determining step.

In view of these considerations, oxidation of [Cr\textsuperscript{III}(CD)(Ino)(H_2O)_2]\textsuperscript{2+} by NBS may proceed by two step one-electron transfer via an inner-sphere mechanism as follows:

$$[\text{Cr}^{\text{III}}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_2]^{2+} + \text{NBS} \leftarrow \frac{K_5}{K_2} \text{Cr}^{\text{IV}} + \text{R}^+ + \text{CD} + \text{Ino} + \text{H}_2\text{O} + \text{Br}^- \hspace{0.5cm} (7)$$

$$[\text{Cr}^{\text{III}}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_2(\text{OH})(\text{NBS})]^+ + \text{H}_2\text{O} \leftarrow \frac{K_3}{K_2} \text{Cr}^{\text{IV}} + \text{R}^+ + \text{CD} + \text{Ino} + \text{H}_2\text{O} + \text{Br}^- \hspace{0.5cm} (8)$$

$$[\text{Cr}^{\text{III}}(\text{CD})(\text{Ino})(\text{H}_2\text{O})_2(\text{OH})(\text{NBS})]^+ \leftarrow \frac{k_4}{k_5} \text{Cr}^{\text{IV}} + \text{R}^+ + \text{CD} + \text{Ino} + \text{H}_2\text{O} + \text{Br}^- \hspace{0.5cm} (9)$$

$$\text{Cr}^{\text{IV}} + \text{R}^+ \leftarrow \frac{k_6}{k_7} \text{Cr}^{\text{V}} + \text{R}^- \hspace{0.5cm} (10)$$

$$\text{Cr}^{\text{V}} + \text{R}^- \leftarrow \frac{k_8}{k_9} \text{Cr}^{\text{VI}} + \text{R}^- \hspace{0.5cm} (11)$$

$$\text{R}^- + \text{H}^+ \leftarrow \frac{k_{10}}{k_{11}} \text{RH} \hspace{0.5cm} (12)$$
where $k_4$ and $k_5$ are rate constants, $R^-$ is succinimide anion and $R^+$ is succinimidyl radical. $R^+$ prefers to abstract $H^+$ to form succinimide (RH) and $R^+$ is an unstable radical, and hence, two succinimidyl radical may dimerize to form bisuccinimidyl $(R-R)^{3+}$.

Our suggestion that the NBS acts as oxidant by a free radical path involving the homolytic dissociation of NBS with reducing metal ions $(Cr^{III})$ to yield $R^+$ and $Br^-$ as intermediates is in good agreement with the theoretical results on calculated bond dissociation energies (BDEs) involving the formation of the $Br^+$, $Br^-$ and $Br^-$ of the N-Br bond. It has been reported that the N-Br BDE of the $Br^-$ formation is lower \(12^\text{th}\) than that of $Br^+$ or $Br^-$. From the above mechanism, the rate of the reaction can be described by Eq. (14):

\[
d[Cr^{VII}]/dt = k_4[[Cr^{III}(CD)(Ino)(H_2O)_2(NBS)]^{2+}]
+ k_5[[Cr^{III}(CD)(Ino)(H_2O)(OH)(NBS)]^+]
\]  

(14)

Since

\[
[[Cr^{III}(CD)(Ino)(H_2O)_2(NBS)]^{2+} =
K_2[NBS][[Cr^{III}(CD)(Ino)(H_2O)_4]^2-]
\]  

(15)

From Eqs (6) and (8) we get Eq. (16).

\[
[[Cr^{III}(CD)(Ino)(H_2O)(OH)(NBS)]^+ =
\{K_1K_5(1/[H^+])\}[NBS][[Cr^{III}(CD)(Ino)(H_2O)_4]^2-]
\]  

(16)

Eqs (15) & (16) and substitution in Eq. (14) give Eq. (17).

\[
d[Cr^{VII}]/dt = k_4K_2[NBS][[Cr^{III}(CD)(Ino)(H_2O)_4]^2-]
+ k_5K_5K_3(1/[H^+])\times [[Cr^{III}(CD)(Ino)(H_2O)_4]^2-]
\]  

(17)

On rearrangement, one gets Eq. (18).

\[
d[Cr^{VII}]/dt = \{k_4K_2+k_5K_4K_5(1/[H^+])\}	imes
[NBS][[Cr^{III}(CD)(Ino)(H_2O)_4]^2-]
\]  

(18)

where,

\[
k_{obs} = \{k_4K_2+k_5K_4K_5(1/[H^+])\}	imes [NBS]
\]  

(19)

This is identical to the experimental rate law (Eq. 4) and therefore from Eqs (5) and (19), we get Eq. (20).

\[
k_3 = k_4K_2, k_2 = k_5K_4K_5
\]  

(20)

In oxidation of the binary and ternary complexes, $[Cr^{III}(Ino)(H_2O)_3]^{3+}$ and $[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$, by NBS at $T = 35$ °C and $I = 0.2$ mol dm$^-3$, the hydroxy complexes, $[Cr^{III}(Ino)(H_2O)_4(OH)]^{2+}$ and $[Cr^{III}(CD)(Ino)(H_2O)_4(OH)]^+$, are significantly more reactive than their conjugate acids. The rate of oxidation of $[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$ is much slower than that of $[Cr^{III}(Ino)(H_2O)_4]^{2+}$, as evidenced by the values of intramolecular electron transfer rate constant. For $[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$ it is $1.43 \times 10^7$ s$^-1$ and for $[Cr^{III}(Ino)(H_2O)_4]^{3+}$ it is $6.90 \times 10^4$ s$^-1$. which can be explained on the basis of crystal field theory. The crystal field stabilization energy ($\Delta_{0}$) due to the electrostatic field of the conjugate base of CD. Therefore, in $[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$, losing the three $t_{2g}$ electrons from the central $Cr^{III}$ ion, during the oxidation reaction becomes more difficult.

Values of enthalpies and entropies of activation for the oxidation of some $Cr^{III}$ complexes by NBS, in which NBS ion coordinates to the $Cr^{III}$ ion of $[Cr^{III}(Ino)(H_2O)_4]^2+$, as evidenced by the values of intramolecular electron transfer rate constant. For $[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$ it is $1.43 \times 10^7$ s$^-1$ and for $[Cr^{III}(Ino)(H_2O)_4]^{3+}$ it is $6.90 \times 10^4$ s$^-1$. which can be explained on the basis of crystal field theory. The crystal field stabilization energy ($\Delta_{0}$) due to the electrostatic field of the conjugate base of CD. Therefore, in $[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$, losing the three $t_{2g}$ electrons from the central $Cr^{III}$ ion, during the oxidation reaction becomes more difficult.

Values of enthalpies and entropies of activation for the oxidation of some $Cr^{III}$ complexes by NBS, in which NBS ion coordinates to the $Cr^{III}$-complexes in the step preceeding the rate determining intra-molecular electron transfer within the precursor complex. Similar behaviour has been observed for a large number of redox reactions.

### Table 3 – Values of $\Delta H^*$ and $\Delta S^*$ for the oxidation of some $Cr^{III}$ complexes by NBS

<table>
<thead>
<tr>
<th>$Cr^{III}$ complexes</th>
<th>$\Delta H^*$ (kJ mol$^-1$)</th>
<th>$\Delta S^*$ (J K$^-1$ mol$^-1$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Cr^{III}(CD)(Ino)(H_2O)_4]^{2+}$</td>
<td>22.328</td>
<td>-339.87</td>
<td>Present work</td>
</tr>
<tr>
<td>$[Cr^{III}(H_2O)_4]^{3+}$</td>
<td>37.8</td>
<td>-148.8</td>
<td>34</td>
</tr>
<tr>
<td>$[Cr^{III}(Ino)(Gly)(H_2O)_4]^{2+}$</td>
<td>59.3</td>
<td>-79.6</td>
<td>17</td>
</tr>
<tr>
<td>$[Cr^{III}(LD)(Urd)(H_2O)_4]^{2+}$</td>
<td>59.57</td>
<td>26.57</td>
<td>33</td>
</tr>
</tbody>
</table>

References