Kinetics and Mechanistic Studies of Oxidation of a Ternary Nitrilotri-Acetatocobalt(II) Complexes Involving DL-valine and DL-aspartic Acid as a Secondary Ligands by Periodate

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Abstract: Oxidation of ternary complexes, \([\text{Co}^{II}(\text{NTA})(L)(\text{H}_2\text{O})_X]\) by periodate in aqueous medium has been studied spectrophotometrically over the (25.0 – 45.0) ± 0.1°C range. The reaction show first order kinetics with respect to both [IO\(_4^-\)] and the complexes, and the rate of the reaction increases over the [H\(^+\)] range (1.05 – 28.20) x 10\(^{-5}\) mol dm\(^{-3}\) in both cases. Preparation and characterization of [Co\(^{III}(\text{NTA})(\text{Asp})(\text{H}_2\text{O})_2]\)\(^2-\) and [Co\(^{III}(\text{NTA})_{\text{Val}}(\text{H}_2\text{O})_2]\)\(^2-\) is performed. Conformation of the formation of the ternary complexes has been done using IR spectrum, TGA, UV-visible spectroscopic and cyclic voltammetry measurements. The thermodynamic activation parameters have been calculated. It is assumed that electron transfer takes place \textit{via} an inner-sphere mechanism.

Keywords: Kinetics, Ternary Co(II) Complexes, Aspartic acid, DL-Valin, UV-spectrophotometer, Inner-Sphere Mechanism, Thermodynamic Activation Parameters

1. Introduction

Amino acid residues are the main constituents of proteins and the study of its sensitivity towards oxidation open up a new area to understand the mechanism involved in the protein and amino acid modification [1].

The use of transition metal complexes of nitrilotriacetic acid have been widely adopted in biology, and are gaining increasing use in biotechnology, particularly in the protein purification technique known as immobilized metal-ion [2].

Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases have attracted much interest as they can display exceptionally high stability and biological important [3, 4].

Periodate oxidation exerts a number of biological effects including the enhancement of lymphocyte activation and increased the frequency of effector to target cell binding [5]. Also, periodate was used in the modification of human serum transferrin by conjugation to oligosaccharide [6].

Oxidation of caffeic acid (3,4-dihydroxycinnamic acid) by means of sodium periodate was reported, that mimics the mechanism of polyphenylenoxidase. The reaction leads to the formation of the antioxidant product 2-S-cysteinylecaffeic adduct which exhibits slightly improved antiradical activity in relation with the parent molecule (caffeic acid) [7]. Also, kinetics studies of periodate oxidations on a series of dextran oligomers, polymers, some dimeric carbohydrates [8] and of chitosans with different chemical composition [9] were investigated to show the dependence of the kinetics on the molecular weight.

Using periodate as an oxidant for inorganic substrates and some transition metals are reported to proceed \textit{via} an inner–sphere mechanism [10-15]. Periodate readily found to oxidize either labile or inert complexes possessing at least one bridging ligand. Initial cobalt(III) products that were transformed to the final cobalt(III) products slowly were identified spectrophotometrically [13-15].

Oxidation of the ternary complexes involving nitrilotriacetatocobaltate(II) succinic acid, [Co\(^{III}\text{NS}(\text{H}_2\text{O})_2]\)\(^2+\), and nitrilotricatetocobaltate(II) malonic acid, [Co\(^{III}\text{NM}(\text{H}_2\text{O})_2]\)\(^2+\) [where N = nitrilotriacetae, S = succinic acid, and M = malonic acid] by periodate has been studied in aqueous medium [16].

Also, oxidation of [Co\(^{III}\text{NMa}(\text{H}_2\text{O})]\)\(^3+\).4\text{H}_2\text{O} and
[Co\textsuperscript{II}NT(H\textsubscript{2}O)\textsuperscript{3-}].4H\textsubscript{2}O by periodate have been studied kinetically in aqueous solution [where, N = nitrilotriacetate, Ma = Maleic acid, and T = tartaric acid] over 25 – 45°C and a variety of pH range [17].

The oxidation of [Co\textsuperscript{II}(nta)(ox)(H\textsubscript{2}O)\textsuperscript{2-}] and [Co\textsuperscript{II}(nta)(ph)(H\textsubscript{2}O)\textsuperscript{2-}] (nta = nitrilotriacetate, ox = oxalic acid and ph = phthalic acid) by periodate have been studied kinetically in aqueous solution over 20–40°C and a variety of pH ranges [18]. These reactions proceeded via the formation of initial cobalt (III) products, which were converted slowly into final cobalt (III) products fitting an inner-sphere mechanism.

A kinetic study of the oxidation of [Co(H\textsubscript{2}L)(H\textsubscript{2}O)\textsuperscript{2+}] (H\textsubscript{2}L = N,N-bis (salicylaldehyde-1,2-diaminoethane) Schiff base) by periodate in aqueous solution was performed at concentrations of Cu(II) increased, and it was independent on Fe(II) concentrations over the ranges studied. An inner-sphere mechanism is proposed for the oxidation pathways of both the protonated and deprotonated Co\textsuperscript{II} complex species [19].

The aim of the present study is to propose the most probable reaction path for the kinetics of oxidation of biologically important ternary nitrilotriacetocobalt(II) complexes involving DL-valine and DL-aspartic acid as a secondary ligand. [Co\textsuperscript{II}(NTA)Asp(H\textsubscript{2}O)\textsubscript{2}] and [Co\textsuperscript{II}(NTA) Val(H\textsubscript{2}O)\textsubscript{2}] were prepared using the same procedure as that for the preparation of Na\textsubscript{3}[Co\textsuperscript{II}NS(H\textsubscript{2}O)\textsubscript{3}] [23]. The elemental analysis data of these complexes are found: C, 25.70; H, 3.02; N, 6.61. Calcd.: C, 24.84; H, 3.11; N, 5.79 and Found: C, 29.46; H, 5.31; N, 6.21; Calcd.:C, 29.66; H, 4.49; N, 6.29, respectively.

IR spectra, thermal gravimetric analysis (TGA), UV Visible spectra and cyclic voltammetric data were carried out to confirm the formula of the complexes.

IR spectra show bands in the (3516 – 3363) cm\textsuperscript{-1} region, were attributed to \nu (OH) of the water molecules. The OH of the carboxylic group disappeared and a new (\nu COO\textsuperscript{-}) appeared in the region (1464 – 1432) cm\textsuperscript{-1} indicating that the carboxylic group of the ligands participates in the coordination with the metal ions through deprotonation.


\textbf{2. Experimental}

\textbf{2.1. Materials and Methods}

All reagent grade or analar chemicals were used without further purification. Co(NO\textsubscript{3})\textsubscript{2} (BDH) solutions were standardized volumetrically with EDTA [20]. A stock solution of (IO\textsubscript{4}) was made up by weight and covered with aluminum foil to avoid photochemical decomposition [21]. Solutions of NaOAC, HOAC, and NaNO\textsubscript{3} were prepared by weighing.

HOAC / NaOAC buffers of known [H\textsuperscript{+}] were used, and the ionic strength was adjusted with NaNO\textsubscript{3}.

Potentiometric measurements were performed with a Metrohm 702 SM titrino. The titroprocessor equipped with a 665 dosimat (Switzerland-Heriau). The titroprocessor and electrode were calibrated with standard buffer solution [22].

Calculations were performed using computer program MINIQUAD-75 loaded on an IBM-550 computer. The solution containing 5.0 ml 0.01 mol dm\textsuperscript{-3} complex, 5.0 ml 0.20 mol dm\textsuperscript{-3} NaNO\textsubscript{3}, 5 ml 0.04 mol dm\textsuperscript{-3} HNO\textsubscript{3} and 25 ml deionized water, was titrated with 0.01 mol dm\textsuperscript{-3} NaOH at 25°C.

Na\textsubscript{3}[Co\textsuperscript{II}(NTA)Asp(H\textsubscript{2}O)\textsubscript{2}] and Na\textsubscript{2}[Co\textsuperscript{II}(NTA) Val(H\textsubscript{2}O)\textsubscript{2}] were prepared using the same procedure as that for the preparation of Na\textsubscript{3}[Co\textsuperscript{II}NS(H\textsubscript{2}O)\textsubscript{3}] [23]. The elemental analysis data of these complexes are found: C, 25.70; H, 3.02; N, 6.61. Calcd.: C, 24.84; H, 3.11; N, 5.79 and Found: C, 29.46; H, 5.31; N, 6.21; Calcd.:C, 29.66; H, 4.49; N, 6.29, respectively.

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All the spectra of the complexes studied showed asym- (\nu COO-Co) band in the region (1582 – 1658) cm\textsuperscript{-1} the bands in the range (2928 – 2967) cm\textsuperscript{-1} in the spectra, are due to \nu (NH) as shown in Figures 1 and 2.

\textbf{Figure 1. Infrared spectra of nitrilotriacetocobalt (II)-Valin[Co\textsuperscript{II}(NTA)(Val)(H\textsubscript{2}O)\textsubscript{2}].}
The thermogram of the complex $\text{Na}_3[\text{Co}^\text{II}(\text{NTA})\text{Asp(H}_2\text{O})_2]$ shows weight loss (6.86) at 151.46°C corresponds to the loss of two coordinated water molecule (calc. 7.45), and the weight loss (46.32) at 394.2°C corresponding to the loss five $\text{CO}_2$ molecules (cal. 45.54).

While the thermogram of the $\text{Na}_3[\text{Co}^\text{II}(\text{NTA})\text{Val(H}_2\text{O})_2]$ complex shows weight loss (8.84) at 145.49°C corresponds to the loss of two coordinated water molecules (calc. 8.09), and weight loss (40.62) at 400.64°C corresponding to the loss four $\text{CO}_2$ molecules (cal. 39.55) as shown in Figures 3 and 4.
Confirmation of the formation of binary and ternary complexes in solution has been carried out by studying the electrochemical behavior (Figures 5-8). Cyclic Voltammetric measurements were operated using potentiostat / Galvaostate winkling PGS 95 with single-compartment Voltametric cell equipped with a platinum working electrode (area = 0.5 cm$^2$). A platinum wire was used as counter electrode, and a SCE as a reference electrode. A sample volume of 25 cm$^3$ containing the free metal ion $3 \times 10^{-3}$ mol dm$^{-3}$, ternary complex $3 \times 10^{-3}$ mol dm$^{-3}$. All solutions are investigated in water at 30°C, the solutions are purged with nitrogen for 120s, and the potential is scanned at the scan rate 25 MVs$^{-1}$ from (+ 1.5 to –1.0) V.

Metal cobalt ion is difficulty oxidized at more positive potential, +732 mV vs. SCE, Figure (3), but the oxidation process of the binary system of Co(II)-nitrilotriacetate becomes slightly easy where the oxidation potential was shifted to more negative value, -375 mV vs. SCE, while in the case of ternary complex involving (aspartic with nitrilotriacetato-cobalt(II), the complex become more stable than binary complex, + 478 mV vs. SCE), but in case of ternary complex involving (valin with nitrilotriacetato-cobalt(II), the complex become less stable than Co$^2$ (NTA)Asp(H$_2$O)$_2$$^2$), because it oxidizes firstly, at +179 mV vs. SCE.

2.2. Kinetic Procedures

The U.V.-visible absorption spectra (Figures 9 and 10) of each species of solution containing Co$^2$ [Co$^2$(NTA)(H$_2$O)$_2$]$^2$, [Co$^2$(NTA)(Asp)(H$_2$O)$_2$]$^3$, [Co$^2$(NTA)(Val)(H$_2$O)$_2$]$^2$ at the concentration (4.0 x 10$^{-3}$ mol dm$^{-3}$) and [H$^+$] = 4.36 x 10$^{-5}$ mol dm$^{-3}$ exhibited an absorption bands over the range of 300-700 nm figure (1, 2). The maxima and molar absorptivity of these compounds were collected Table (1). Peaks shifting and molar absorptivity indicated the formation of complex [Co$^2$(NTA)(Asp)(H$_2$O)$_2$]$^3$, [Co$^2$(NTA)(Val)(H$_2$O)$_2$]$^2$. 

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**Figure 5.** Cyclic voltammogram for the $3 \times 10^{-3}$ M of CO(II) solution on Pt electrode at 300K with the scan rate of 25mVs$^{-1}$.

**Figure 6.** Cyclic voltammogram for the $3 \times 10^{-3}$ M of CO(II)-NTA solution on Pt electrode at 300K with the scan rate of 25mVs$^{-1}$.

**Figure 7.** Cyclic voltammogram for the $3 \times 10^{-3}$ M of CO(II)-NTA-Val solution on Pt electrode at 300K with the scan rate of 25mVs$^{-1}$.

**Figure 8.** Cyclic voltammogram for the $3 \times 10^{-3}$ M of CO(II)-NTA-Asp solution on Pt electrode at 300K with the scan rate of 25mVs$^{-1}$.

**Figure 9.** Change in absorbance for (Co$^2$) (Co$^2$(NTA), and Co$^2$(NTA)Asp at the same concentration (4 x 10$^{-3}$moldm$^{-3}$), and pH = 5.
by the presence of a large excess of IO$_4^-$ absorbance was commenced.

The required amount of separately thermostated IO$_4^-$ stock solution was rapidly mixed, and then the recording of monitoring the absorbance of initial Co$^{II}$ complexes absorbance was commenced. The [H$^+$] of the reaction mixture was measured using a Chertsey, Surrey, 7065 pH-meter.

Pseudo-first order conditions were maintained in all runs by the presence of a large excess of IO$_4^-$ (> 10-fold). The ionic strength was kept constant by addition of NaNO$_2$. All reactants, except IO$_4^-$, were equilibrated at required temperature for 15–20 min. The required amount of separately thermostated IO$_4^-$ stock solution was rapidly mixed, and then the recording of absorbance was commenced.

The [H$^+$] of the reaction mixture was measured using a Milton-Roy 601 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 initial Co$^{III}$ complexes absorbance at 572 and 558 nm, respectively. All reactants, except IO$_4^-$, were equilibrated at required temperature for 15–20 min. The required amount of separately thermostated IO$_4^-$ stock solution was rapidly mixed, and then the recording of absorbance was commenced.

The limits for results are calculated using Microcal Origin® (Version 6.0). The error limits for results are calculated using Microcal Origin® (Version 6.0).

2.3. Oxidation Product

The U.V.-vis. Absorption spectra of the oxidation product of [Co$^{II}$NTA]Asp(H$_2$O)$_2$$^{3-}$ and [Co$^{II}$NTA]Val(H$_2$O)$_2$$^{3-}$ by periodate were recorded on Jasco UV-530 spectrophotometer as a function of time over the 300-700 nm range (Figures 11 and 12) respectively. The maxima and molar absorptivity coefficients of the final cobalt (III) product at [H$^+$] = 4.36 x 10$^{-2}$ mol dm$^{-3}$ of oxidation of aspartic ternary complex were $\varepsilon_{\text{max}}^{395} = 158$ and $\varepsilon_{\text{max}}^{572} = 135$ dm$^3$ mol$^{-1}$ cm$^{-1}$, while the coefficients of the valin ternary complex were $\varepsilon_{\text{max}}^{395} = 156$ and $\varepsilon_{\text{max}}^{558} = 157$ dm$^3$ mol$^{-1}$ cm$^{-1}$.

![Figure 10. Change in absorbance for (Co$^{II}$), Co$^{II}$(NTA), and Co$^{II}$(NTA)Val. At the same concentration (4 x 10$^{-3}$mol dm$^{-3}$), pH = 5.](image)

![Figure 11. Change in absorbance as a function of time in the reaction between [Co$^{II}$(NTA)Asp(H$_2$O)$_2$$^{3-}$ and [IO$_4^-$]. Curve (6) shows the spectra of the final cobalt (III) product.](image)

![Figure 12. Change in absorbance as a function of time in the reaction between [Co$^{II}$(NTA)Val(H$_2$O)$_2$$^{3-}$ and [IO$_4^-$]. Curve (6) shows the spectra of the final cobalt (III) product.](image)

| [Co$^{II}$] | $\varepsilon_{\text{max}}^{395}$ | $\varepsilon_{\text{max}}^{572}$ |
|-------------|-----------------|-----------------|
| dm$^3$ mol$^{-1}$ cm$^{-1}$ | dm$^3$ mol$^{-1}$ cm$^{-1}$ |
| [Co$^{II}$ (NTA)Asp(H$_2$O)$_2$$^{3-}$] | 59 | 26 |
| [Co$^{II}$ (NTA)Val(H$_2$O)$_2$$^{3-}$] | 121.8 | 79 |
| [Co$^{II}$ (NTA)Val(H$_2$O)$_2$$^{3-}$] | 105 | 107 |
| [Co$^{II}$ (NTA)Val(H$_2$O)$_2$$^{3-}$] | 79.67 | 98.25 |

### 3. Results

Kinetics of $\frac{d [\text{Co}^{III} \text{(NTA)Asp(H}_2\text{O)}_2^{3-}]}{dt} = k_{\text{obs}} [\text{Co}^{II} \text{(NTA)Asp(H}_2\text{O)}_2^{3-}]_o$ (1)
Plots of \( k_{\text{obs}} \) against \([\text{IO}_4^-]\) were found to be linear, (Figures 13 and 14). The dependence of \( k_{\text{obs}} \) on \([\text{IO}_4^-]\), Table (2 & 3), is described by

\[
k_{\text{obs}} = k_1[\text{IO}_4^-]
\]

The kinetics of the reaction was studied over \([\text{H}^+]\) range \((1.05 - 28.20) \times 10^{-5} \text{ mol dm}^{-3}\) at different temperatures Table (4 & 5) lists the variation of \( k_1 \) with \([\text{H}^+]\) at different temperatures which indicate that the reaction rate increased gradually with decreasing \([\text{H}^+]\). Plots of \( k_1 \) versus \([\text{H}^+]\) were linear, with intercepts as shown in (Figures 15 and 16). This behavior can be described by equation 3.

\[
k_1 = k_2 + k_3 / [\text{H}^+]
\]

Values of \( k_2 \) and \( k_3 \) were calculated at different temperatures, and were listed in Table (6 & 7).

The thermodynamic activation parameters were calculated by using the transition state theory equation. The enthalpies of activation, \( \Delta H^* \), and \( \Delta H^*_3 \) for \([\text{Co}^{II}(\text{NTA})\text{Asp(H}_2\text{O)}_2]\) were reported as 44.6 ± 0.12 and 76.9 ± 0.18 kJmol\(^{-1}\), respectively. The corresponding entropies of activation, \( \Delta S^*_2 \) and \( \Delta S^*_3 \) were −128.0 ± 0.03 and −114.4 ± 0.1 JKmol\(^{-1}\) respectively.

Also, The enthalpies of activation, \( \Delta H^*_2 \) and \( \Delta H^*_3 \) for \([\text{Co}^{II}(\text{NTA})\text{Val(H}_2\text{O)}_2]\) were reported as 49.1 ± 0.12 and 65.8 ± 0.18 kJmol\(^{-1}\), respectively. The corresponding entropies of activation, \( \Delta S^*_2 \) and \( \Delta S^*_3 \) were −115.2 ± 0.03 and −153.8 ± 0.1 JKmol\(^{-1}\) respectively. Furthermore, the reaction rate increased with an increase in ionic strength, over a 0.30 – 0.60 mol dm\(^{-3}\) range as shown in Table (2, 3).

From equations 1, 2 and 3 the experimental rate law was derived, as:

\[
\text{Rate} = (k_2+k_3/[\text{H}^+]) ([\text{Co}^{II}(\text{NTA})\text{L(H}_2\text{O)}_x])_o [\text{IO}_4^-]
\]
Table 2. Dependence of the reaction rate constant, $10^6 k_{obs}$ s$^{-1}$, on $[\text{Co}^2(\text{NTA})\text{Asp(H}_2\text{O})_2]^{2-}$, $[\text{IO}_4]^{-}$, $T$ and temperatures at $[H^+]=28.2 \times 10^{-3}$ mol dm$^{-3}$.

| $[\text{IO}_4]^{-}$, M | $10^6 k_{obs}$ s$^{-1}$ |
|-------------------------|--------------------------|
| $T = 25^\circ$ | $T = 30^\circ$ | $T = 35^\circ$ |
| 5.0 | 8.08 ± 0.04 | 11.23 ± 0.03 | 17.05 ± 0.02 |
| 4.0 | 6.93 ± 0.03 | 9.68 ± 0.04 | 13.63 ± 0.01 |
| 3.0 | 4.73 ± 0.01 | 6.57 ± 0.03 | 11.07 ± 0.01 |
| 2.0 | 3.27 ± 0.02 | 3.43 ± 0.02 | 7.43 ± 0.03 |
| 1.0 | 1.97 ± 0.02 | 1.93 ± 0.02 | 3.30 ± 0.02 |
| 0.5 | 0.83 ± 0.02 | 1.22 ± 0.12 | 1.41 ± 0.01 |

$[\text{Co}^2(\text{NTA})\text{Asp(H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-1}$ mol dm$^{-3}$, $I^-$ = 0.25 mol dm$^{-3}$.

Table 3. Variation of the reaction rate constant, $10^6 k_{obs}$ s$^{-1}$, on $[\text{Co}^2(\text{NTA})\text{Val(H}_2\text{O})_2]^{2-}$, $[\text{IO}_4]^{-}$, $T$ at temperatures at $[H^+]=28.2 \times 10^{-3}$ mol dm$^{-3}$.

| $[\text{IO}_4]^{-}$, M | $10^6 k_{obs}$ s$^{-1}$ |
|-------------------------|--------------------------|
| $T = 25^\circ$ | $T = 30^\circ$ | $T = 45^\circ$ |
| 5.0 | 7.18 ± 0.01 | 8.34 ± 0.01 | 27.67 ± 0.01 |
| 4.0 | 5.58 ± 0.02 | 7.20 ± 0.02 | 20.57 ± 0.04 |
| 3.0 | 4.40 ± 0.015 | 5.12 ± 0.011 | 14.28 ± 0.013 |
| 2.0 | 2.62 ± 0.017 | 3.43 ± 0.015 | 7.78 ± 0.004 |
| 1.0 | 1.60 ± 0.010 | 1.97 ± 0.012 | 3.42 ± 0.010 |
| 0.5 | 0.69 ± 0.021 | 0.95 ± 0.10 | ------ |

$[\text{Co}^2(\text{NTA})\text{Val(H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-1}$ mol dm$^{-3}$, $I^-$ = 0.25 mol dm$^{-3}$, $[\text{IO}_4]^{-}$ = 0.02 mol dm$^{-3}$, and $[H^+] = 4.36 \times 10^{-3}$ mol dm$^{-3}$.

Table 4. Variation of $k_1$ with $[H^+]$ at $[\text{Co}^2(\text{NTA})\text{Asp(H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-1}$ mol dm$^{-3}$, $I = 0.25$ mol dm$^{-3}$, different $[\text{IO}_4]^{-}$ and different temperatures.

| $[\text{IO}_4]^{-}$ mol dm$^{-3}$ | 102 K1, (M-1s-1) |
|------------------------------|------------------|
| $T = 25^\circ$ | $T = 30^\circ$ | $T = 45^\circ$ |
| 28.2 | 1.61 ± 0.09 | 2.37 ± 0.01 | 4.61 ± 0.03 |
| 15.1 | 1.90 ± 0.01 | 2.72 ± 0.02 | 5.45 ± 0.04 |
| 4.36 | 2.39 ± 0.01 | 3.74 ± 0.02 | 8.20 ± 0.05 |
| 1.05 | 3.42 ± 0.03 | 6.43 ± 0.03 | 14.54 ± 0.06 |

Table 5. Dependence of $k_1$ with $[H^+]$ at $[\text{Co}^2(\text{NTA})\text{Val(H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-1}$ mol dm$^{-3}$, $I = 0.25$ mol dm$^{-3}$, different $[\text{IO}_4]^{-}$ and different temperatures.

| $[\text{IO}_4]^{-}$ mol dm$^{-3}$ | $10^3 k_{1c}$ (M$^{-1}$s$^{-1}$) |
|-------------------------------|-----------------------------|
| $T = 25^\circ$ | $T = 30^\circ$ | $T = 45^\circ$ |
| 28.2 | 1.43 ± 0.06 | 2.03 ± 0.04 | 4.26 ± 0.02 |
| 15.1 | 1.68 ± 0.01 | 2.31 ± 0.02 | 4.48 ± 0.03 |
| 4.36 | 1.97 ± 0.01 | 2.83 ± 0.02 | 5.82 ± 0.05 |
| 1.05 | 2.96 ± 0.03 | 4.90 ± 0.03 | 10.07 ± 0.06 |

Table 6. Variation of $k_2$ and $k_3$ with temperatures at $[\text{Co}^2(\text{NTA})\text{Asp(H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-1}$ mol dm$^{-3}$, $I = 0.25$ mol dm$^{-3}$, different $[\text{IO}_4]^{-}$ and different $[H^+]$.

| $T$, $^\circ$C | $10^5 k_{2c}$ (M$^{-1}$s$^{-1}$) | $10^5 k_{3c}$ (M$^{-1}$s$^{-1}$) | $10^5 k_{3c}$ s$^{-1}$ |
|---------------|-----------------------------|-----------------------------|---------------------|
| 25 | 17.52 ± 0.015 | 1.81 ± 0.010 | 5.31 ± 0.03 |
| 30 | 24.63 ± 0.030 | 4.20 ± 0.009 | 5.87 ± 0.03 |
| 35 | 32.40 ± 0.034 | 8.30 ± 0.010 | 7.76 ± 0.04 |
| 40 | 48.84 ± 0.050 | 10.30 ± 0.013 | 13.94 ± 0.07 |
| 45 | 54.04 ± 0.065 | 13.70 ± 0.017 | ------ |

Table 7. Variation of $k_2$ and $k_3$ with temperatures at $[\text{Co}^2(\text{NTA})\text{Val(H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-1}$ mol dm$^{-3}$, $I = 0.25$ mol dm$^{-3}$, different $[\text{IO}_4]^{-}$ and different $[H^+]$.

| $T$, $^\circ$C | $10^5 k_{2c}$ (M$^{-1}$s$^{-1}$) | $10^5 k_{3c}$ s$^{-1}$ |
|---------------|-----------------------------|---------------------|
| 25 | 15.01 ± 0.013 | 1.56 ± 0.014 |
| 30 | 20.53 ± 0.020 | 3.00 ± 0.019 |
| 35 | 28.59 ± 0.031 | 4.00 ± 0.012 |
| 40 | 41.49 ± 0.040 | 6.25 ± 0.023 |
| 45 | 52.78 ± 0.055 | 9.15 ± 0.019 |
4. Discussion

The lability of cobalt(II) reactants and the inertness of cobalt(III) products could be utilized as a diagnostic tool for ascertaining inner-sphere electron transfer [10, 13-15]. Oxidation of some cobalt(II) complexes by periodate, where an initial cobalt (III) product was observed, was interpreted in terms of this mechanism.

An inner-sphere mechanism is proposed for the bath way of oxidation of both two Co^{II} complexes Co^{II}(NTA)Asp(H_2O)_2]^{3-} and [Co^{II}(NTA)Val(H_2O)_2]^{2-}. This proposal seems to be supported for the following reasons:

- Formation of the initial cobalt (III) products, which were slowly converted to the final cobalt products [13, 15, 24].
- Periodate ion is capable of acting as a ligand, as evidenced from its coordination to copper(III) [25] and nickel [26].

In aqueous acidic medium the Co^{II}(NTA)Asp(H_2O)_2]^{3-} and [Co^{II}(NTA)Val(H_2O)_2]^{2-}, complexes are in equilibria:

\[ \text{Co}^{II}(\text{NTA})\text{Asp(H}_2\text{O})_2^{3-} \rightleftharpoons \left[\text{Co}^{II}(\text{NTA})\text{Asp(OH)(H}_2\text{O})\right]^{+} + \text{H}^{+} \ (K_1) \]

(5)

\[ \text{Co}^{II}(\text{NTA})\text{Val(H}_2\text{O})_2^{2-} \rightleftharpoons \left[\text{Co}^{II}(\text{NTA})\text{Val(OH)(H}_2\text{O})\right]^{+} + \text{H}^{+} \ (K_2) \]

(6)

K_1 and K_2 were potentiometrically determined as 1.38 \times 10^{-3} and 5.01 \times 10^{-7}, respectively. It was observed from values of K_1 and K_2 at the employed pH range that these equilibriums were not prevailing and the protonated Co^{II}-complex species was the predominant.

In aqueous solutions, periodate species are found in the equilibria [27].

\[ \text{H}_3\text{IO}_6^{--} \rightleftharpoons \text{H}_3\text{IO}_6^{2-} + \text{H}^{+} \ (K_3 = 1.0 \times 10^{-3}) \]

(7)

\[ \text{H}_3\text{IO}_6^{2-} \rightleftharpoons 2\text{H}_2\text{O} + \text{IO}_4^{2-} \ (K_4 = 43) \]

(8)

\[ \text{H}_3\text{IO}_6^{2-} \rightleftharpoons \text{H}_3\text{IO}_5^{2-} + \text{H}^{+} \ (K_5 = 5.0 \times 10^{-6}) \]

(9)

Thus, it may be concluded that over the [H^+] range used, the periodate species likely to be present are H_3IO_6 and H_3IO_5.

The hydrogen ion dependence of the reaction rate of both complexes is in agreement with the involvement of both deprotonated and protonated forms of periodate in the rate determining steps, proceeded by a rapid deprotonation equilibrium and in which both forms are reactive.

The concomitant reaction rate increase with the increase of ionic strength may be attributed to that the reaction rate, in the rate determining step, occurred between two species of the same sign.

In view of the above considerations, kinetics of oxidation of [Co^{II}(NTA)L(H_2O)_3]^{8-} by periodate proceeds by one first – order pathway in each reactant.

The mechanism could be described by the following equations (10-14).

\[ \text{H}_3\text{IO}_6^{--} \rightleftharpoons \text{H}_3\text{IO}_6^{2-} + \text{H}^{+} \ (K_3 = 1.0 \times 10^{-3}) \]

(10)

\[ \text{H}_3\text{IO}_6^{2-} \rightleftharpoons 2\text{H}_2\text{O} + \text{IO}_4^{2-} \ (K_4 = 43) \]

(11)

\[ \text{H}_3\text{IO}_6^{2-} \rightleftharpoons \text{H}_3\text{IO}_5^{2-} + \text{H}^{+} \ (K_5 = 5.0 \times 10^{-6}) \]

(12)

\[ \text{Co}^{II}(\text{NTA})\text{Asp(H}_2\text{O})_2^{3-} + \text{H}^{+} \ (K_1) \rightarrow \left[\text{Co}^{II}(\text{NTA})\text{Asp(OH)(H}_2\text{O})\right]^{+} \]

(13)

\[ \text{Co}^{II}(\text{NTA})\text{Val(H}_2\text{O})_2^{2-} + \text{H}^{+} \ (K_2) \rightarrow \left[\text{Co}^{II}(\text{NTA})\text{Val(OH)(H}_2\text{O})\right]^{+} \]

(14)

From the above mechanism, the rate of the reaction can be described by Equation (14),

\[ \text{Rate} = k_{10} \text{K}_6 \left[\text{Co}^{II}(\text{NTA})\text{L(H}_2\text{O})_3^{8-}\right] \left[\text{H}_3\text{IO}_6\right] \]

(15)

Substituting [H_3IO_6] from equation (7) gives,

\[ \text{Rate} = \left[\text{Co}^{II}(\text{NTA})\text{L(H}_2\text{O})_3^{8-}\right] \left[\text{H}_3\text{IO}_6\right] \]

(16)

\[ k_{10} \text{K}_6 \left( k_{11} \text{K}_5 / \text{H}^{+}\right) \]

(17)

Values of k_2 and k_3 were obtained by comparison of Equations (17) and (3), as follows:

\[ k_2 = k_{10} \text{K}_6 \text{K}_3 \]

(18)

The initial cobalt(III) product of oxidation of [Co^{II}(NTA)Asp(H_2O)_2]^{3-} by IO_4^- may be converted to final products according to the equation (18),

\[ \text{NTA(L)Co}^{II-}\text{OIO}_3^{2-} + \text{x H}_2\text{O} \rightarrow [\text{Co}^{III}\text{NTA (L(H}_2\text{O})_3]^{8-} + \text{I}^{VI} \]

(19)

In comparison, using cyclic voltammetric measurements, Co^{II}(NTA)Asp(H_2O)_2]^{3-} is difficultly oxidized at more positive potential, + 478 mV vs. SCE. While in the case of [Co^{II}(NTA)Val(H_2O)_2]^{2-} the complex is more easy oxidized at less positive potential, + 179 mV vs. SCE. Thus the sequence of stability is Asp > Val. Complexes.

According to crystal field theory, Co^{2+} has d^7 distributed as (t_2g)^5 and (e_g)^2. Increase of crystal field energy \Delta_e between t_2g and e_g orbital, by strong field ligands, labilize the free electron in e_g. Values of pK_a for valine and aspartic acid are
2.3 and 1.88 respectively, i.e. strength of conjugate bases are in the sequence Asp > Val. Therefore $\Delta_e$ for aspartate ligand is more than both valinate. Thus, loss of e$_s$ electron from the central Co$^{III}$ ion is easier in case of [Co$^{III}$(NTA)Val(H$_2$O)$_2$]$^{2-}$ than Co$^{III}$(NTA)Asp(H$_2$O)$_2$]$^{3-}$. This is consistent with the order of stability of these complexes.

The high negative entropies of activation for this reaction were climbed to be largely the result of the charge concentration on the formed encounter complex, which causes substantial mutual ordering of the solvated water molecules [28]. The intramolecular electron transfer steps are endothermic as indicated by the value of $\Delta H^*$. The contributions of $\Delta H^*$ and $\Delta S^*$ to the rate constant seem to compensate each other. This fact suggests that the reaction were climbed to be largely the result of the charge concentration on the formed encounter complex, which causes substantial mutual ordering of the solvated water molecules.

Oxidation of Co$^{II}$ complexes shows the formation of an initial Co$^{III}$ product. This may be due to the oxidation process being inner sphere. This is consistent with inner sphere oxidation which is generally proposed for IO$_3^-$ reactions. Through transformation of initial to final Co$^{II}$ product an I$^{VI}$ in the initial product is probably substituted by a water molecule with a slow rate due to inertness of Co$^{II}$ and Co$^{II}$-OIO$_3$ bond is being stronger than Co-H$_2$O bond.

5. Conclusion

Ternary Co$^{II}$ complexes involving NTA and the secondary ligand Valin and Aspartic acid are prepared and their structures were confirmed by different methods.

From the kinetic studies on the oxidation of [Co$^{II}$(NTA)(Val)(H$_2$O)$_2$]$^{2-}$ and [Co$^{II}$(NTA)(Asp)(H$_2$O)]$^{3-}$ by periodate, the following results are concluded:-

(1)-The presence of $1/[H^+]$ dependence in the acid medium of the reaction and the rate law suggests involving of the deprotonated form of the cobalt (II) complexes is the reactive species.

(2)-The using of Mn$^{II}$ as a catalyst in the reaction mixture is responsible for the oxidation of the complexes.

(3)-Oxidation of Co$^{II}$(NTA)(Val)(H$_2$O)$_2$]$^{2-}$ and [Co$^{II}$(NTA)(Asp)(H$_2$O)]$^{3-}$ is a first –order reaction with respect to [Co$^{II}$(NTA)(Asp)(H$_2$O)]$^{3-}$.

(4)-The rate of oxidation of [Co$^{III}$(NTA)(Asp)(H$_2$O)]$^{3-}$ is faster than [Co$^{III}$(NTA)(Val)(H$_2$O)$_2$]$^{2-}$ as evidenced from the two complexes.

(5)-The high negative entropies of activation for which reaction were climbed to be largely the result of the charge concentration on the formed encounter complex, which causes substantial mutual ordering of the solvated molecules of the solvated complex. The intramolecular electron transfer steps are endothermic as indicated by the value of $\Delta H^*$.

The contributions of $\Delta H^*$ and $\Delta S^*$ to the rate constant seem to compensate each other. This fact suggests that the factor controlling $\Delta H^*$ must be closely related to those controlling $\Delta S^*$. Therefore, the solubility state of the encounter complex would be important in determining $\Delta H^*$. Thus, the relatively small enthalpy of activation, $\Delta H^*$, can be explained in terms of the formation of more solved complex.

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