

Kinetic and Mechanistic Studies of Oxidation of Amine-N-Polycarboxylates Complexes of Cobalt(II) by Periodate Ions in Aqueous Medium

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The kinetics and mechanism of interaction of periodate ion with $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ [L = trimethylenediaminetetraacetic acid (TMDTA)] and ethylene glycol bis(2-aminoethyl ether) N,N,N',N'-tetraacetic acid (EGTA) have been studied spectrophotometrically by following an increase in absorbance at $\lambda_{\text{max}} = 550 \text{ nm}$ in acetate buffer medium as a function of pH, ionic strength, temperature, various concentration of periodate and $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ under pseudo-first order conditions. The experimental observations have revealed that the intermediates having sufficiently high half life are produced during the course of both the reactions which finally get converted into a corresponding $[\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})]^{3-n}$ complexes as a final reaction product. The reaction is found to obey the general rate law $\text{Rate} = (k_2 [\text{IO}_4^-] + k_3 [\text{IO}_4^-]^2) [\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$. This rate law is consistent with a four step mechanistic scheme (vide supra) where electron transfer proceeds through an inner sphere complex formation. The value of rate constant k_2 is independent of pH over the entire pH range which suggest that unprotonated form of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ is the only predominant species. The value of k_2 is invariant to ionic strength variation in both the systems. The value of k_3 is also found to be almost invariant to ionic strength in case of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}-[\text{IO}_4^-]$ system but it decreases considerably in case of $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}-[\text{IO}_4^-]$ system with the corresponding decrease in ionic strength. The activation parameters have been computed and given in support of proposed mechanistic scheme.

Keywords: Kinetics and mechanism, Electron transfer, $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$, TMDTA, EGTA, Periodate

INTRODUCTION

There has been plenty of studies on the oxidation of several inorganic [1-4] and organic [5-6] substrate by periodate ion in aqueous medium. In the past several years, the periodate ion oxidation of varieties of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ complexes (L = EDTA, HEDTA, NTA, DTPA, PDTA, and HPDTA) have been the subject of interest for several investigators including us [10]. The comprehensive kinetic and spectroscopic studies have shown that the oxidations of

periodate ion proceeds through an inner-sphere electron transfer mechanism involving the formation of precursor complexes of the type $[\text{LCo}^{\text{II}}\text{-OIO}_3]^{1-n}$ and $[\text{LCo}^{\text{II}}\text{-(OIO}_3)_2]^{1-n}$ which eventually get converted slowly to produce $[\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})]^{3-n}$ complex as final reaction product. A similar type of inner sphere electron transfer process was also observed in the reaction of periodate ions with aqua-ions of V(IV) [2], Fe(II) [4], and Cr(III) [11]. The recent studies on the VO_2^+ oxidation of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ [L = HEDTA and EDTA] [12-13] have further revealed the formation of an intermediate which converted slowly to penta-co-ordinated $[\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})]^{3-n}$ as final reaction product and provides

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additional support to the proposed mechanistic scheme (vide supra) for the reacting system at hand.

Therefore, as an attempt to verify the consistency in the kinetics of oxidation of amine-N-polycarboxylates complexes of Co(II) by periodate ions. We have considered it worthwhile to investigate the kinetics and mechanism of oxidation of two more $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ complexes [where L = trimethylene diaminetetraaceticacid (TMDTA) and ethylene glycol bis(2-aminoethyl ether) N,N,N',N'-tetraaceticacid (EGTA)] by periodate ion in acidic buffer medium is in further confirmation of our earlier proposed mechanistic scheme. The experimental results obtained from the present study enabled us to suggest that the oxidation of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ by periodate ion proceeds through two parallel pathways where the unprotonated forms of Co(II) complex as well as of periodate ion were the predominant reacting species under the chosen experimental conditions.

EXPERIMENTAL

Materials

Fresh solution of sodium meta periodate was prepared and wrapped with aluminium foil to avoid photochemical decomposition [14]. The ligand trimethylenediaminetetraaceticacid (TMDTA) was prepared by an excellent method described by Weyh and Ham [15] in good yield, the ligand ethylene glycol bis(2-aminoethyl ether) N,N,N',N'-tetraaceticacid (EGTA) was obtained from (CDH, India) and used without any further purification. Calculated amount of the ligands *viz.* TMDTA and EGTA were used for preparing their stock solutions by adding appropriate amount of sodium hydroxide (BDH) in order to dissolve them properly in the solution. Solution of Co(II) nitrate (Merck) was prepared and standardized against EDTA volumetrically. Sodium acetate and sodium nitrate (BDH) were prepared by weighing their calculated amounts. The standard solution of acetic acid (A.R. BDH) was prepared by titrating it against sodium hydroxide using phenolphthaline indicator. Doubly distilled water was used for preparing all the required solutions.

Apparatus and Kinetic Measurements

The progress of reaction was monitored by using a

Shimadzu double beam spectrophotometer model UV-240 equipped with a thermostated cell compartment. The UV-visible spectrum of reactants and products as well as the repetitive spectral scans of the reaction mixture were also recorded using the above stated spectrophotometer. A digital pH meter model (CL-46 India) was standardized from time to time using a standard buffers of pH = 4.0 and 7.0 before measuring the pH of desired solutions.

The kinetics of oxidation of both the $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ complexes by periodate ions was carried out under pseudo first order condition as a function of concentration, pH, ionic strength and temperature. The reaction have been investigated at $\lambda_{\text{max}} = 550 \text{ nm}$ where $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ and IO_4^- have negligible absorption. The fresh solutions of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ were prepared by using stoichiometric amounts of cobalt nitrate and at least 10% excess of TMDTA as well as EGTA in order to ensure complete complexation. It is to be noted that the excess ligand taken in the above preparation further reduces the possibility of any catalysis of periodate oxidations due to trace metal ions such as Cu(II) [16] and Mn(II) [17] present as impurities for periodate oxidation. The fresh solutions of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ complexes were prepared by the method discuss above immediately before each kinetic run in order to minimize any air oxidation of cobalt(II) complexes as reported in literature [18-19]. The kinetics of oxidation of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ complexes were studied in pH range 2.0-5.0 where the air oxidation of cobalt(II) complexes were negligible. The plots of $\log(A_\infty - A_t)$ *vs.* time exhibit reasonably good linearity over 90% of the reaction. The value of pseudo-first order rate constant were computed from the slopes of these plots.

RESULTS AND DISCUSSION

Effect of $[\text{IO}_4^-]$ on Its Reaction with $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$

The kinetics of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ oxidation by periodate were studied spectrophotometrically at $\lambda_{\text{max}} = 550 \text{ nm}$, pH = 4.00 ± 0.02 , I = 0.1 M ($\text{CH}_3\text{COONa} + \text{NaNO}_3$) and temperature = 15.0 ± 0.1 °C, 20.0 ± 0.1 °C, and 25.0 ± 0.1 °C under pseudo-first order condition by taking large excess of periodate concentration over $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$. The plots of $\log(A_\infty - A_t)$ *vs.* time were

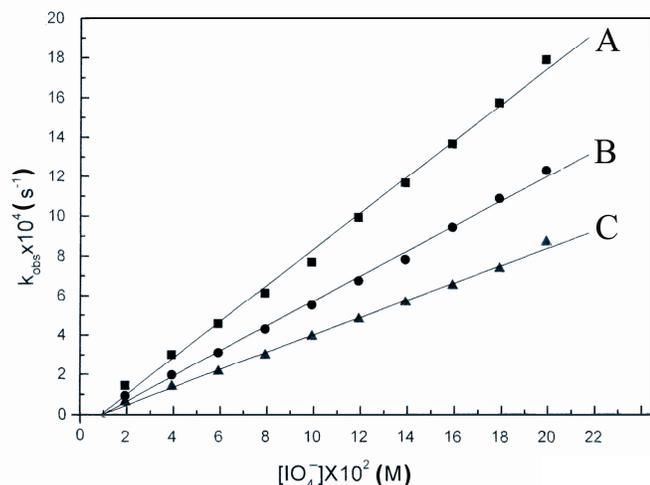


Fig. 1. The periodate concentration dependence of observed rate constant for $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{-2}$ - $[\text{IO}_4^-]$ reaction system at three different temperatures: (A) 25 °C, (B) 20 °C, (C) 15 °C. Conditions: $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{-2}$, 2.0×10^{-3} M; I, 0.1 M ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$); pH, 4.00 ± 0.02 .

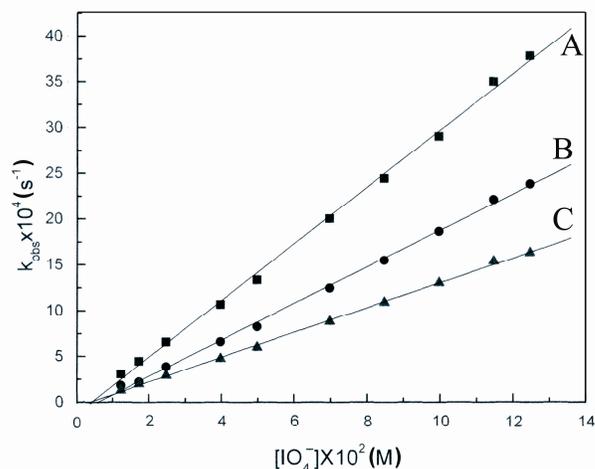


Fig. 2. The periodate concentration dependence of observed rate constant for $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{-2}$ - $[\text{IO}_4^-]$ reaction system at three different temperatures: (A) 25 °C, (B) 20 °C, (C) 15 °C. Conditions: $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{-2}$, 1.25×10^{-3} M; I, 0.1 M ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$); pH, 4.0 ± 0.02 .

found to be linear up to 90% of the reactions where A_∞ and A_t are absorbances at infinity and time t , respectively. The values of pseudo first order rate constants (k_{obs}) were determined in each case from the slopes of the above plot. It was also observed that the values of k_{obs} increases with increasing concentration of periodate ion. Figures 1 and 2 show that the linear least square computed fits of the plots of k_{obs} vs. $[\text{IO}_4^-]$ yields a straight line.

The linear least square computed fits of the plots of $k_{\text{obs}}/[\text{IO}_4^-]$ vs. $[\text{IO}_4^-]$ were found to be linear in both systems (Figs. 3 and 4). The dependence of k_f on $[\text{IO}_4^-]$ was found to be consistent with Eq. (1).

$$\frac{k_{\text{obs}}}{[\text{IO}_4^-]} = k_2 + k_3 [\text{IO}_4^-] \quad (1)$$

The values of k_2 and k_3 were calculated from the intercepts and slopes of linear least square computed plots as given in Figs. 3 and 4 at three different temperatures. The variations of

k_2 and k_3 with temperature for both the systems are compiled in Table 1. The value of k_2 obtained from intercepts of the plots given in Figs. 3 and 4 are in fairly good agreement with the value of (k_f) .

Effect of Complex Concentration on Reaction of $[\text{IO}_4^-]$ with $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$

At experimental conditions pH = 4.00 ± 0.02 , I = 0.1 M ($\text{CH}_3\text{COONa} + \text{NaNO}_3$), $[\text{IO}_4^-] = 6.0 \times 10^{-2}$ M, for $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{-2}$ - $[\text{IO}_4^-]$, and pH = 4.00 ± 0.02 , and I = 0.1 M ($\text{CH}_3\text{COONa} + \text{NaNO}_3$), $[\text{IO}_4^-] = 2.0 \times 10^{-2}$ M for $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{-2}$ - $[\text{IO}_4^-]$, the variations in rate constant with increasing complex concentration were studied at three different temperatures. The dependence of rate on $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ was found to be invariant within the chosen concentration range (Tables 2 and 3). The values of k_f ($k_f = k_{\text{obs}}/[\text{IO}_4^-]$) also do not depend on the concentration of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{-2}$ as well as $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{-2}$.

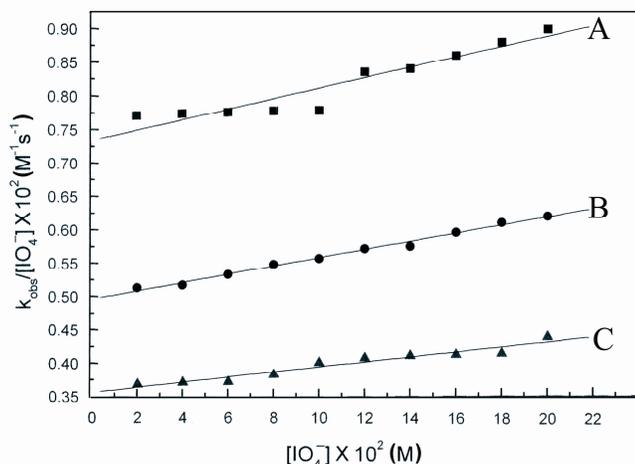


Fig. 3. The periodate concentration dependence of forward rate constant for $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$ - $[\text{IO}_4^-]$ reaction at different temperatures: (A) 25 °C, (B) 20 °C, (C) 15 °C. Conditions: same as Fig. 1.

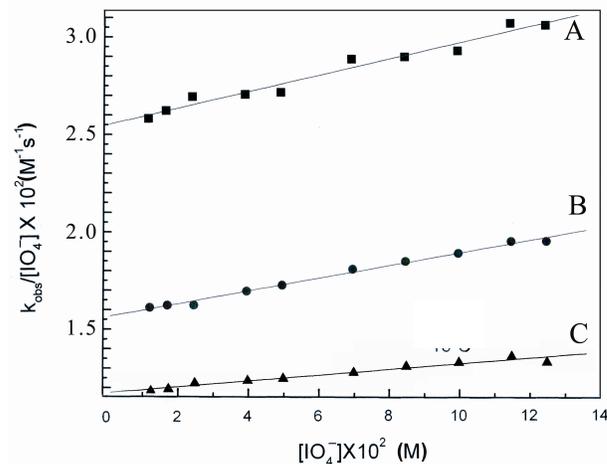


Fig. 4. The periodate concentration dependence of forward rate constant for $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{2-}$ - $[\text{IO}_4^-]$ reaction different temperatures: (A) 25 °C, (B) 20 °C, (C) 15 °C. Conditions: same as Fig. 2.

Table 1. Variation of k_2 and k_3 with Temperature^a

Reaction system	$10^2 \times k_2$ ($\text{M}^{-1} \text{s}^{-1}$)			$10^2 \times k_3$ ($\text{M}^{-2} \text{s}^{-1}$)		
	15.0 °C	20.0 °C	25.0 °C	15.0 °C	20.0 °C	25.0 °C
$[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$ - $[\text{IO}_4^-]$	0.36 ± 0.03	0.49 ± 0.02	0.74 ± 0.03	0.39 ± 0.04	0.63 ± 0.02	0.79 ± 0.02
$[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{2-}$ - $[\text{IO}_4^-]$	1.17 ± 0.05	1.56 ± 0.04	2.54 ± 0.05	1.36 ± 0.05	3.18 ± 0.06	4.13 ± 0.05

^a $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-} = 2.0 \times 10^{-3} \text{ M}$; $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{2-} = 1.25 \times 10^{-3} \text{ M}$, $\text{pH} = 4.0 \pm 0.02$, $I = 0.1 \text{ M}$ ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$).

Effect of pH on the Reaction of $[\text{IO}_4^-]$ with $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$

The effect of pH on oxidation of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{2-}$ complexes by periodate ion was investigated in pH range 2.0-5.0, keeping all other variables constant. The data represented in Tables 4 and 5 show that the rate constants k_{obs} and k_f do not depend on the pH of the reaction medium in both systems. This indicates that the $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ complexes mostly exist in their unprotonated form during the course of reaction. However, the oxidation of $[\text{Co}^{\text{II}}\text{HEDTA}(\text{H}_2\text{O})]^{1-}$ by vanadate ion in aqueous medium has been reported to be depend on the pH of solution with

maximum rate of reaction at $\text{pH} = 2.1$ [12].

Effect of Ionic Strength on the Reaction of $[\text{IO}_4^-]$ with $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$

The rate of oxidation of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})_2]^{2-}$ by periodate ion was investigated as a function of ionic strength in the range 0.1-0.4 and 0.05-0.3, respectively, keeping all other variables constant. The values of k_2 and k_3 were computed for both the systems at different ionic strengths from the intercepts and slopes of $k_{\text{obs}}/[\text{IO}_4^-]$ vs. $[\text{IO}_4^-]$ plots, respectively, and compiled in Table 6. As seen, k_2 is almost invariant to ionic strength variation in both the

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Table 2. First Order Dependence on $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ at $[\text{IO}_4^-] = 6.0 \times 10^{-2} \text{ M}$, $\text{pH} = 4.00 \pm 0.02$, $I = 0.1 \text{ M}$ ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$)

$[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-} \times 10^3$ (M)	$10^4 \times k_{\text{obs}} (\text{s}^{-1})$			$10^2 \times k_f (\text{M}^{-1} \text{s}^{-1})$		
	15.0 °C	20.0 °C	25.0 °C	15.0 °C	20.0 °C	25.0 °C
0.5	2.19	3.38	4.60	3.65	5.63	7.67
1.0	2.25	3.47	4.74	3.75	5.78	7.90
2.5	2.14	3.33	4.52	3.57	5.55	7.53
3.0	2.17	3.36	4.58	3.62	5.60	7.63
4.0	2.20	3.40	4.65	3.67	5.67	7.75
5.0	2.25	3.45	4.70	3.75	5.75	7.83
(Average)	2.20 ± 0.04	3.40 ± 0.05	4.63 ± 0.07	3.67 ± 0.07	5.66 ± 0.08	7.72 ± 0.12

Table 3. First Order Dependence on $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ at $[\text{IO}_4^-] = 2.0 \times 10^{-2} \text{ M}$, $\text{pH} = 4.00 \pm 0.02$, $I = 0.1 \text{ M}$ ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$)

$[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-} \times 10^3$ (M)	$10^4 \times k_{\text{obs}} (\text{s}^{-1})$			$10^2 \times k_f (\text{M}^{-1} \text{s}^{-1})$		
	15.0 °C	20.0 °C	25.0 °C	15.0 °C	20.0 °C	25.0 °C
0.20	2.51	3.61	5.30	1.26	1.81	2.65
0.25	2.54	3.67	5.36	1.27	1.84	2.68
0.30	2.57	3.68	5.39	1.29	1.84	2.69
0.35	2.57	3.70	5.41	1.29	1.85	2.71
0.40	2.51	3.61	5.28	1.26	1.81	2.64
0.50	2.53	3.62	5.33	1.27	1.81	2.66
(Average)	2.54 ± 0.02	3.65 ± 0.04	5.35 ± 0.05	1.27 ± 0.01	1.83 ± 0.02	2.67 ± 0.02

Table 4. Effect of pH on the Reaction of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ with $[\text{IO}_4^-]$ at $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-} = 4.0 \times 10^{-3} \text{ M}$, $[\text{IO}_4^-] = 6.0 \times 10^{-2} \text{ M}$, $I = 0.1 \text{ M}$ ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$)

pH	$[\text{H}^+] \times 10^5$	$10^4 \times k_{\text{obs}} (\text{s}^{-1})$			$10^3 \times k_f (\text{M}^{-1} \text{s}^{-1})$		
		15.0 °C	20.0 °C	25.0 °C	15.0 °C	20.0 °C	25.0 °C
4.0	10.00	2.21	3.42	4.65	3.68	5.70	7.75
3.5	31.62	2.09	3.22	4.39	3.48	5.37	7.32
3.0	100.00	2.14	3.31	4.51	3.57	5.52	7.52
2.5	316.23	2.19	3.38	4.62	3.65	5.63	7.70
2.0	1000.00	2.21	3.41	4.65	3.68	5.68	7.75
(Average)		2.17 ± 0.07	3.35 ± 0.07	4.56 ± 0.07	3.61 ± 0.060	5.58 ± 0.06	7.61 ± 0.06

Table 5. Effect of pH on the Reaction of $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ with $[\text{IO}_4^-]$ at $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-} = 1.25 \times 10^{-3} \text{ M}$, $[\text{IO}_4^-] = 2.0 \times 10^{-2} \text{ M}$, $I = 0.1 \text{ M}$ ($\text{NaNO}_3 + \text{CH}_3\text{COONa}$)

pH	$[\text{H}^+] \times 10^5$	$10^4 \times k_{\text{obs}} \text{ (s}^{-1}\text{)}$			$10^3 \times k_f \text{ (M}^{-1} \text{ s}^{-1}\text{)}$		
		15.0 °C	20.0 °C	25.0 °C	15.0 °C	20.0 °C	25.0 °C
4.99	1.02	2.54	3.66	5.35	1.27	1.83	2.67
4.63	2.34	2.52	3.62	5.30	1.26	1.81	2.65
4.27	3.39	2.53	3.64	5.33	1.27	1.82	2.66
3.72	19.05	2.51	3.62	5.29	1.26	1.81	2.64
3.42	38.02	2.52	3.63	5.31	1.26	1.82	2.65
(Average)		2.52 ± 0.03	3.63 ± 0.03	5.32 ± 0.03	1.26 ± 0.001	1.82 ± 0.01	2.65 ± 0.01

Table 6. Effect of Ionic Strength Variation on the Reaction of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-}$ with $[\text{IO}_4^-]$ at $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-} = 4.0 \times 10^{-3} \text{ M}$, $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-} = 1.25 \times 10^{-3} \text{ M}$, $\text{pH} = 4.00 \pm 0.02$, $\text{Temp.} = 25.0 \pm 0.1 \text{ °C}$

Reaction system	I (M)	$10^2 \times k_2 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$10^2 \times k_3 \text{ (M}^{-2} \text{ s}^{-1}\text{)}$
$[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}-[\text{IO}_4^-]$	0.400	0.742	0.144
	0.200	0.735	0.122
	0.150	0.740	0.109
	0.100	0.730	0.092
$[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}-[\text{IO}_4^-]$	0.300	2.532	8.760
	0.275	2.563	7.502
	0.250	2.550	5.981
	0.100	2.542	4.553
	0.050	2.501	3.290

systems. On the other hand the value of k_3 is almost constant in case of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}-[\text{IO}_4^-]$ system and decreases remarkably in the case of $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}-[\text{IO}_4^-]$ system with the corresponding decrease in ionic strength of the medium.

Effect of Temperature on the Reaction of $[\text{IO}_4^-]$ with $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$

The influence of temperature on oxidation of both $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ by periodate ion was studied in the temperature range 288-298 K. The activation parameters corresponding to k_2 and k_3 were

calculated using the Arrhenius and Eyring equations. The values of evaluated activation parameters are compiled in Table 7.

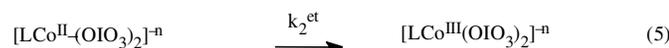
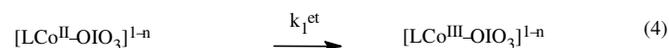
In both cases, the oxidation of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-}$ to $[\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})]^{1-}$ by periodate ion is thermodynamically favorable. The mechanism of oxidation of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ by periodate seems to proceed *via* an inner-sphere electron transfer mechanism in which an intermediate Co(III) complex is formed which finally gives the desired product. The first path exhibits a first order dependence in each reactant. In the second path, the rate of reaction is third order, first order in

Table 7. Activation Parameters for Reactions Associated with k_2 and k_3

Reaction system	E_a (kJ M ⁻¹)	(ΔH^\ddagger) (kJ M ⁻¹)	(ΔS^\ddagger) (J M ⁻¹ K ⁻¹)	Reaction condition
[Co ^{II} TMDTAH ₂ O] ²⁻				[Co ^{II} TMDTAH ₂ O] ²⁻ = 2.0 × 10 ⁻³ M, pH = 4.0 ± 0.02, I = 0.1 M (NaNO ₃ + CH ₃ COONa)
k_2	56.52	54.04	-284.82	
k_3	52.36	49.88	-283.82	
[Co ^{II} EGTA(H ₂ O)] ²⁻				[Co ^{II} EGTA(H ₂ O)] ²⁻ = 1.25 × 10 ⁻³ M, pH = 4.0 ± 0.02, I = 0.1 M (NaNO ₃ + CH ₃ COONa)
k_2	57.93	55.45	-279.50	
k_3	82.46	79.98	-272.02	

each [Co^{II}L(H₂O)]²⁻ⁿ complex and second order in the oxidant concentration.

The following most possible mechanistic scheme is proposed through equations (2-5):



where L = EGTA and TMDTA and (-n) is the charge on each ligand. The experimental observations and its confirmation with our earlier proposed mechanisms for the oxidations of [Co^{II}L(H₂O)]²⁻ⁿ (L = PDTA, HPDTA) by periodate ions [10] gives further support to the proposed mechanism. The general rate law for the above reactions can be given by equation (6).

$$\text{Rate} = k_f [\text{Co}^{\text{II}}\text{L}^{2-n}] [\text{IO}_4^-] \quad (6)$$

Since periodate ion is present in large excess, equation (6) can be transformed to equation (7)

$$\text{Rate} = k_{\text{obs}} [\text{Co}^{\text{II}}\text{L}^{2-n}] \quad (7)$$

where

$$k_{\text{obs}} = k_f [\text{IO}_4^-] \quad (8)$$

Equation (8) is valid for the first pathway only if step (4) is

considered as the rate determining step.

$$\text{Rate} = k_1^{\text{et}} [\text{LCo}^{\text{II}}\text{-OIO}_3]^{1-n} \quad (9)$$

Equation (9) is further reduced to equation (10) with the help of equation (2).

$$\text{Rate} = K_1 k_1^{\text{et}} [\text{Co}^{\text{II}}\text{L}^{2-n}] [\text{IO}_4^-] \quad (10)$$

Comparison of equations (6) and (10) gives:

$$k_f = K_1 k_1^{\text{et}} \quad (11)$$

Thus the slope of the plot of k_{obs} vs. $[\text{IO}_4^-]$ is found to be equal to $K_1 k_1^{\text{et}} = k_f$. Hence the experimental and theoretical rate law for the first pathway are the same provided $k_f = K_1 k_1^{\text{et}}$.

Since the periodate ion is present in large excess, a second IO_4^- ion further adds to form $[\text{LCo}^{\text{II}}\text{(OIO}_3)_2]^{1-n}$ as an intermediate. In this situation, both steps (4) and (5) are to be considered simultaneously as the rate determining step for the second pathway of reaction and the rate law is given by equation (12).

$$\text{Rate} = k_1^{\text{et}} [\text{LCo}^{\text{II}}\text{-OIO}_3]^{1-n} + k_2^{\text{et}} [\text{LCo}^{\text{II}}\text{-(OIO}_3)_2]^{1-n} \quad (12)$$

Equation (12) can be further transformed to equation (13) with the help of equations (2) and (3).

$$\text{Rate} = k_1^{\text{et}} K_1 [\text{Co}^{\text{II}}\text{L}^{2-n}] [\text{IO}_4^-] + k_2^{\text{et}} K_1 K_2 [\text{Co}^{\text{II}}\text{L}^{2-n}] [\text{IO}_4^-]^2$$

or

$$\text{Rate} = \{k_1^{\text{et}} K_1 + k_2^{\text{et}} K_1 K_2 [\text{IO}_4^-]\} [\text{Co}^{\text{II}}\text{L}^{2-n}] [\text{IO}_4^-] \quad (13)$$

Now on comparing equation (13) with equation (6) one gets.

$$k_f = k_1^{\text{et}} K_1 + k_2^{\text{et}} K_1 K_2 [\text{IO}_4^-] \quad (14)$$

From equation (14) and equation (8) we get

$$\frac{k_{\text{obs}}}{[\text{IO}_4^-]} = k_1^{\text{et}} K_1 + K_1 K_2 k_2^{\text{et}} [\text{IO}_4^-] \quad (15)$$

The theoretical rate law for the second path of reaction given by equation (15) is in agreement with the empirical experimental rate law given by equation (1), where $k_2 = k_1^{\text{et}} K_1$ and $k_3 = K_1 K_2 k_2^{\text{et}}$

The existence of initial Co(III) products in the systems under investigation render additional support in favor of the above proposed mechanism. The oxidation process having second order dependence in $[\text{IO}_4^-]$, probably proceeds *via* an inner-sphere mechanism as well. This conclusion is also in line with the hypothesis that periodate is an inner-sphere oxidant [1,3-5]. Two periodate ions could substitute a water molecule and set free a carboxylate arm in $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$. A second order dependence in $[\text{IO}_4^-]$ was also reported in its reaction with V(IV) [20], and precursor $[\text{VO}(\text{IO}_4)_2]$. The possibility of second order dependence in $[\text{IO}_4^-]$ due to dimerization of periodate ion is ruled out as this process takes place at higher pH values [21].

The fairly constant values of pseudo-first order rate constant k_{obs} with increasing value of pH of reaction medium (Tables 4 and 5) clearly shows that the unprotonated forms of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ are the predominant reacting species with periodate ion throughout the entire pH region. The structures of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ and $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ are not known in solution phase or in solid phase. However, the penta co-ordination of Ni(II) complexes with EDTA, PDTA, and TMDTA has been verified in an aqueous solution by Evilia [22].

In absence of the structures of the complexes under investigation, the exact nature of the reactivities of protonated and unprotonated forms of the above complexes could not be understood. However, on the basis of protonation constants of the complexes, it can be inferred that the unprotonated forms of these complexes are stable and their reaction with periodate ion is slower in comparison to their protonated counterparts. A similar conclusion were made by Y. Sulfab *et al.* [9] on $[\text{Co}^{\text{II}}\text{DTPA}(\text{H}_2\text{O})]^{3-}$ - $[\text{IO}_4^-]$ system and also by Anis and Mansour on $[\text{Cr}^{\text{III}}\text{NTMP}]$ - $[\text{IO}_4^-]$ system [11]. The NMR study shows that the three nitrogens of deprotonated forms of DTPA are coordinated to Co(II). The proton addition decreases the number of coordinated nitrogens [23]. The conclusion is also in further agreement with $[\text{Cu}^{\text{II}}\text{DTPA}]$ complexes proposed by Chabarek *et al.* [24].

As is obvious from Table 6, the k_2 values for both complexes and also k_3 values for $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ are almost invariant but k_3 values for $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ decreased by decreasing ionic strength. Therefore, it has a positive effect on k_3 values.

The evaluated values of heat of activation (ΔH^\ddagger) corresponding to the rate constant k_2 is relatively high in comparison to k_3 for $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ - $[\text{IO}_4^-]$ system. This is probably attributed to the formation of $[\text{Co}^{\text{II}}\text{OIO}_3]^{1-n}$ species in an endothermic manner. The entry of second periodate ion to $[\text{LCo}^{\text{II}}\text{-OIO}_3]^{1-n}$ is probably exothermic in nature and thus has relatively low value of enthalpy of activation for $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ - $[\text{IO}_4^-]$ system. On the other hand, the low values of enthalpy of activation corresponding to k_2 in comparison to k_3 in the case of $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ - $[\text{IO}_4^-]$ system probably accounts for the exothermic and endothermic behaviors, respectively, due to the formation of $[\text{LCo}^{\text{II}}\text{-OIO}_3]^{1-n}$ and $[\text{LCo}^{\text{II}}\text{-OIO}_2]^{1-n}$ species during the course of reaction.

Finally, the repetitive spectral scan of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})]^{2-}$ - $[\text{IO}_4^-]$ reaction system (Fig. 5) reveals that there is a continuous increase in absorbance with time at both 375 nm and 550 nm. This increase in absorbance as a function of time is attributed to the formation of a Co(III) intermediate. The absorbance at 375 nm and 550 nm were finally found to decrease after 110 min (Fig. 5) of reaction. This suggests the conversion of Co(III) intermediate to other final product. The kinetics of conversion of this Co(III)

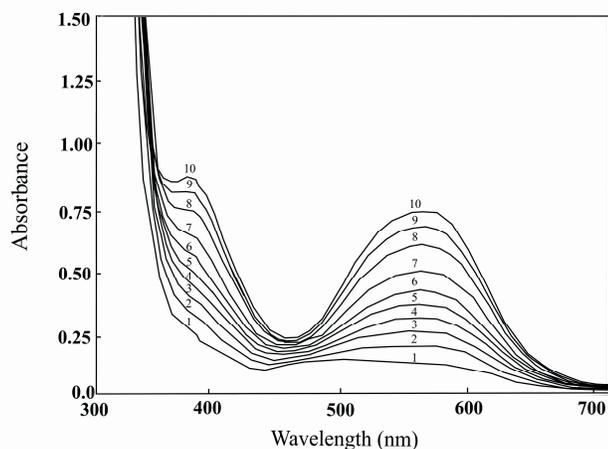


Fig. 5. Time dependence of electronic spectrum of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$ - $[\text{IO}_4^-]$ system. The time periods are: (1) 0, (2) 5, (3) 12, (4) 25, (5) 35, (6) 50, (7) 65, (8) 80, (9) 95, and (10) 110 min. Conditions: $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$, 2.0×10^{-3} M; pH, 4.00 ± 0.02 ; I, 0.1 M ($\text{CH}_3\text{COONa} + \text{NaNO}_3$); $[\text{IO}_4^-]$, 6.0×10^{-2} M; Temp., 25.0 ± 0.1 °C.

intermediate was not studied in detailed. However, preliminary kinetic observations made on the conversion of Co(III) intermediate suggest that the rate of reaction is extremely slow. The final form of spectrum is almost identical to the spectra of $[\text{Co}^{\text{III}}\text{TMDTA}(\text{H}_2\text{O})]^{1-}$ which is the final product of oxidation of $[\text{Co}^{\text{II}}\text{TMDTA}(\text{H}_2\text{O})_2]^{2-}$ by periodate ion. An exactly similar behavior was also observed in the case of $[\text{Co}^{\text{II}}\text{EGTA}(\text{H}_2\text{O})]^{2-}$ - $[\text{IO}_4^-]$ reaction system. Thus, it can be concluded that $[\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})]^{3-n}$ is the final product in the oxidations of $[\text{Co}^{\text{II}}\text{L}(\text{H}_2\text{O})]^{2-n}$ by periodate ion.

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REFERENCES

[1] Y. Salfab, J. Inorg. Nucl. Chem. 38 (1976) 2271.

- [2] Y. Sulfab, A.L. Abu-Shadi, Inorg. Chem. Acta 21 (1977) 115.
- [3] A.Y. Kasim, Y. Sulfab, Inorg. Chem. Acta 24 (1977) 247.
- [4] F.R. El-Eziri, Y. Sulfab, Inorg. Chem. Acta 25 (1977) 15.
- [5] G.J. Buist, in: C.H. Boneford, C.F.H. Tripper (Eds.), Comprehensive Chemical Kinetics, Elsevier Amsterdam, 1972, pp. 435-456.
- [6] A. Indelli, F. Ferranti, F. Secco, J. Phys. Chem. 70 (1966) 631.
- [7] A.A. Abdel-Khalek, Y. Sulfab, J. Inorg. Nucl. Chem. 43 (1981) 3257.
- [8] M.A. Hussein, A.A. Abdel-Khalek, Y. Sulfab, J. Chem. Soc. Dalton Trans. (1983) 317.
- [9] Y. Sulfab *et al.*, Polyhedron 9 (1990) 99.
- [10] R.M. Naik, J. Sarkar, D.D. Chaturvedi, A. Verma, S.K. Singh Indian J. Chem. Sec. 42A (2003) 1639.
- [11] S.S. Anis, M.A. Mansour, Trans. Metal. Chem. 26 (2001) 695.
- [12] M.A. Mansour, Trans. Metal. Chem. 28 (2003) 276.
- [13] G.R. Babu, K. Ramakrishna, G. Venkateswarlu, P.V. Subba Rao, Indian J. Chem. 42A (2003) 1053.
- [14] F.S.H. Head, H.A. Standing, J. Chem. Soc. (1957) 1457.
- [15] J.A. Wegh, R.E. Hasmm, Inorg. Chem. 7 (1968) 2431.
- [16] D.H. Huchital, R.J. Hodges, Inorg. Chem. Acta 12 (1973) 1004.
- [17] H.A. Mottala, H. Freiser, Anal. Chem. 39 (1967) 1294.
- [18] A.Y. Kasim, Y. Sulfab, Inorg. Chem. Acta 22 (1977) 169.
- [19] E. Norkus, A. Vas Kelis, A. Griguociene, G. Rohovskrs, H.S.J. Reklai, P. Norkus, Trans. Metal. Chem. 26 (2001) 465.
- [20] D.J.B. Galiford, J.M. Ottaway, Analyst 91 (1972) 415.
- [21] B.J. Buist, W.C.P. Hipperson, J.D. Lewis, J. Chem. Soc. A (1969) 307.
- [22] D.S. Everhart, R.F. Evilia, Inorg. Chem. 14 (1975) 27.
- [23] L.L. Grazyński, B.J. Trzebiatowska, Coord. Chem. 10 (1980) 159.
- [24] S. Chabarek, A.E. Frost, M.A. Doran, N.J. Bicknell, J. Inorg. Nucl. Chem. 11 (1959) 184.