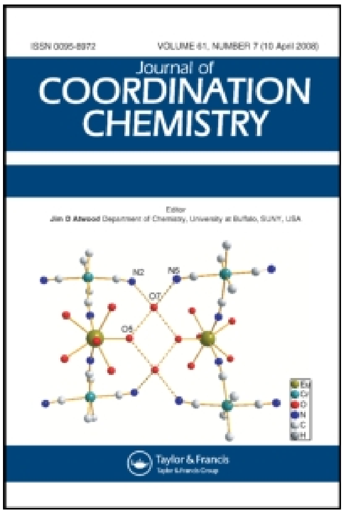

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Kinetics and mechanism of the oxidation of a ternary complex of cobalt(II) involving nitrilotriacetate and benzoate by periodate in acetate medium. Evidence for manganese(II) as a catalyst

Hassan A. Ewais[a]
[a] Faculty of Science, Chemistry Department, Beni-Suef University, Beni-Suef City, Egypt

To cite this Article Ewais, Hassan A.(2009) 'Kinetics and mechanism of the oxidation of a ternary complex of cobalt(II) involving nitrilotriacetate and benzoate by periodate in acetate medium. Evidence for manganese(II) as a catalyst', Journal of Coordination Chemistry, 62: 6, 940 — 950

To link to this Article: DOI: 10.1080/00958970802381190

URL: http://dx.doi.org/10.1080/00958970802381190

Journal of Coordination Chemistry
Vol. 62, No. 6, 20 March 2009, 940–950

Kinetics and mechanism of the oxidation of a ternary complex of cobalt(II) involving nitrilotriacetate and benzoate by periodate in acetate medium. Evidence for manganese(II) as a catalyst

HASSAN A. EWAIS*

Faculty of Science, Chemistry Department, Beni-Suef University,
Beni-Suef City, Egypt

(*Received 15 January 2008; in final form 6 June 2008*)

Kinetics of the oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ (nta = nitrilotriacetate and bz = benzoate) by periodate in acetate medium have been investigated spectrophotometrically at 580 nm under pseudo first order condition by taking large excess of IO_4^- over the 15.0–35.0°C range at pH = 4.99 and $I = 0.50$ M. The kinetics in acetate medium obeyed the rate law:

$$\frac{d[Co^{III}]}{dt} = (k_2 + k_3[CH_3CO_2^-])[Co^{II}(nta)(bz)(H_2O)_2]^{2-}[IO_4^-]$$

Also, the oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate in the presence of Mn(II) as a catalyst was carried out. The rate of reaction increases as the concentration of Mn(II) increases. Initial cobalt(III) products were formed and slowly converted to final products, fitting an inner-sphere mechanism. The enthalpy and entropy of activation were measured using the transition state theory equation.

Keywords: Kinetic studies; Nitrilotriacetic acid; Ternary complexes of cobalt(II); Periodate oxidation; Thermodynamic activation parameters

1. Introduction

The activity of periodic acid as an oxidizing agent varies as a function of pH; periodate is a stronger oxidant in acid medium than alkaline medium. The reduction potential of the IO_4^-/IO_3^- couple is +1.6 V and +0.70 V in acid and alkaline media, respectively [1]. Oxidations of inorganic substrates [2–4] and transition metal complexes [5–8] by periodate are reported to proceed through an inner-sphere mechanism. Periodate readily oxidizes either labile or inert complexes possessing at least one bridging ligand. Initial cobalt(III) products that were transformed to the final cobalt(III) products were slowly identified spectrophotometrically [5–8].

---

*Email: hshalby2002@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802381190

Oxidations by periodate are catalyzed with trace amounts of metal ions [2, 9, 10]. Iron(II) catalyzes oxidation of chromium(III)-DL-aspartic acid complex by periodate in acetate buffer, due to formation of iron(III) which acts as the oxidizing agent [9]. Catalysis by Cu(II) in oxidation of $Fe(CN)_6^{4-}$ by periodate in acid medium is well established and results from oxidation of Cu(II) to Cu(III) which acts as the oxidizing agent [2]. The kinetics and mechanism of oxidation of the $[Co^{II}DPTA]^{3-}$ (DPTA = diethylenetriaminepentaacetate) by periodate in acetate medium in the presence of Mn(II) as a catalyst show that an initial cobalt(III) product is not formed and the oxidation process is outer-sphere with only $[Co^{III}DTPA]^{2-}$ produced [10].

The kinetics of oxidation of cobalt(II) complexes of propylenediaminetetraacetate (PDTA) [11], 1,3-diamino-2-hydroxypropanetetraacetate (HPDTA) [11], trimethylenediaminetetraacetate (TMDTA) [12] and ethyleneglycol,bis(2-aminoethyl)ether, *N*,*N*,*N*′,*N*′-tetraacetate (EGTA) [12] by periodate in aqueous medium show electron transfer through an inner-sphere mechanism and gave only the final product [11, 12].

Kinetics and mechanism of the oxidation of ternary complexes, $[Co^{II}(nta)(S)(H_2O)_2]^{3-}$ [13] (S = succinate) and $[Co^{II}(nta)(M)(H_2O)]^{3-}$ [13] (M = malonate), by periodate were studied. Initial cobalt(III) products were formed and changed slowly to final products. It was proposed that the reaction is inner-sphere with relatively faster rates of ring closure than oxidation [13].

In this paper, the kinetics of oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ (nta = nitrilotriacetate and bz = benzoate) by periodate are reported to study the effect of benzoate as a secondary ligand on the stability of $[Co^{II}(nta)(H_2O)_2]^{-}$ [7] towards oxidation. Also, the catalytic effect of Mn(II) on the rate of oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate was reported to compare with oxidation of $Co^{II}DTPA$ by periodate [10] under the same conditions.

2. Experimental

2.1. *Materials and solutions*

All chemicals used in this study were of reagent grade (Analar, BDH, Sigma). Cobalt(II) nitrate solution was standardized volumetrically against EDTA [14]. Buffer solutions were prepared from acetic acid and sodium acetate of known concentrations. $NaNO_3$ was used to adjust ionic strength in the different buffered solutions. Doubly distilled water was used in all kinetic runs. A stock solution of $NaIO_4$ (Aldrich) was prepared by accurate weighing and wrapped in aluminum foil to avoid photochemical decomposition [15].

$Na_2[Co^{II}(nta)(bz)(H_2O)_2]$ was prepared using the procedure for preparation of Co^{II}-nta [16]. (Found: C, 33.95; H, 3.25; N, 2.92. $Na_2Co^{II}C_{13}H_{15}NO_{10}$ Calcd: C, 34.67; H, 3.33; N, 3.11%). To confirm the formula of the complex, IR spectra and TGA data were recorded. In the IR spectrum, bands in the 3520–3253 cm^{-1} region were attributed to $\nu(OH^-)$ of the coordinated water molecule. The OH^- band disappeared and a new COO^- band appeared in the 1464–1432 cm^{-1} region. The thermogram of the complex shows that weight loss (8.23) begins at 185.2°C, corresponding to the loss of two coordinated water molecules (Calcd 8.0).

2.2. *Kinetic procedures*

The oxidation rates were measured by monitoring absorbance of the Co^{III}-complex at 580 nm on a Jenway 6300 spectrophotometer. The pH of the reaction mixture was measured using a G-C825 pH-meter. The temperature of the cuvette compartment was also maintained at the required temperature by a circulatory water arrangement from a Thermostate (Gallen Kamp Griffin, BGL 240 V).

Pseudo-first order conditions were maintained in all runs by using large excess (>10-fold) of IO_4^-. The ionic strength was kept constant by addition of $NaNO_3$. The values of pseudo-first order rate constant k_{obs} were obtained from the slopes of $\ln(A_\infty - A_t)$ *versus* time plots, where A_t and A_∞ are absorbance at time t and infinity, respectively.

Enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) have been calculated by plotting $\ln k/\mathrm{T}$ *versus* $1/\mathrm{T}$ using Eyring equation:

$$\ln\frac{k}{T} = \ln\frac{\mathrm{K}}{\mathrm{h}} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

where k = the rate constant, K = the Boltzman constant, h = Plank's constant, R = universal gas constant and T = absolute temperature.

2.3. *Oxidation products*

The UV–Visible absorption spectra (shown in figure 1) of the products of oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate were recorded on a Unicam UV-700 spectrophotometer. An initial cobalt(III) product was formed and then changed slowly to the final cobalt(III) product. Both initial and final products were blue. There has been some controversy in the literature regarding the correct formulation of cobalt(III)-nta complexes [17–19]. The blue complex has been designated by Thacker and Higginson [17] as the β-form. The maxima and molar absorption coefficients of final cobalt(III) product at pH = 4.99 were $\varepsilon_{max}^{392} = 146$ and $\varepsilon_{max}^{596} = 137\ \mathrm{mol^{-1}\,cm^{-1}\,dm^3}$.

3. Results and discussion

The kinetics of oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate were studied at fixed temperatures and ionic strength over a range of pH, periodate and complex concentrations.

Plots of $\ln(A_\infty – A_t)$ *versus* time were linear up to 90% reaction. Pseudo-first order rate constants, k_{obs}, obtained from the slopes of these plots, are shown in table 1. The constancy of k_{obs} over concentration range $(1.0–3.0) \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$, shown in table 1, is in agreement with equation (1).

$$\frac{d[Co^{III}]}{dt} = k_{obs}\left[Co^{II}(nta)(bz)(H_2O)_2^{2-}\right] \qquad (1)$$

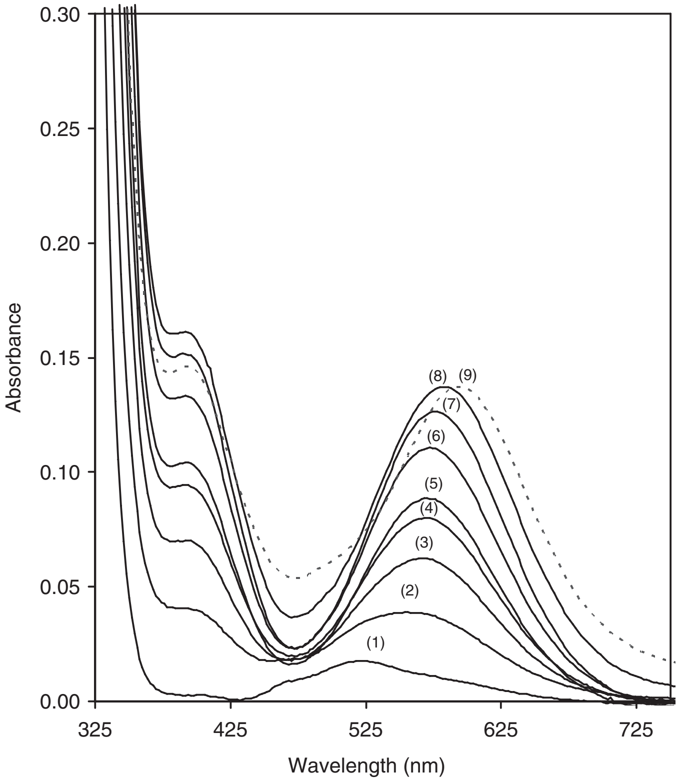

Figure 1. Change in absorbance as a function of time. Curves (1)–(8) were recorded at 2, 10, 15, 20, 30, 40, 60 and 180 min. respectively from the time of initiation of the reaction; curve (9) represents the final products. $[Co^{II}(nta)(bz)(H_2O)2]^{2-} = 1.0 \times 10^{-3}$ mol dm^{-3}, $[IO_4^-] = 0.02$ mol dm^{-3}, I = 0.5 mol dm^{-3} (NaNO3), pH = 4.99 and $T = 25°C$.

Table 1. Dependence of the $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}/IO_4^-$ reaction rate on $[Co^{II}(nta)(bz)(H_2O)_2]^2$, $[IO_4^-]$ and pH at $I = 0.50$ mol dm^{-3} and $T = 25.0°C$.

pH	I (mol dm^{-3})	10^3 $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ (mol dm^{-3})	10^2 $[IO_4^-]$ (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^2 k_1 (dm^3 mol^{-1} s^{-1})
4.99	0.50	1.00	5.00	10.2 ± 0.30	2.03 ± 0.06
			4.00	8.88 ± 0.20	2.22 ± 0.05
			3.00	7.13 ± 0.10	2.37 ± 0.03
			2.00	4.16 ± 0.04	2.08 ± 0.02
			1.50	3.80 ± 0.06	2.53 ± 0.04
			1.00	2.71 ± 0.05	2.71 ± 0.05
			0.50	1.03 ± 0.02	2.06 ± 0.04
		1.50	2.00	4.38 ± 0.05	2.17 ± 0.02
		2.00	2.00	4.26 ± 0.03	2.13 ± 0.02
		2.50	2.00	4.13 ± 0.02	2.07 ± 0.01
		3.00	2.00	4.21 ± 0.04	2.11 ± 0.02
4.27			2.00	4.18 ± 0.18	2.09 ± 0.09
4.45			2.00	4.33 ± 0.19	2.17 ± 0.10
4.63			2.00	4.59 ± 0.26	2.29 ± 0.13
5.23			2.00	5.12 ± 0.27	2.56 ± 0.14
4.99	0.30		2.00	3.46 ± 0.04	1.73 ± 0.02
	0.40		2.00	3.84 ± 0.03	1.92 ± 0.02
	0.60		2.00	4.76 ± 0.06	2.38 ± 0.03

Note: ($k_1 = k_{obs}/[IO_4^-]$).

The dependence of k_{obs} on IO_4^- was examined over the concentration range $(0.5\text{–}5.0) \times 10^{-2}\,mol\,dm^{-3}$ at fixed $[Co^{II}(nta)(bz)(H_2O)_2^{2-}]$, pH, ionic strength and temperature, showing that k_{obs} varies linearly with $[IO_4^-]$ according to equation (2).

$$k_{obs} = k_1[IO_4^-] \tag{2}$$

The dependence of the reaction rate on pH was investigated over the pH range 4.27–5.23 with k_{obs} increasing with increasing pH. The value of k_{obs} increased by *ca.* 25% over one unit of pH increase at ionic strength of $0.5\,mol\,dm^{-3}$ ($NaNO_3$). Since nta complexes of bivalent metals are not protonated in this pH range [20], the pH effect probably results from the breakdown of constant ionic strength, particularly when such large and highly charged ions are reactants [21]. Table 1 indicates that the rate of reaction increases with increasing ionic strength, attributed to the fact that the reaction takes place between species of the same charge.

3.1. *Kinetics of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}/IO_4^-$ reaction in acetate medium*

Oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate was carried out at constant pH and ionic strength using different acetate ion concentrations. The results (table 2 and figure 2) show that k_1 depends on acetate concentration, with the variation of k_1 with $[CH_3CO_2^-]$ described by equation (3).

$$k_1 = k_2 + k_3[CH_3CO_2^-] \tag{3}$$

From equations (1)–(3) the rate law for the oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by IO_4^- in acetate medium is given by equation (4).

$$\frac{d[Co^{III}]}{dt} = (k_2 + k_3[CH_3CO_2^-])[Co^{II}(nta)(bz)(H_2O)_2]^{2-}[IO_4^-] \tag{4}$$

The values of k_2 and k_3 collected in table 3 were obtained from the intercepts and the slopes, respectively, of figure 2. The enthalpies of activation ΔH_2^* and ΔH_3^* associated with k_2 and k_3 were calculated from the Eyring equation as 76 ± 4 and $33 \pm 4\,kJ\,mol^{-1}$, respectively. The corresponding entropies of activation ΔS_2^* and ΔS_3^* were calculated as -29 ± 3 and $-150 \pm 10\,J\,K^{-1}\,mol^{-1}$, respectively.

The ternary cobalt(II) complex of nta with benzoic acid may be formulated as $Na_2[Co^{II}(nta)(bz)(H_2O)_2]$, where nta is tridentate and benzoic acid is monodentate.

Table 2. Variation of k_1 with acetate ion concentration at $I = 0.50\,mol\,dm^{-3}$, pH = 4.99 at different temperatures.

	$10^2\,k_1$ ($dm^3\,mol^{-1}\,s^{-1}$)			
$[CH_3CO_2^-]$ ($mol\,dm^{-3}$)	$T = 15.0°C$	$T = 20.0°C$	$T = 25.0°C$	$T = 30.0°C$
0.05	0.72 ± 0.01	1.02 ± 0.01	1.70 ± 0.03	2.59 ± 0.01
0.10	1.13 ± 0.02	1.43 ± 0.02	2.08 ± 0.02	2.93 ± 0.02
0.20	1.63 ± 0.04	2.26 ± 0.06	2.85 ± 0.03	4.23 ± 0.03
0.30	2.37 ± 0.04	3.13 ± 0.03	3.97 ± 0.06	6.55 ± 0.04
0.40	3.13 ± 0.06	3.97 ± 0.05	4.88 ± 0.08	7.53 ± 0.09
0.50	3.95 ± 0.07	5.08 ± 0.08	6.3 ± 0.1	9.1 ± 0.1

Note: ($k_1 = k_{obs}/[IO_4^-]$).

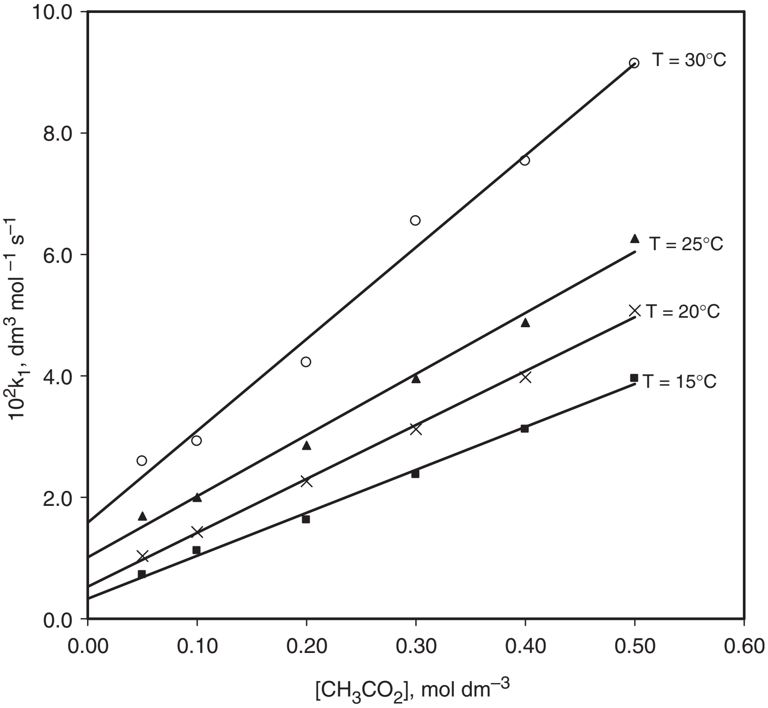

Figure 2. Dependence of k_1 on $[CH_3CO_2^-]$ at different temperatures.

Table 3. Variation of acetate-independent rate constant k_2 and acetate-dependent rate constant k_3 with temperature.

Temperature (°C)	$10^2\ k_2$ (dm^3 mol^{-1} s^{-1})	$10^2\ k_3$ (dm^6 mol^{-2} s^{-1})
15.0	0.33 ± 0.06	7.1 ± 0.3
20.0	0.52 ± 0.07	8.9 ± 0.2
25.0	1.0 ± 0.2	10.1 ± 0.5
30.0	1.6 ± 0.3	15.1 ± 0.8

The lability of cobalt(II) reactant and the inertness of cobalt(III) product can be utilized as a diagnostic tool for ascertaining inner-sphere electron transfer [2, 5–7].

Periodate oxidation of $[Co^{II}(nta)(bz)(H_2O)]^{2-}$ in the presence of acetate proceeds via initial formation of cobalt(III) products changing slowly to final cobalt(III) products. The rate of reaction increases with increasing acetate concentration (table 2), indicating $[Co^{II}(nta)(bz)(H_2O)]^{2-}$ and $[Co^{II}(nta)(bz)(CH_3CO_2)(H_2O)]^{3-}$ are the reactive species. Coordination of acetate to $[Co^{II}(nta)(bz)(H_2O)]^{2-}$ prior to oxidation by periodate. The rate law obtained also requires acetate in a step preceding the rate-determining one.

The mechanism of the $[Co^{II}(nta)(bz)(H_2O)]^{2-}$ oxidation by periodate in acetate may be described by the following equations:

$$[Co^{II}(nta)(bz)(H_2O)_2]^{2-} + [CH_3CO_2]^- \rightleftharpoons [Co^{II}(nta)(bz)(CH_3CO_2)(H_2O)]^{3-} + H_2O \qquad K_1 \tag{5}$$

Table 4. Variation of k_1 with [Mn(II)] at $[\mathrm{Co^{II}(nta)(bz)(H_2O)_2}]^{2-} = 1.00 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{IO_4}^-] = 2.00 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, Ph = 4.99, $I = 0.50\,\mathrm{mol\,dm^{-3}}$ and different temperatures.

	$10^2\,k_1$ ($\mathrm{mol^{-1}\,dm^{-3}\,s^{-1}}$)			
$10^5\,[\mathrm{Mn^{II}}]$ ($\mathrm{mol\,dm^{-3}}$)	$T = 15.0$°C	$T = 20.0$°C	$T = 25.0$°C	$T = 30.0$°C
2.50	1.23 ± 0.02	1.83 ± 0.04	3.19 ± 0.03	3.98 ± 0.02
5.00	1.56 ± 0.01	2.26 ± 0.03	3.53 ± 0.02	5.18 ± 0.07
7.50	1.98 ± 0.04	3.00 ± 0.05	5.09 ± 0.06	6.17 ± 0.09
10.0	2.78 ± 0.05	4.14 ± 0.04	5.98 ± 0.05	7.2 ± 0.2
12.5	3.61 ± 0.07	4.58 ± 0.07	7.6 ± 0.1	8.4 ± 0.2
15.0	4.28 ± 0.06	5.86 ± 0.09	8.3 ± 0.1	10.4 ± 0.3

Note: ($k_1 = k_{\mathrm{obs}}/[\mathrm{IO_4^-}]$).

$$[\mathrm{Co^{II}(nta)(bz)(H_2O)_2}]^{2-} + \mathrm{IO_4^-} \rightleftharpoons [\mathrm{Co^{II}(nta)(bz)(H_2O)(OIO_3)}]^{3-} + \mathrm{H_2O} \qquad K_2 \tag{6}$$

$$[\mathrm{Co^{II}(nta)(bz)(CH_3CO_2)(H_2O)}]^{3-} + \mathrm{IO_4^-} \longrightarrow [\mathrm{Co^{II}(nta)(bz)(CH_3CO_2)(OIO_3)}]^{4-} + \mathrm{H_2O} \qquad K_3 \tag{7}$$

$$\mathrm{Co^{II}(nta)(bz)(H_2O)(OIO_3)}]^{3-} \longrightarrow [\mathrm{Co^{III}(nta)(bz)(H_2O)(OIO_3)}]^{2-} \qquad k_4 \tag{8}$$

$$[\mathrm{Co^{II}(nta)(bz)(CH_3CO_2)(OIO_3)}]^{4-} \longrightarrow [\mathrm{Co^{III}(nta)(bz)(CH_3CO_2)(OIO_3)}]^{3-} \qquad k_5 \tag{9}$$

Assuming that K_1, K_2 and K_3 are small, the rate law in equation (10), which is consistent with the experimental results, is derived from the above mechanism.

$$\frac{\mathrm{d}[\mathrm{Co^{III}}]}{\mathrm{d}t} = \{k_4K_2 + k_5K_1K_3[\mathrm{CH_3CO_2^-}]\}[\mathrm{Co^{II}(nta)(bz)(H_2O)_2}]^{2-}[\mathrm{IO_4^-}] \tag{10}$$

A comparison of equations (4) and (10) shows that $k_2 = k_4K_2$ and $k_3 = k_5K_1K_3$.

An inner-sphere mechanism is proposed for both the acetate dependent and independent pathways. Acetate ion in one reaction pathway is not surprising as several ligands are known to coordinate to $[\mathrm{Co^{II}(nta)(H_2O)_2}]^-$ [22].

3.2. *Kinetics of oxidation of $[\mathrm{Co^{II}(nta)(bz)(H_2O)_2}]^{2-}$ in the presence of Mn(II) as catalyst*

Catalysis by Mn(II) was carried out at constant pH and ionic strength using different Mn(II) concentrations $(2.50\text{–}15.0) \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ from 15.0–30.0°C. The data in tables 1 and 4 show the comparison between reaction noncatalyzed and catalyzed by Mn(II); the rate of reaction increases in the presence of Mn(II) as a catalyst. The results in table 4 and figure 3 show that the rate constant, k_1, depends on Mn(II) concentration. Figure 3 shows that variation of k_1 with $[\mathrm{Mn^{II}}]$ is described by equation (11) at the temperature used.

$$k_1 = k_6 + k_7[\mathrm{Mn^{II}}] \tag{11}$$

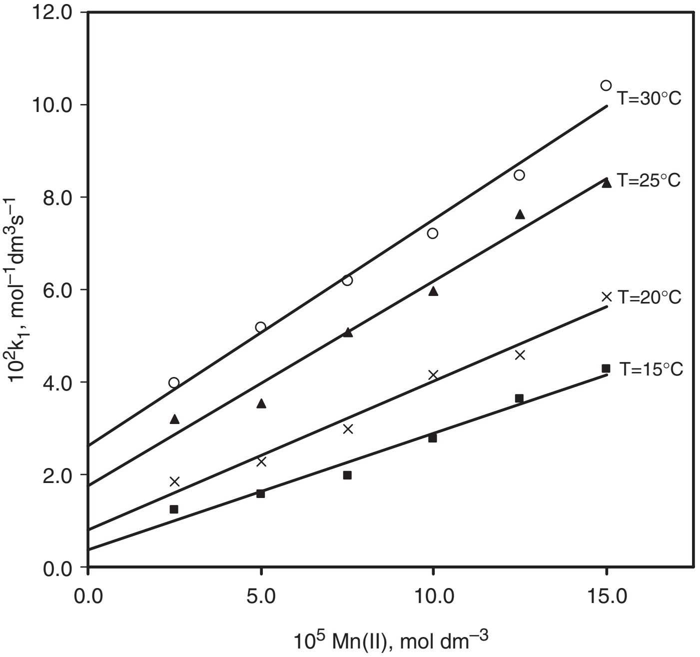

Figure 3. Dependence of k_1 on [Mn(II)] at different temperatures.

Table 5. Variation of Mn^{II}-independent rate constant k_6 and Mn^{II}-dependent rate constant k_7 with temperature.

Temperature (°C)	$10^2\ k_6$ ($dm^3\,mol^{-1}\,s^{-1}$)	$10^{-2}\ k_7$ ($dm^6\,mol^{-2}\,s^{-1}$)
15.0	0.36 ± 0.02	2.5 ± 0.2
20.0	0.80 ± 0.02	3.2 ± 0.2
25.0	1.75 ± 0.03	4.4 ± 0.3
30.0	2.61 ± 0.03	4.9 ± 0.3

From equations (1), (2) and (11) the rate law for the catalyzed oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate is given by equation (12).

$$\frac{d[Co^{III}]}{dt} = (k_6 + k_7[Mn(II)][Co^{II}(nta)(bz)(H_2O)_2]^{2-}[IO_4^-] \tag{12}$$

and

$$k_{obs} = (k_6 + k_7[Mn^{II}])[IO_4^-] \tag{13}$$

The values of k_6 and k_7 (table 5) were obtained from the intercepts and slopes of figure 3 and enthalpies of activation associated with k_6 and k_7 were calculated from the Eyring equation as ΔH_6^* and ΔH_7^* are 96 ± 7 and $17 \pm 2\,kJ\,mol^{-1}$, respectively. The corresponding entropies of activation ΔS_6^* and ΔS_7^* were calculated as -43 ± 5 and $-140 \pm 20\,JK^{-1}\,mol^{-1}$, respectively.

Mn(II) catalyzed oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate in acetate buffer occur through formation of a $Mn^{III}I^{VI}$ complex, which is more reactive than free periodate [23, 24]. Cu(II) and Mn(II) catalyze periodate oxidations [2, 10]. The oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate in the presence of Mn(II) may proceed in two pathways, one independent of Mn(II) and the second dependent on it, as shown in the following equations.

$$Mn^{II} + I^{VII} \rightleftharpoons Mn^{III} - I^{VI} \qquad K_4 \quad (14)$$

$$[Co^{II}(nta)(bz)(H_2O)]^{2-} + I^{VII} \rightleftharpoons [Co^{III}(nta)(bz)(H_2O)(I^{VII})]^{3-} + H_2O \quad K_5 \quad (15)$$

$$[Co^{II}(nta)(bz)(H_2O)_2]^{2-} + Mn^{III} - I^{VI} \longrightarrow [Co^{III}(nta)(bz)(H_2O)(I^{VI})]^{3-} + Mn^{II} \qquad k_8 \quad (16)$$

$$[Co^{II}(nta)(bz)(H_2O)(I^{VII})]^{3-} \longrightarrow [Co^{III}(nta)(bz)(H_2O)(I^{VI})]^{3-} \qquad k_9 \quad (17)$$

The rate law derived from the above mechanism, assuming that K_4 and K_5 are small, is

$$\frac{d[Co^{III}]}{dt} = (K_5k_9 + K_4k_8[Mn^{II}])[Co^{II}(nta)(bz)(H_2O)_2]^{2-}[I^{VII}] \qquad (18)$$

and

$$k_{obs} = (K_5k_9 + K_4k_8[Mn^{II}])[I^{VII}] \qquad (19)$$

From a comparison of equations (13) and (19), $k_6 = K_5k_9$ and $k_7 = K_4k_8$. Equation (19) contains two terms, the first independent of Mn(II) and the second dependent on Mn(II).

The initial cobalt(III) products converted to final products according to equations (20)–(22).

$$[(nta)(bz)(H_2O)Co^{III}{-}OIO_3]^{2-} \xrightarrow{H_2O} [Co^{III}(nta)(bz)(H_2O)_2]^{2-} + I^{VI} \qquad (20)$$

$$[(nta)(bz)(CH_3CO_2)Co^{III}{-}OIO_3)]^{3-} \xrightarrow{H_2O} [Co^{III}(nta)(bz)(CH_3CO_2)(H_2O)]^{3-} + I^{VI} \qquad (21)$$

$$[(nta)(bz)(H_2O)Co^{III}{-}OIO_3]^{3-} \xrightarrow{H_2O} [Co^{III}(nta)(bz)(H_2O)_2]^{3-} + I^{VI} \qquad (22)$$

$$2I^{VI} \longrightarrow IO_4^- + IO_3^- \qquad (23)$$

From the above reactions, an I^{VI} in the initial product is probably substituted by a water molecule with a very slow rate due to inertness of Co^{III} and Co^{II}–OIO_3 bond being stronger than Co–H_2O [25].

The comparison between oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ [7] and $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate under the same conditions show that the initial cobalt(III) product is formed and changed slowly to the final product in both cases. The value of the intramolecular electron transfer rate constant, k_3, for oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ ($1.0 \times 10^{-2}\,dm^3\,mol^{-1}\,s^{-1}$) is lower than the value of k_2 ($2.47 \times 10^{-2}\,dm^3\,mol^{-1}\,s^{-1}$) for oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ due to benzoate as a secondary ligand, making the ternary complex, $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$, more stable toward oxidation by periodate than the binary complex, $[Co^{II}(nta)(H_2O)_2]^-$.

Also, periodate oxidation of $[Co^{II}DTPA]^{3-}$ [10] in the presence of Mn(II) as a catalyst, unlike $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$, did not show the formation of an initial cobalt(III) product. This may be due to oxidation being outer-sphere and hence, only $[Co^{III}DTPA]^{2-}$ was produced. Alternatively, the oxidation process may be inner-sphere, but because the rate of ring closure is faster than that of oxidation, the initial cobalt(III) product was not observed. The oxidation rate of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ under the same conditions is lower than that of $[Co^{II}DTPA]^{3-}$. Thus, $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ is more stable towards oxidation by periodate than $[Co^{II}DTPA]^{3-}$.

The mechanism of oxidation of $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$ by periodate proceeds via an inner-sphere electron transfer mechanism in which initial cobalt(III) product slowly converted to a final cobalt(III) product [5–8, 13]. Outer-sphere electron transfer would lead directly to formation of final cobalt(III) product [10–12]. Periodate ion is capable of acting as a ligand, as evidenced from coordination to copper(III) [26] and nickel(IV) [27].

Negative entropies of activation for redox reactions between reactants with charges of the same sign are largely the result of charge concentration on encounter complex formation, which causes substantial ordering of the solvated water molecules [28]. The intramolecular electron transfer step is endothermic as indicated by the positive enthalpy of activation and hence, the contributions of H^* and S^* to the rate constant compensate each other, suggesting that the factors controlling ΔH^* must be closely related to those for ΔS^*; therefore, the solvation state of the activated complex is important in determining ΔH^* [28]. Also, the oxidation of the cobalt(II) complex to the cobalt(III) complex by periodate is thermodynamically favorable [12]. The relatively low enthalpies of activation calculated for the k_3 and k_7 process for both reactions are probably due to formation of $[Co^{II}(nta)(bz)(CH_3CO_2)(OIO_3)]^{4-}$ and $[Co^{II}(nta)(bz)(H_2O)(I^{VII})]^{3-}$ being exothermic.

References

[1] F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 5th Edn, p. 569, Wiley, New York (1988).
[2] Y. Sulfab. *J. Inorg. Nucl. Chem.*, **38**, 2271 (1976).
[3] D.J.B. Galliford, J.M. Ottaway. *Analyst*, **91**, 415 (1972).
[4] F.R. El-Ziri, Y. Sulfab. *Inorg. Chim. Acta*, **25**, 15 (1977).
[5] A.Y. Kassim, Y. Sulfab. *Inorg. Chim. Acta*, **24**, 247 (1977).
[6] A.A. Abdel-Khalek, Y. Sulfab. *J. Inorg. Nucl. Chem.*, **43**, 3257 (1981).
[7] M.A. Hussein, A.A. Abdel-Khalek, Y. Sulfab. *J. Chem. Soc., Dalton Trans.*, **839**, 317 (1983).
[8] A.A. Abdel-Khalek. *Polyhedron*, **8**, 51 (1989).
[9] A.A. Abdel-Khalek, A.A. Mohamed, H.A. Ewais. *Transition Met. Chem.*, **24**, 233 (1999).
[10] H.A. Ewais. *Egypt J. Chem.*, **47**, 555 (2004).
[11] M.R. Naik, J. Sarker, D.D. Chaturvedi, A. Verma, K.S. Singh. *Indian J. Chem. Sect. A*, **42**, 1639 (2003).
[12] M.R. Naik, A. Srivastava, K.A. Tiwari, S.B.S. Yadav, K.A. Verma. *Iran. Chem. Soc.*, **4**, 63 (2007).
[13] H.A. Ewais. *Int. J. Chem. Kinet.*, **40**, 103 (2008).
[14] A.I. Vogel. *A Textbook of Quantitative Inorganic Analysis*, 3rd Edn, p. 433, Longmans, London (1961).
[15] M.C.R. Symons. *J. Chem. Soc.*, 2794 (1955).
[16] M. Mori, M. Shibata, E. Kyuno, Y. Okubo. *Bull. Chem. Soc. Jpn.*, **31**, 940 (1958).

[17] M.A. Thacker, W.C.E. Higginson. *J. Chem. Soc., Dalton Trans.*, **7**, 704 (1975).
[18] B.B. Smith, D.T. Sawyer. *Inorg. Chem.*, **7**, 922 (1968).
[19] M. Mori, M. Shibata, E. Kyuno, Y. Okubo. *Bull. Chem. Soc. Jpn.*, **31**, 1958 (1940).
[20] G. Schwarzenbach, W. Beidermann. *Helv. Chim. Acta*, **31**, 331 (1948).
[21] J. Doyle, A.G. Sykes. *J. Chem. Soc. A*, 795 (1967).
[22] D.D. Perrin. *Stability Constants of Metal Complexes*, p. 420, Pergamon Press, Oxford (1974).
[23] F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 3rd Edn, p. 849, Wiley, New York (1972).
[24] G.R. Waterbury, A.M. Hayes, D.S. Martin. *J. Am. Chem. Soc.*, **74**, 15 (1952).
[25] V.S. Sharma, D.L. Leussing. *Inorg. Chem.*, **11**, 138 (1972).
[26] I. Hadinec, L. Jensovsky, A. Linek, V. Synecek. *Naturwiss.*, **47**, 377 (1960).
[27] P. Ray. *Inorg. Synth.*, **5**, 201 (1957).
[28] M.J. Weaver, E.L. Yee. *Inorg. Chem.*, **19**, 1936 (1980).