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Kinetics and mechanism of oxidation of the ternary complex of cobalt(II) involving N-(2-acetamido) iminodiacetic acid and malonate by periodate in acetate medium

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ABSTRACT

The kinetics of the oxidation of $[Co^{II}(ADA)(M)(H_2O)_2]^{2-}$ (ADA = N-(2-acetamido)iminodiacetic and M = Malonate) by periodate in acetate medium have been investigated spectrophotometrically at 580 nm under pseudo first order condition by taking large excess of oxidant (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: $d[Co^{III}]/dt = (k_2 + k_3[CH_3CO_2^-])[Co^{II}(ADA)(M)(H_2O)_2]^{2-}[IO_4^-]$. The initial cobalt(III) products were formed and slowly converted to final products, fitting an inner-sphere mechanism. The enthalpy and the entropy of the activation were measured using the transition state theory equation.

KEYWORDS

Kinetic studies;
N-(2-acetamido)
iminodiacetic;
Ternary complexes of
cobalt(II);
Periodate oxidation;
Thermodynamic activation
parameters.

INTRODUCTION

The activity of periodic acid as an oxidizing agent varies greatly as a function of pH and is capable of suitable control. 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 by periodate are reported to proceed through an inner-sphere mechanism[2-4]. Also, oxidation of transition metal complexes, was found to proceed via the inner sphere mechanism[5-8]. This mechanism could be drawn from reactions of this oxidant with transition metal complexes. It was found that 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 slowly were identified spectrophotometrically[6-8].

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 the formation of iron(III) which acts as the oxidizing agent[9]. Catalysis by Cu(II) ions in the oxidation of $[Fe(CN)_6]^{4-}$ by periodate in acid medium is well established and is seen to result from the oxidation of Cu(II) to Cu(III) which acts as an 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 were investigated[10]. It is observed that an initial cobalt(III) product is not formed and the oxidation process being outer-sphere so, the only final product [Co^{III}DTPA]$^{2-}$ was produced[10].

The kinetics of oxidation of cobalt(II) complexes of propylene- diaminetetraacetate (PDTA)[11], 1,3-diamino-2-hydroxypro panetetraacetate (HPDTA)[11], trimethylenediaminetetraacetate (TMDTA)[12] and ethyleneglycol, bis(2-aminoethyl) ether, N, N, N′, N′-tetraacetate (EGTA)[12] by periodate in aqueous medium have been investigated. In all cases, the electron transfer takes place through an inner-sphere mechanism and gave only the final product[11,12].

Kinetics and mechanism of the oxidation of a ternary complexes, [Co^{II}(nta)(S)(H$_2$O)$_2$]$^{3-}$[13] (S = succinate) and [Co^{II}(nta)(M)(H$_2$O)]$^{3-}$[13] (M = malonate) by periodate were studied. The initial cobalt(III) products were formed and changed slowly to final cobalt(III) products. It is proposed that the reaction obeys an inner-sphere mechanism which suggested that the relatively faster rates of ring closure were compared to the oxidation step[13].

In this paper, the kinetics of oxidation of [Co^{II}(ADA)(M)(H$_2$O)$_2$]$^{2-}$ (ADA = N-(2-acetamido) iminodiacetic and M = Malonate) by periodate are reported in order to study the effect of malonate as a secondary ligand on the stability of [Co^{II}(ADA)-(H$_2$O)$_3$][14] towards oxidation.

EXPERIMENTAL

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[15]. 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[16].

Na$_2$[Co^{II}(ADA)(M)(H$_2$O)] was prepared using the same procedure used for the preparation of Co^{II}-ADA[14]. (Found: C, 27.01; H, 3.57; N, 7.04. Na$_2$Co^{II}C$_9$H$_{12}$N$_2$O$_9$ Calcd.: C, 25.96; H, 3.85; N, 6.73 %). To confirm the formula of the complex, i.r. spectra and t.g.a. data were recorded. In the IR spectrum, bands in the 3405-3155 cm^{-1} region, were attributed to ν(OH$^-$) of the coordinated water molecule. The OH$^-$ band disappeared and a new COO$^-$ band appeared in the 1422-1400cm^{-1} region. The thermogram of the complex shows that weight loss (34.74 %) begins at 292C corresponding to the loss of one coordinated water molecule and three molecules of CO$_2$ (Calcd.: 36.05 %).

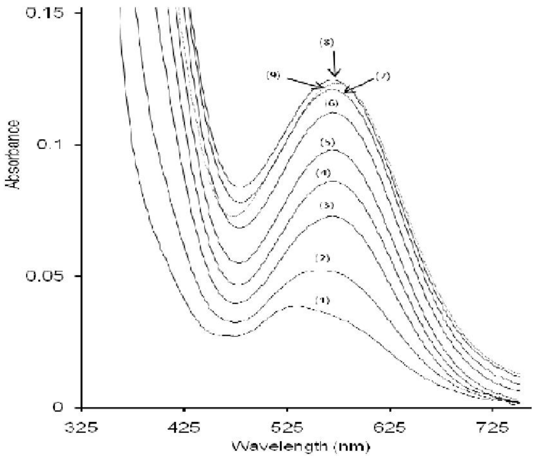

Figure 1 : Change in absorbance as a function of time curves (1)-(8) were recorded at 5, 10, 20, 30, 40, 60, 90 and 120 min. respectively from the time of initiation of the reaction; curve (9) represents the final products

Kinetic procedures

The reaction rates were measured by monitoring the absorbance of the Co^{III}-complex at 565nm on a Milton & Roy SP 601 spectrophotometer. The pH of the reaction mixture was measured using a G-C825 pH-meter. The temperature of the cuvette compartment too was 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 the presence of a large excess of IO$_4^-$ (>10-fold). The ionic strength was kept constant by addition of NaNO$_3$ solution. The pH of the reaction mixture was found to be always constant during the reaction run. 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$_\infty$ are absorbance at time t and infinity, respectively. Enthalpy of activation (ΔH*) and entropy

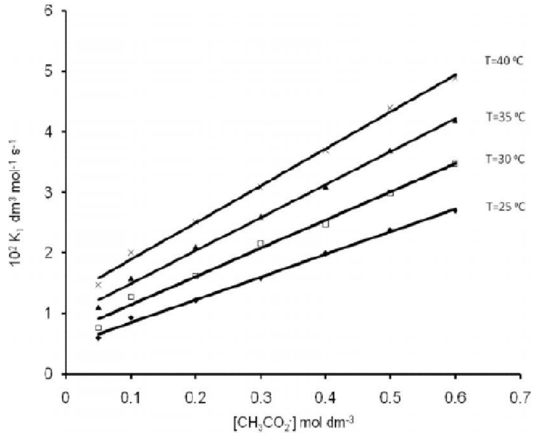

Figure 2 : Dependence of K_1 on [CH_3CO_2] at different temperatures

of activation (ΔS*) have been calculated by plotting ln k/T versus 1/T using Eyring equation:

ln k/T = ln K/h + ΔS*/R-ΔH*/RT

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

Oxidation products

The UV-visible absorption spectra of complexes and the oxidation products of complexes (Figure 1) were recorded on a JASCO UV-530 spectrophotometer as a function of time over the 325-725nm range spectrophotometer as shown in figure 1. The maxima and molar absorption coefficients of final cobalt(III) product at pH = 4.99 were $\varepsilon_{max}^{572} = 124$ mol^{-1}cm^{-1}dm^3.

RESULTS AND DISCUSSION

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

Plots of ln(A_∞-A_t) versus time were linear up to 86 % of 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 the complex concentration range (1.0–3.0)×10^{-3} mol dm^{-3}, shown in TABLE 1 is in agreement with equation (1).

$$d[Co^{III}]/dt = k_{obs}[Co^{II}(ADA)(M)(H_2O)]^{2-} \quad (1)$$

The dependence of k_{obs} on IO_4^- was examined over the concentration range (0.5-5.0)×10^{-2} mol dm^{-3} at fixed [Co^{II}(ADA)(M)(H_2O)]$^{2-}$, pH, ionic strength and temperature. The results in TABLE 1 show that k_{obs} varies linearly with [IO_4^-] according to equation (2).

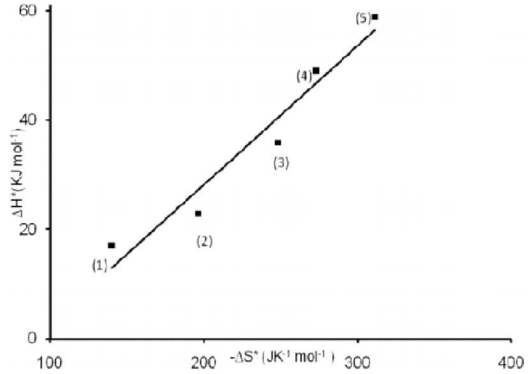

Figure 3 : Isokinetic relationship for the oxidation of ternary cobalt(II) complexes: (1) [Co^{II} (nta) (bz) ($H_2O)_2$]^2, (2) [CoII (ADA) (M) (H_2O)]$^{2-}$, (3) [CoII (nta) (ox) ($H_2O)_2$]$^{3-}$, (4) [CoII (nta) (T) (H_2O)]$^{3-}$, (5) [CoII (nta) (Ma) (H_2O)]$^{3-}$

$$k_{obs} = k_1[IO_4^-] \quad (2)$$

The dependence of the reaction rate on pH was investigated over the pH range 4.27-5.23. It was found that k_{obs} increases with increasing pH. The value of k_{obs} increased by ca. 30 % over one unit of pH increase when the ionic strength of 0.5 mol dm^{-3} is made up with $NaNO_3$. It was decided to examine whether the apparent pH dependence arises from a medium effect, since ADA complexes of bivalent metals are not protonated in this pH range[17]. The proposed medium probably results from the breakdown of the principle of constant ionic strength, particularly when such large and highly charged ions are reactants[18]. TABLE 1 indicates that the rate of reaction increases with increasing of ionic strength. This phenomenon has been attributed to the fact that the reaction takes place between species of the same charge.

Oxidation of [Co^{II}(ADA)(M)$(H_2O)_2$]$^{2-}$ by periodate was carried out at constant pH and ionic strength using different acetate ion concentrations. The results in TABLE 2 and figure 2, show that k_1 depends on acetate ion concentration. It can be seen from figure 2 that the variation of k_1 with [$CH_3CO_2^-$] is described by equation (3) at the temperature employed.

$$k_1 = k_2 + k_3[CH_3CO_2^-] \quad (3)$$

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

$$d[Co^{III}]/dt = (k_2 + k_3[CH_3CO_2^-])\,[Co^{II}(ADA)(M)(H_2O)]^{2-}[IO_4^-] \quad (4)$$

TABLE 1 : Dependence of the $[Co^{II}(ADA)(M)(H_2O)]^{2-}/IO_4^-$ reaction rate on $[Co^{II}(ADA)(M)(H_2O)]^{2-}$,$[IO_4^-]$ and pH at I = 0.50 mol dm^{-3} and T = 25.0°

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}	10^4k_{obs} s^{-1}	10^2k_1 dm^3 mol^{-1}s^{-1}
4.99	0.50	1.00	5.00	9.37±0.09	1.87±0.02
			4.00	7.87±0.08	1.96±0.02
			3.00	5.33±0.05	1.78±0.02
			2.00	4.07±0.04	2.03±0.02
			1.50	2.83±0.03	1.88±0.02
			1.00	1.80±0.02	1.80±0.01
			0.50	0.81±0.01	1.62±0.01
		1.50	2.00	3.83±0.04	1.91±0.02
		2.00	2.00	4.33±0.03	2.16±0.02
		2.50	2.00	4.23±0.04	2.11±0.02
		3.00	2.00	4.07±0.05	2.03±0.02
4.27			2.00	2.63±0.02	1.31±0.01
4.45			2.00	2.94±0.03	1.47±0.02
4.63			2.00	3.32±0.03	1.66±0.02
5.23			2.00	4.05±0.06	2.02±0.03
4.99	0.30		2.00	2.67±0.04	1.33±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

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

The values of k_2 and k_3 collected in TABLE 3 at the temperature used were obtained from the intercepts and the slopes respectively of figure 2. The enthalpy of activation ΔH_2^* and ΔH_3^* associated with k_2 and k_3, were calculated from the Eyring equation as 48.2±1.4 and 23.00±2.0 kJmol^{-1}, respectively. The corresponding entropies of activation ΔS_2^* and ΔS_3^* were calculated as -127.2±4.8 and -196.5±8.5 JK^{-1} mol^{-1} respectively.

The ternary cobalt(II) complex of ADA may be formulated as $[Co^{II}(ADA)(M)(H_2O)]^{2-}$, where ADA is functioning as tridentate ligand and malonate as bidentate ligand. The lability of cobalt(II) reactant and the inertness of cobalt(III) product could be utilized as a diagnostic tool for ascertaining inner-sphere electron transfer[4,7-9].

Periodate oxidation of $[Co^{II}(ADA)(M)(H_2O)]^{2-}$ in the presence of acetate ions 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 $[Co^{II}(ADA)(M)(H_2O)]^{2-}$ and $[Co^{II}(ADA)(M)(CH_3CO_2)]^{3-}$ are the reactive species. Coordination of acetate to $[Co^{II}(ADA)(M)(H_2O)]^{2-}$ prior to oxidation by periodate .The rate law obtained also requires acetate in a step preceding the rate-determining one.

TABLE 2 : Variation of k_1 with acetate ion concentration at I = 0.50 mol dm^{-3}, pH = 4.99 and different temperatures. ($k_1 = k_{obs}$ / $[IO_4^-]$)

$[CH_3CO_2^-]$ mol.dm^{-3}	10^2 k_1 dm^{3}mol^{-1} s^{-1}			
	T = 25.0°C	T= 30.0°C	T= 35.0°C	T= 40.0°C
0.05	0.60±0.01	0.77±0.02	1.10±0.02	1.48±0.03
0.10	0.93±0.02	1.28±0.03	1.58±0.03	2.01±0.04
0.20	1.22±0.02	1.62±0.03	2.10±0.04	2.52±0.05
0.30	1.58±0.03	2.16±0.04	2.61±0.05	3.10±0.06
0.40	1.99±0.04	2.48±0.05	3.10±0.07	3.70±0.07
0.50	2.38±0.04	3.00±0.05	3.70±0.07	4.40±0.08
0.60	2.70±0.05	3.48±0.06	4.20±0.08	4.90±0.09

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

$$\begin{gathered}[Co^{II}(ADA)(M)(H_2O)]^{2-} + [CH_3CO_2]^- \\ \downarrow\uparrow \\ [Co^{II}(ADA)(M)(CH_3CO_2)]^{3-} + H_2O \; K_1 \end{gathered} \qquad (5)$$

$$\begin{gathered}[Co^{II}(ADA)(M)(H_2O)]^{2-} + IO_4^- \\ \downarrow\uparrow \\ [Co^{II}(ADA)(M)(OIO_3)]^{3-} + H_2O \; K_2 \end{gathered} \qquad (6)$$

$$\begin{gathered}[Co^{II}(ADA)(M)(CH_3CO_2)]^{3-} + IO_4^- \\ \downarrow \\ [Co^{II}(ADA)(M)(CH_3CO_2)(OIO_3)]^{4-} + H_2O \; K_3 \end{gathered} \qquad (7)$$

$$\begin{gathered}[Co^{II}(ADA)(M)(OIO_3)]^{3-} \\ \downarrow \\ [Co^{III}(ADA)(M)(OIO_3)]^{2-} \; k_4 \end{gathered} \qquad (8)$$

$$\begin{gathered}[Co^{II}(ADA)(M)(CH_3CO_2)(OIO_3)]^{4-} \\ \downarrow \\ [Co^{III}(ADA)(M)(CH_3CO_2)(OIO_3)]^{3-} \; k_5 \end{gathered} \qquad (9)$$

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

$$\begin{gathered} d[Co^{III}]/dt = \{k_4K_2 + k_5K_1K_3[CH_3CO_2^-]\} \\ [Co^{II}(ADA)(M)(H_2O)]^{2-} \end{gathered} \qquad (10)$$

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. The entry of acetate in one reaction pathway is not surpris-

TABLE 3 : Variation of acetate-independent rate constant k_2 and acetate dependent rate constant k_3 with temperature

Temp. (°C)	10^2k_2 ($dm^3\ mol^{-1}\ s^{-1}$)	10^2k_3 ($dm^6\ mol^{-2}\ s^{-1}$)
25	0.477±0.08	3.75±0.29
30	0.677±0.08	4.67±0.36
35	0.949±0.08	5.46±0.42
40	1.284±0.08	6.10±0.47

TABLE 4 : Values of ΔH* and ΔS* for the oxidation of ternary cobalt(II) complexes by periodate

Reference	-ΔS* ($JK^{-1}\ mol^{-1}$)	ΔH*($KJ\ mol^{-1}$)	Complex
23	20 ± 140	2 ± 17	$[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$
This work	8 ± 196	2 ± 23	$[Co^{II}(ADA)(M)(H_2O)]^{2-}$
8	18 ± 248	4 ± 36	$[Co^{II}(nta)(ox)(H_2O)_2]^{3-}$
24	3 ± 2527	2 ± 49	$[Co^{II}(nta)(T)(H_2O)]^{3-}$
24	28 ± 311	3 ± 59	$[Co^{II}(nta)(Ma)(H_2O)]^{3-}$

ing as several ligands are known to coordinate to the complex $[Co^{II}(ADA)(M)(H_2O)]^{2-}$[19].

The mechanism of oxidation of the $[Co^{II}(ADA)(M)(H_2O)]^{2-}$ by periodate proceeds via an inner-sphere electron transfer mechanism in which the formation of initial cobalt(III) product slowly converted to a final cobalt(III) product[6-8]. Outer-sphere electron transfer would lead directly to the formation of final cobalt(III) product[10-12]. Periodate ion is capable of acting as a ligand, as evidenced from its coordination to copper(III)[20] and nickel(IV)[21].

The negative entropies of activation for redox reactions between reactants with charges of the same sign are largely the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules[22]. The intramolecular electron transfer step is endothermic as indicated by the positive enthalpy of activation value and hence, the contributions of H* and S* to the rate constant seem to compensate each other. This suggests that the factors controlling ΔH* must be closely related to those ΔS*; therefore the solvation state of the activated complex would be important in determining ΔH*[22]. Also, the oxidation of the cobalt(II) complex to the cobalt(III) complex by periodate is thermodynamically favorable[11]. The relatively low enthalpies of activation calculated for the k_3 and k_7 process for both reactions is probably due to the formation of $[Co^{II}(ADA)(M)(CH_3CO_2)(OIO_3)]^{4-}$ and $[Co^{II}(ADA)(M)(H_2O)(I^{VII})]^{3-}$ being exothermic.

Enthalpies and entropies of activation for the oxidation of ternary complexes of cobalt(II), $[Co^{II}(nta)(bz)(H_2O)_2]^{2-}$[23], $[Co^{II}(ADA)(M)(H_2O)]^{2-}$, $[Co^{II}(nta)(ox)(H_2O)_2]^{3-}$[8], $[Co^{II}(nta)(T)(H_2O)]^{3-}$[24] and $[Co^{II}(nta)(Ma)(H_2O)_2]^{3-}$[24] with periodate are collected in Table. A plot of ΔH* versus ΔS* for these complexes is shown in figure 3. Similar linear plots were found for a large number of redox reactions[25,26] and for each reaction series a common rate-determining step is proposed. An excellent linear relationship is seen; this isokinetic relationship lends support to a common mechanism for the oxidation of cobalt(II) complexes, reported here, by periodate. This consists of periodate ion coordination to the cobalt(II) complexes in step preceding the rate-determining intramolecular electron transfer within the precursor complex. Isokinetic compensation between ΔH* and ΔS* in a series of related reactions usually implies that one interaction between the reactants varies within the series, the remainder of the mechanism being invariant[27]. The electron transfer reactivities of these complexes with periodate are comparable, as the coordination of periodate with these complexes are identical. All of this suggests that the excellent correlation often observed between ΔS* and ΔH* mainly reflects the fact that both thermodynamic parameters are in reality two measures of the same thing, and that measuring a compensation temperature is just a rather indirect way of measuring the average temperature at which the experiments were carried out. As this temperature will often be in a range that the experimenter expects to have some biological significance, it is not surprising if the compensation temperature turns out to have a biologically suggestive value[28].

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