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Inner-sphere Oxidation of Diaqua(nitrilotriacetato)cobaltate(II) by Periodate in Acetate Medium. Isokinetic Relationship for the Oxidation of (Aminopolycarboxylato)cobalt(II) Complexes by Periodate

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The kinetics of oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ (nta = nitrilotriacetate) by periodate in acetate medium has been found to obey equation (i). Formation of initial cobalt(III) products, which were slowly converted to final cobalt(III) products, appears to fit an inner-sphere mechanism. A common

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

mechanism for the oxidation of (aminopolycarboxylato)cobalt(II) complexes by periodate is proposed, and this is supported by an excellent isokinetic relationship between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for these reactions.

Periodate oxidations of organic substrates, when bridging groups (*e.g.* OH, NH_2, and CO) are in the 1,2-positions, proceed through the formation of cyclic intermediates.[1] In the oxidation of the iodide ion by periodate, oxygen atom transfer with the formation of an intermediate HOI was invoked.[2] It thus seems that periodate oxidations follow an inner-sphere mechanism.

The oxidations of some transition metal aqua-ions and complexes have been interpreted in terms of an inner-sphere mechanism.[3-6] In the oxidation of Fe^{2+}, stopped-flow traces showed rapid formation and slow decomposition of an intermediate.[4] Initial cobalt(III) products were identified, spectrophotometrically, in the oxidation of cobalt(II) complexes of ethylenediaminetetra-acetate (edta),[5] *N*-(2-hydroxyethyl)-ethylenediaminetriacetate (hedta),[6] and ethylenediamine-*NN'*-diacetate (edda).[6] Additional support for an inner-sphere oxidation of these cobalt(II) complexes may also be drawn from a consideration of their rate laws. The rate law for the reaction of $[Co^{II}(edta)]^{2-}$ with IO_4^- is described by equation (1); the rates of the $[Co^{II}(hedta)]^-$ and $[Co^{II}(edda)]$ reactions with IO_4^- are governed by equation (2) [6] (L = $hedta^{3-}$ or $edda^{2-}$). In equation (1) a fast equilibrium step

$$d[Co^{III}]/dt = k^{e.t.}K[Co^{II}(edta)^{2-}][IO_4^-]/(1 + K[IO_4^-]) \quad (1)$$

$$d[Co^{III}]/dt = k_1^{e.t.}K_1[Co^{II}L][IO_4^-] + k_2^{e.t.}K_1K_2[Co^{II}L][IO_4^-]^2 \quad (2)$$

precedes the slow intramolecular electron-transfer (e.t.) step. The pathway which is first order in each reactant in equation (2) almost certainly proceeds *via* an inner-sphere mechanism. This is necessitated by the pathway that is second order in $[IO_4^-]$, since a rapid pre-equilibrium between $[Co^{II}L]^n$ and IO_4^- is required to account for the intermolecular reaction.[7]

The second-order dependence on the reductant concentration observed in periodate oxidation of the aqua-ions Fe^{2+} (ref. 4) and Cr^{3+} (ref. 8) seems to support an inner-sphere mechanism. In these processes, two one-electron transfers in a single activated complex were proposed. Two-electron transfer is believed to occur *via* an inner-sphere mechanism.[9]

The oxidation of diaqua(nitrilotriacetato)cobaltate(II), $[Co^{II}(nta)(H_2O)_2]^-$, by periodate is expected to proceed by a mechanism similar to that of the cobalt(II) complexes of edta, hedta, and edda. A periodate ion may replace a co-ordinated water molecule prior to electron transfer. The formation of an initial cobalt(III) product would thus serve as additional proof for inner-sphere oxidation by periodate.

It was observed that in the oxidation of the closely related series of cobalt(II) complexes of edta, hedta, and edda by periodate only a relatively small variation in the rate occurred under identical conditions. This may be due to parallel changes in the enthalpy, $\Delta H^\ddagger$, and the entropy, $\Delta S^\ddagger$, of activation. A linear relationship between $\Delta H^\ddagger$ and $\Delta S^\ddagger$, which is indicative of small variations in the free energy of activation, $\Delta G^\ddagger$, may be considered as strong support for a common mechanism for the series.[10] The existence of an isokinetic relationship for this related series of cobalt(II) complexes is examined below.

Experimental

Reagent grade chemicals were used without further purification. Stock solutions of periodate, wrapped in foil to avoid photochemical decomposition,[11] and of nta were made up by weight. Cobalt(II) nitrate solution was standardized volumetrically against edta.[12] Sodium acetate–acetic acid buffers of known concentrations were used. Ionic strength was adjusted with sodium nitrate.

Oxidation Products.—The u.v.–visible absorption spectra of the products of the oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ by IO_4^-, in the absence and presence of acetate ions, recorded on a Unicam SP8000 spectrophotometer are shown in Figures 1 and 2. In both cases, initial cobalt(III) products were formed and these changed slowly to final cobalt(III) products. Both the initial and the final products were blue. There has been some controversy in the literature regarding the correct formulation of cobalt(III)–nta complexes.[13-15] The blue complex has been designated by Thacker and Higginson [13] as the β form. The maxima and molar absorption coefficients of the acetate-free final cobalt(III) product at pH 5 were $\varepsilon_{max.}^{398} = 120$ and $\varepsilon_{max.}^{598} = 125$ dm^3 mol^{-1} cm^{-1}. In acetate medium these values were $\varepsilon_{max.}^{398} = 133$ and $\varepsilon_{max.}^{596} = 145$ dm^3 mol^{-1} cm^{-1}. The molar absorbance of the final cobalt(III) product, in acetate buffer, varies with acetate ion concentration.

The cobalt(III) product of the oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ by $S_2O_8^{2-}$ was different from that obtained with

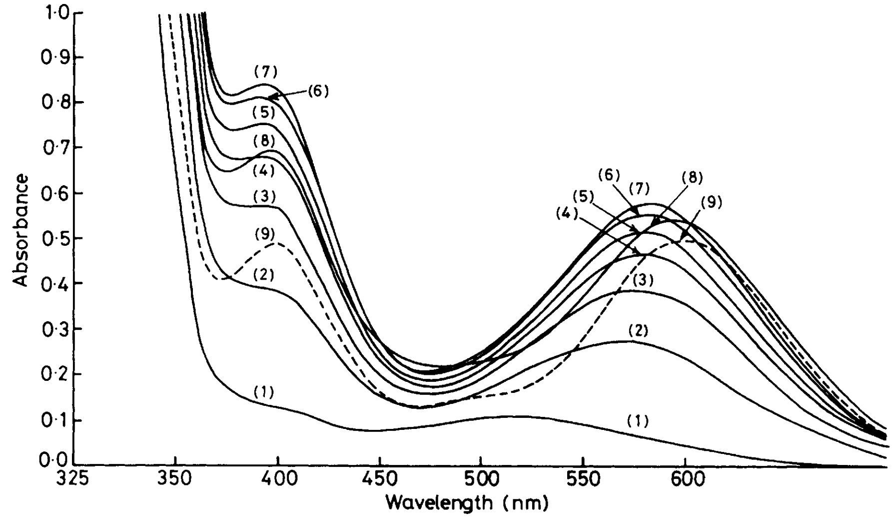

Figure 1. Change in absorbance as a function of time. Curves (1)—(8) were recorded at 1, 5, 10, 15, 20, 30, 50, and 320 min respectively from the time of initiation of the reaction; curve (9) represents the final product. $[Co^{II}(nta)(H_2O)_2^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[IO_4^-] = 0.05$ mol dm^{-3}, $I = 0.50$ mol dm^{-3} ($NaNO_3$), pH 5.20 (unbuffered), and $T = 25.0$ °C; path-length 4.0 cm

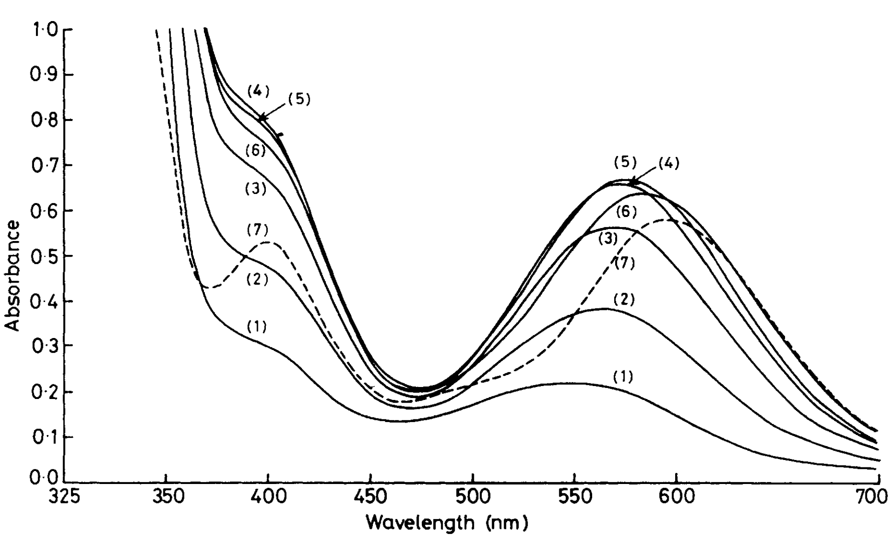

Figure 2. Change in absorbance as a function of time in acetate buffer. Curves (1)—(6) were recorded at 2, 4, 8, 15, 30, and 95 min respectively from the time of initiation of the reaction; curve (7) represents the final product. $[Co^{II}(nta)(H_2O)_2^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[IO_4^-] = 0.05$ mol dm^{-3}, $[CH_3CO_2^-] = 0.25$ mol dm^{-3}, $I = 0.50$ mol dm^{-3} ($NaNO_3$), pH 5.02, and $T = 25.0$ °C; path-length 4.0 cm

IO_4^-. The cobalt(III) product of the $[Co^{II}(nta)(H_2O)_2]^-/S_2O_8^{2-}$ reaction was designated as the α form.[16]

Kinetic Procedure.—The kinetic procedure was similar to that described for the $[Co^{II}(edta)]^{2-}/IO_4^-$ reaction.[5] The $[Co^{II}(nta)(H_2O)_2]^-$ complex was made up in solution and contained about 20% excess of the ligand to ensure complete formation as a precipitate occurred, when the metal ion : ligand ratio was 1 : 1. The rate of the reaction was monitored at 590 nm on a Unicam SP700 spectrophotometer. The pH of the reaction mixture was measured by means of a Radiometer digital pH-meter model PHM 62.

Pseudo-first-order conditions were maintained in all runs by using at least a ten-fold excess of periodate concentration over that of the complex. The effect of varying the pH, acetate ion concentration, and temperature on the reaction rate was studied.

Results

In the oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ by IO_4^-, an initial cobalt(III) product was formed in the absence as well as in presence of acetate ions, and in both cases the initial product was slowly converted to a final cobalt(III) product.

At fixed periodate concentration, ionic strength, pH, and temperature, plots of $\ln(A_\infty - A_t)$ *versus* time, where A_∞ and A_t are absorbances at infinity and time t, respectively, were linear to at least 85% of reaction. The pseudo-first-order rate constant, $k_{obs.}$, was calculated from the slopes of the first-order plots using a linear least-squares program. The constancy of $k_{obs.}$, over the complex concentration range $(5.0—20.0) \times 10^{-4}$ mol dm^{-3}, shown in Table 1, is in agreement with equation (3).

$$d[Co^{III}]/dt = k_{obs.}[Co^{II}(nta)(H_2O)_2^-] \qquad (3)$$

Table 1. Dependence of the $[Co^{II}(nta)(H_2O)_2]^-/IO_4^-$ reaction rate on $[Co^{II}(nta)(H_2O)_2^-]$, $[IO_4^-]$, and pH at $I = 0.5$ mol dm^{-3} (Na[O$_2$CMe]) and 25.0 °C [a]

pH	$10^2[IO_4^-]$/ mol dm^{-3}	$10^3k_{obs.}$/ s^{-1}	$10k_2$/ dm^3 mol^{-1} s^{-1}
5.0	0.5	0.50 ± 0.02	1.00 ± 0.04
5.0	1.0	1.05 ± 0.05	1.05 ± 0.05
5.0	2.0	2.05 ± 0.06	1.03 ± 0.03
5.0	2.5	2.63 ± 0.08	1.05 ± 0.03
5.0	3.0	3.24 ± 0.09	1.08 ± 0.03
5.0	4.0	4.24 ± 0.10	1.06 ± 0.02
5.0	4.0	4.10 ± 0.12 [b]	1.03 ± 0.03
5.0	4.0	4.13 ± 0.13 [c]	1.03 ± 0.03
5.0	4.5	4.80 ± 0.14	1.07 ± 0.03
5.0	5.0	5.23 ± 0.20	1.05 ± 0.04
5.25	5.0	5.70 ± 0.20	1.14 ± 0.04
5.11	5.0	5.60 ± 0.18	1.12 ± 0.04
4.48	5.0	5.00 ± 0.10	1.00 ± 0.02
4.23	5.0	4.43 ± 0.08	0.89 ± 0.02

[a] Unless otherwise stated, $[Co^{II}(nta)(H_2O)_2^-] = 5.0 \times 10^{-4}$ mol dm^{-3}. [b] $[Co^{II}(nta)(H_2O)_2^-] = 1.5 \times 10^{-3}$ mol dm^{-3}. [c] $[Co^{II}(nta)(H_2O)_2^-] = 2.0 \times 10^{-3}$ mol dm^{-3}.

Table 2. Variation of k_2 with acetate ion concentration at $I = 0.5$ mol dm^{-3} (Na[O$_2$CMe] + NaNO$_3$), pH = 5.0 ± 0.1, at different temperatures

$[CH_3CO_2^-]$/ mol dm^{-3}	10^2k_2/dm^3 mol^{-1} s^{-1}			
	19.4 °C	25.0 °C	30.0 °C	35.2 °C
0.05	1.92 ± 0.01	3.21 ± 0.03	4.56 ± 0.02	7.18 ± 0.09
0.10	2.57 ± 0.01	4.44 ± 0.04	6.03 ± 0.05	8.81 ± 0.12
0.25	4.35 ± 0.04	6.91 ± 0.06	9.56 ± 0.08	
0.35		9.13 ± 0.18		
0.40	6.17 ± 0.04		13.35 ± 0.32	17.31 ± 0.32
0.50	7.96 ± 0.12	11.39 ± 0.22	15.76 ± 0.18	20.67 ± 0.36

The dependence of $k_{obs.}$ on IO_4^- was examined over the concentration range (5.0—50.0) × 10^{-3} mol dm^{-3} at fixed $[Co^{II}(nta)(H_2O)_2^-]$, pH, ionic strength, and temperature. The results in Table 1 show that $k_{obs.}$ varies linearly with $[IO_4^-]$, according to equation (4).

$$k_{obs.} = k_2[IO_4^-] \qquad (4)$$

The dependence of the reaction rate on pH was investigated over the range pH 4.23—5.25. It was found that $k_{obs.}$ increases with increasing pH. The value of $k_{obs.}$ increased by *ca.* 25% over one unit of pH increase. It was decided to examine whether the apparent pH dependence arises from a mechanistic path or a medium effect, since nta complexes of bivalent metals are not protonated in this pH range.[17] Kinetic runs were then carried out at constant pH and ionic strength using different acetate ion concentrations. The results in Table 2 and Figure 3 show that k_2 depends on acetate ion concentration. It can be seen from Figure 3 that the variation of k_2 with $[CH_3CO_2^-]$ is described by equation (5) at the

$$k_2 = k_2' + k_3[CH_3CO_2^-] \qquad (5)$$

temperature employed. From equations (3), (4), and (5) the rate law for the oxidation of $[Co^{II}(nta)(H_2O)_2]^-$ by IO_4^- in acetate medium is given by equation (6). The values of k_2'

$$d[Co^{III}]/dt = (k_2' + k_3[CH_3CO_2^-])[Co^{II}(nta)(H_2O)_2^-][IO_4^-] \qquad (6)$$

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

T/°C	$10^2k_2'$/ dm^3 mol^{-1} s^{-1}	$10k_3$/ dm^6 mol^{-2} s^{-1}
19.4	1.21 ± 0.18	1.30 ± 0.05
25.0	2.47 ± 0.20	1.82 ± 0.07
30.0	3.42 ± 0.08	2.47 ± 0.03
35.2	5.75 ± 0.19	2.95 ± 0.06

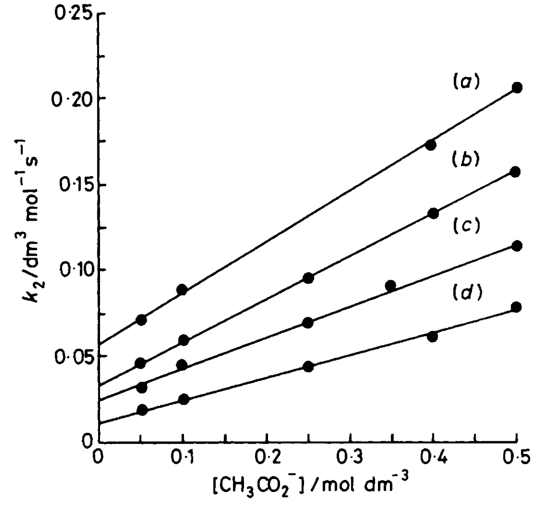

Figure 3. Dependence of k_2 on $[CH_3CO_2^-]$ at (*a*) 35.2, (*b*) 30.0, (*c*) 25.0, and (*d*) 19.4 °C

and k_3, collected in Table 3, at the temperature used, were obtained from the intercepts and the slopes respectively, of Figure 3. The enthalpies of activation $\Delta H_2^‡$ and $\Delta H_3^‡$, associated with k_2' and k_3, were calculated from a linear least-squares fit to the transition-state theory equation as 67.7 ± 5.0 and 35.5 ± 2.5 kJ mol^{-1}, respectively. The corresponding entropies of activation $\Delta S_2^‡$ and $\Delta S_3^‡$ were calculated as −48.5 ± 16.7 and −140.0 ± 8.4 J K^{-1} mol^{-1}, respectively.

Enthalpies and entropies of activation of the oxidation of cobalt(II) complexes of the aminopolycarboxylate ligands edta, hedta, edda, and nta with periodate are collected in Table 4. For the cobalt(II) complexes of hedta and edda, only $\Delta H^‡$ and $\Delta S^‡$ values for the pathway that is first order in each reactant were considered.[6] A composite $\Delta H^‡$ for the $[Co^{II}(edta)]^{2-}/IO_4^-$ reaction was obtained from a summation of the enthalpy of formation, associated with the precursor complex, and the enthalpy of activation of the intramolecular electron-transfer step.[5] A composite $\Delta S^‡$ was also calculated in the same manner. A plot of $\Delta H^‡$ against $\Delta S^‡$ for these cobalt(II) complexes is shown in Figure 4, and an excellent linear relationship was obtained.

Discussion

Periodate oxidation of $[Co^{II}(nta)(H_2O)_2]^-$, in the absence and presence of acetate ions, proceeds *via* the formation of initial cobalt(III) products. Formation of initial cobalt(III) products was also observed in the oxidation of cobalt(II) complexes of edta, hedta, and edda with periodate. The initial cobalt(III) products gave different final cobalt(III) products in the absence and presence of acetate ions. This indicates different cobalt(II) reactive species, the most likely species being

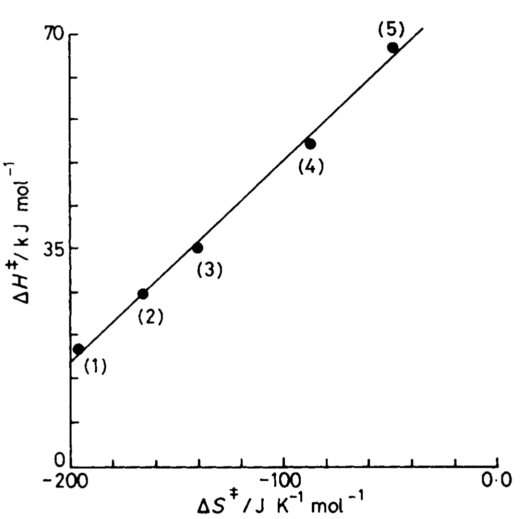

Figure 4. Isokinetic plot for the oxidation of (aminopolycarboxylato)cobalt(II) complexes: (1) $[Co^{II}(edda)(H_2O)_2]$, (2) $[Co^{II}(hedta)(H_2O)]^-$, (3) $[Co^{II}(nta)(CH_3CO_2)(H_2O)]^{2-}$, (4) $[Co^{II}(edta)]^{2-}$, and (5) $[Co^{II}(nta)(H_2O)_2]^-$ by periodate

$[Co^{II}(nta)(H_2O)_2]^-$ and $[Co^{II}(nta)(CH_3CO_2)(H_2O)]^{2-}$. Co-ordination of the acetate ion to $[Co^{II}(nta)(H_2O)_2]^-$ prior to oxidation by IO_4^- seems to be supported by the change in the spectrum of the cobalt(II) complex observed on addition of acetate ion. The rate law obtained also requires the entry of an acetate ion in a step preceding the rate-determining one.

The mechanism of the $[Co^{II}(nta)(H_2O)_2]^-/IO_4^-$ reaction in acetate buffer may be described by equations (7)—(11).

$$[Co^{II}(nta)(H_2O)_2]^- + CH_3CO_2^- \rightleftharpoons [Co^{II}(nta)(CH_3CO_2)(H_2O)]^{2-} + H_2O \quad K_1 \qquad (7)$$

$$[Co^{II}(nta)(H_2O)_2]^- + IO_4^- \rightleftharpoons [(nta)(H_2O)Co^{II}{-}OIO_3]^{2-} \quad K_2 \qquad (8)$$

$$[Co^{II}(nta)(CH_3CO_2)(H_2O)]^{2-} + IO_4^- \rightleftharpoons [(nta)(CH_3CO_2)Co^{II}{-}OIO_3]^{3-} \quad K_3 \qquad (9)$$

$$[(nta)(H_2O)Co^{II}{-}OIO_3]^{2-} \longrightarrow [(nta)(H_2O)Co^{III}{-}OIO_3]^{2-} \quad k_1^{e.t.} \qquad (10)$$

$$[(nta)(CH_3CO_2)Co^{II}{-}OIO_3]^{3-} \longrightarrow [(nta)(CH_3CO_2)Co^{III}{-}OIO_3]^{3-} \quad k_2^{e.t.} \qquad (11)$$

Assuming that K_1, K_2, and K_3 are small, the rate law given by equation (12), which is consistent with the experimental results, is derived from the above mechanism. A comparison

$$d[Co^{III}]/dt = (k_1^{e.t.}K_2 + k_2^{e.t.}K_1K_3[CH_3CO_2^-])[Co^{II}(nta)(H_2O)_2^-][IO_4^-] \qquad (12)$$

of equations (6) and (12) shows that $k_2' = k_1^{e.t.}K_2$ and $k_3 = k_2^{e.t.}K_1K_3$.

An inner-sphere mechanism is proposed for both the acetate-dependent and -independent pathways. This proposition is based upon the formation of initial cobalt(III) products. Outer-sphere electron transfer would lead directly to the formation of final cobalt(III) products. Periodate ion is capable of acting as a ligand, as evidenced from its co-ordination to copper(III),[18] and nickel(IV).[19] The entry of the acetate ion in one reaction pathway is not surprising as several ligands are known to co-ordinate to the complex $[Co^{II}(nta)(H_2O)_2]^-$.[20] The acetate-ion-dependent pathway, as revealed by the composite enthalpy of activation, appears to furnish a route requiring lower energy.

Table 4. Enthalpies and entropies of activation for the oxidation of some (aminopolycarboxylato)cobalt(II) complexes by periodate

Complex	10^2k_2 [a]/ dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	Ref.
$[Co^{II}(edda)(H_2O)_2]$	12.1 ±0.1	18.8 ±2.1	−196.0 ±3.3	6
$[Co^{II}(hedta)(H_2O)]^-$	16.4 ±0.4	28.0 ±1.7	−166.0 ±5.4	6
$[Co^{II}(nta)(CH_3CO_2)(H_2O)]^{2-}$	18.2 ±0.7	35.5 ±2.5	−140.0 ±8.4	*b*
$[Co^{II}(edta)]^{2-}$	24.0 [c]	51.8 ±2.1	−87.8 ±8.4	5
$[Co^{II}(nta)(H_2O)_2]^-$	24.7 ±0.20	67.7 ±5.0	−48.5 ±16.7	*b*

[a] Values of k_2 at 25.0 °C. [b] This work. [c] Value obtained from $Kk^{e.t.}$ of equation (1).

The initial cobalt(III) products may be converted to final products according to equations (13) and (14).

$$[(nta)(H_2O)Co^{III}{-}OIO_3]^{2-} \xrightarrow{H_2O} [Co^{III}(nta)(H_2O)_2] + I^{VI} \qquad (13)$$

$$[(nta)(CH_3CO_2)Co^{III}{-}OIO_3]^{3-} \xrightarrow{H_2O} [Co^{III}(nta)(CH_3CO_2)(H_2O)]^- + I^{VI} \qquad (14)$$

$$2\,I^{VI} \longrightarrow IO_4^- + IO_3^- \qquad (15)$$

The small changes in the rates of the oxidation of aminopolycarboxylatocobalt(II) complexes (Table 4) are shown to arise from parallel changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. These parallel changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ seem to lead to only small changes in $\Delta G^{\ddagger}$ and for such a closely related series a common mechanism is proposed.[10] Similar linear plots were found for a large number of redox reactions [21-23] and for each reaction series a common rate-determining step is proposed. The isokinetic relation lends support to a common mechanism for the oxidation of cobalt(II) complexes, reported here, by periodate. This consists of a periodate ion co-ordination to the cobalt(II) complex in a step preceding the rate-determining intramolecular electron transfer within the precursor complex.

Acknowledgements

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