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KINETICS AND MECHANISM OF OXIDATION OF Co (II) EDTA BY CHROMIUM (VI) : EFFECT OF MICELLE

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ABSTRACT

The kinetics of oxidation of metal ion complex [Co (II) EDTA] by chromium (VI) in perchloric acid medium has been investigated spectrophotometrically at 535 nm. The reaction is first order with respect to complex and the oxidant, and markedly inhibited by H^+ under the conditions [Cr(VI)] << [Co(II)EDTA]. The reaction obeys the following rate law with respect to EDTA is as follows.

$$\frac{d}{dt}[\mathrm{CoYH_2O^{2-}}] = \frac{kK_a\,[\mathrm{Co(II)\,EDTA}]_t\,[\mathrm{Cr(VI)}]}{K_a + [H^+]}$$

where Y = EDTA in the tetra negative form.

In the oxidation of Co (II) EDTA by Cr (VI) anionic micelle (sodium dodecyl sulphate) caused acceleration at sub micelle concentration; where as neutral micelle (triton X-100) caused deceleration in rate. A possible mechanism consistent with the observed results is proposed.

Key words: Co (II) EDTA, Chromium (VI), Oxidation, Sodium dodecyl sulphate, Triton X-100.

INTRODUCTION

The EDTA complex of cobalt (II) continues to be of considerable interest as a reductant in mechanistic studies, particularly where stereo chemical information is sought, since the product of Co (II) EDTA i.e., {Co (III) EDTA} is chiral and non labile[1,2]. Inner sphere oxidation of cobalt (II) complexes of ethylenediaminetetraacetate[3] by periodate were investigated. The detailed mechanism of electron transfer however is not easily assigned, as

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*Author for correspondence; E-mail: dsuryakala@yahoo.co.in the Co (II) complex is labile and consequently there exists the possibility of inner-sphere as well as outer-sphere paths. Also the Co (III)-EDTA$^-$ ion is an extremely strong complex, with a log K value of 41.4, while that of Co (II)- EDTA^{2-} is 16.45.[4] The present authors have taken up the kinetic study of oxidation of this complex by chromium (VI) and micelle effects on the kinetics. The micelle effects have been studied using Berezin's kinetic approach. These effects have been explained by considering the hydrophobic and electrostatic interactions between the reactants and the surfactants[5,6] in terms of the proposed mechanisms.

EXPERIMENTAL

Materials and methods

All solutions were prepared using double-distilled water rendered free from all ionic impurities by passage through an ion-exchanger. E. Merck pro analysis sample of cobalt (II) nitrate[7], Analar BDH sample of Ethylenediaminetetraaceticacid di-sodium salt (EDTA) were standardized[8] and the complex is prepared by mixing an equimolar solutions of cobalt (II) and EDTA[9]. Aqueous chromium (VI) is prepared[10]. A fluka sample of sodium dodecyl sulphate (SDS)[11], Triton X-100 (TX-100)[12] have been used in the preparation of 0.1 mol dm^{-3} solution. 5.0 mol dm^{-3} perchloric acid solution is prepared from 60% perchloric acid (Merck) and was standardized. Ionic strength was adjusted using sodium perchlorate solution.

The course of the reaction was followed spectrophotometrically at known intervals of time on a "Perkin Elmer Lamda25 UV/VIS spectrophotometer" using a 1 cm quartz cell at 535 nm under pseudo first order conditions [Co (II) EDTA] >> [Cr (VI)] where the product obeys Beer's law. The pseudo first order rate constants were determined from the slopes of the plots of log $(A_\alpha - A_t)$ versus time where A_α is the absorbance after the completion of the reaction and A_t is the same at time't'.

Product analysis

The formation of cobalt (III) EDTA as the product of oxidation of cobalt (II) EDTA by Cr (VI) was established by scanning the absorption spectrum, which overlapped with the spectrum of Co (III) EDTA, prepared by the electrolytic oxidation of the same concentration of Co (II) EDTA, using platinum gauze electrode. The product has maximum absorbance at 535 nm (ε_{535} = 319 dm^3 mol^{-1} cm^{-1}) (€ $_{598}$ = 120 dm^3 mol^{-1} cm^{-1}), which is in agreement with the reported value[4], (ε_{535} = 320 dm^3 mol^{-1} cm^{-1}) and (€$_{598}$ = 125 dm^3 mol^{-1} cm^{-1}) for the same complex. At this wavelength, the Beer's law is obeyed and all other materials have negligible absorbance (Fig. 1). The hydrogen ion concentration is at least 100 times higher than that of Co (II) EDTA complex. Hence change in hydrogen ion concentration during the reaction is negligibly small, which also proved by the observed constancy in pH of the reaction mixture with time.

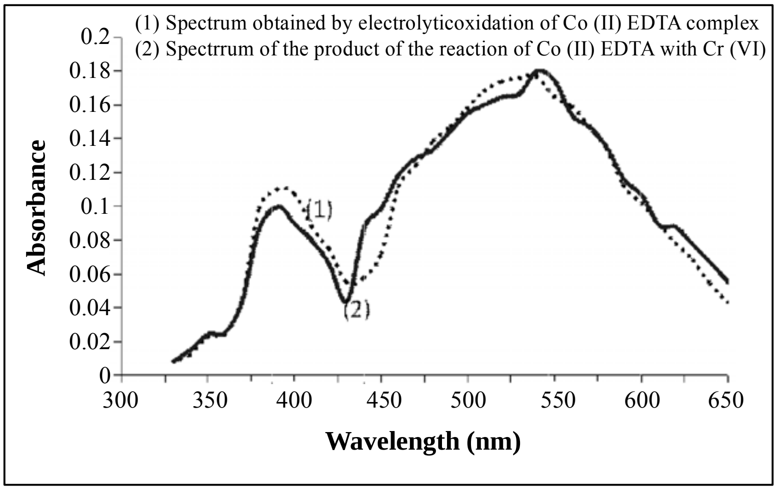


Fig 1: Spectra of the product of the reaction of Co (II) EDTA with Cr (VI) at [Co (II) EDTA] = [Cr (VI)] = 4.0 x 10^{-3} mol dm^{-3}, [H^+] = 0.1 mol dm^{-3}, μ = 0.5 mol dm^{-3}, Temp. = 30 ± 0.1°C

To determine the stoichiometry of the reaction a known concentration of [Co (II) EDTA] is mixed independently with different concentrations of Cr (VI) at [H^+] = 0.1 mol dm^{-3} in water. The reaction mixtures were kept overnight for the completion of the reaction and the absorbance of the products were measured at 535 nm. The absorbance increased with increasing [Cr (VI)] initially and further increase in concentration of Cr (VI) did not produce any change in absorbance. The results shown that three moles of Co (II) EDTA requires one mole of Cr (VI).

$$3\ \text{Co (II) EDTA} + 1\ \text{Cr (VI)} \longrightarrow 3\ \text{Co (III) EDTA} + 1\ \text{Cr (III)}$$

Determination of binding constants

The binding constants have been determined using equation.

$$\frac{1}{\left(A_M - A_W^0\right)} = \frac{1}{\left(A_M^0 - A_W^0\right)} + \frac{1}{\left(A_M^0 - A_W^0\right) K_s C} \quad ....(1)$$

Where A_M and A_W^0 are the absorbances in the absence and presence of micelle, respectively. A_M^o is limiting absorbance in the presence of micelle, $1/(A_M-A_W^0)$ is plotted against 1/ C {C=([surfactant] – CMC)} and from slopes and intercepts of these plots, the binding constant of Co (II) EDTA complex with SDS (272 nm) was determined to be $1.125 \pm 0.20 \times 10^3$ dm^3 mol^{-1}. Interestingly, the spectrum of the Co (II) EDTA complex did not show any change in the presence of triton X-100 indicating that the binding constant is very small with this complex. The binding constant of Cr (VI) with SDS[13] (at 330 nm) has been reported to be 98.0 ± 0.5 dm^3 mol^{-1} and with triton X-100 [14] the value is 54.0 dm^3 mol^{-1}.

RESULTS AND DISCUSSION

To study the effect of varying [Cr (VI)] in the range of (2.0 to 10.0) x 10^{-3} mol dm^{-3} on the reaction rate, its concentration is varied under pseudo-first order conditions and keeping all other parameters constant. The linear plots of log $(A_\alpha-A_t)$ versus time, under the conditions [Co (II) EDTA] >> [Cr (VI)] and were found to be linear with identical slopes, shown the first order with respect to Cr (VI). The pseudo first order rate constants calculated are presented in the Table 1.

Table 1: Kinetic data for the reaction between [Co (II) EDTA] and [Cr (VI)] at $\mu = 0.3$ mol dm^{-3}, Temp. = 30°C ± 0.1°C

S. No.	10^4 [Cr (VI)] mol dm^{-3}	10^3 [Co (II) EDTA] mol dm^{-3}	$[H^+]$ mol dm^{-3}	10^2 k_1 sec^{-1}
1	0.4	4.0	0.1	1.14 ± 0.02
2	1.0	4.0	0.1	1.16 ± 0.03
3	2.0	4.0	0.1	1.19 ± 0.04
4	4.0	4.0	0.1	1.12 ± 0.02
5	1.0	2.0	0.1	0.56 ± 0.03
6	1.0	4.0	0.1	1.15 ± 0.04
7	1.0	6.0	0.1	1.44 ± 0.03
8	1.0	8.0	0.1	1.87 ± 0.02
9	1.0	10.0	0.1	2.28 ± 0.02
10	1.0	4.0	0.02	5.0 ± 0.04
11	1.0	4.0	0.04	2.63 ± 0.16
12	1.0	4.0	0.06	1.85 ± 0.02
13	1.0	4.0	0.08	1.43 ± 0.03
14	1.0	4.0	1.0	1.24 ± 0.04

The observed rate constants k_1 varies linearly with [Co (II) EDTA] at fixed reaction conditions as shown (Fig. 2) in Table 1. The kinetic runs were carried out at different $[H^+]$, under the constant reaction conditions. The results in Table 1 show that $[H^+]$ ion inhibits the reaction and plot of $1/k_1$ versus $[H^+]$ is linear with a positive intercept (Fig. 3). This type of H^+ dependence of rate indicates a rate-law of the form $k_1 = ak / (b + [H^+])$.

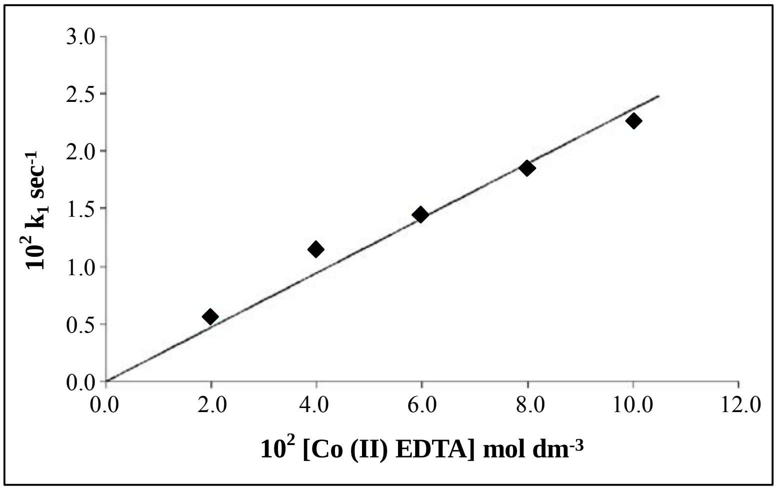


Fig. 2: Effect of varying [Co (II) EDTA] on reaction rate at [Cr (VI)] = 1.0 x 10^{-4} mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3}, μ = 0.3 mol dm^{-3}, Temp. = 30°C ± 0.1°C

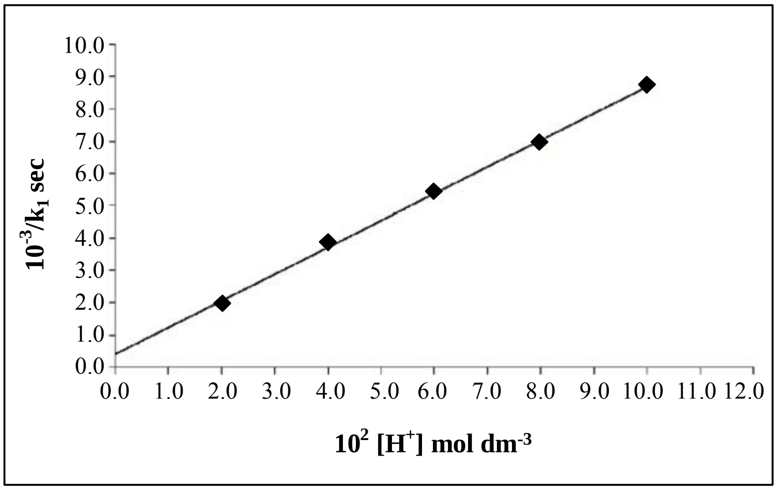


Fig. 3: Plot of $[H^+]$ versus $1/k_1$ at [Cr (VI)] = 1.0 x 10^{-4} mol dm^{-3}, [Co (II) EDTA] = 4.0 x 10^{-3} mol dm^{-3}, μ = 0.3 mol dm^{-3}, Temp. = 30°C ± 0.1°C

Effect of micelle

To investigate micellar effects of sodium dodecyl sulphate (SDS) and TX-100 on the rate, the kinetic runs were carried out at different initial concentrations of SDS and TX-100, respectively by keeping [Cr (VI)], [Co (II) EDTA] and [H^+] constant. The results are presented in Table 2 and 3, respectively.

Table 2: Effect of SDS on the oxidation of [Co (II) EDTA] by [Cr (VI)] at [Cr (VI)] = 1.0 x 10^{-4} mol dm^{-3}; [Co (II) EDTA] = 4.0 x 10^{-3} mol dm^{-3}; [H^+] = 0.2 mol dm^{-3}; μ = 0.3 mol dm^{-3}; Temp. = 30°C ± 0.1°C

10^2 [SDS] (mol dm^{-3})	10^3 k_1 (sec^{-1})
0.0	5.95 ± 0.02
0.2	9.72 ± 0.02
0.4	16.88 ± 0.03
0.8	16.12 ± 0.04
1.2	11.77 ± 0.05
1.6	10.74 ± 0.02
2.0	9.72 ± 0.02
2.4	8.18 ± 0.03

Table 3: Effect of triton X-100 on the oxidation of [Co (II) EDTA] by [Cr (VI)] at [Cr (VI)] = 1.0 x 10^{-4} mol dm^{-3}, [Co (II) EDTA] = 4.0 x 10^{-3} mol dm^{-3}; [H^+] = 0.1 mol dm^{-3}; μ = 0.3 mol dm^{-3}; Temp. = 30°C ± 0.1°C

10^4 [TX-100] (mol dm^{-3})	10^3 k_1 (sec^{-1})
0.0	11.20 ± 0.02
6.8	9.40 ± 0.05
13.6	9.00 ± 0.02
27.2	8.72 ± 0.05
40.8	8.30 ± 0.04
54.4	8.00 ± 0.03

In the case of Co (II) EDTA by Cr (VI), anionic micelles (sodium dodecyl sulphate) caused acceleration at sub micellar concentration, and further increase in surfactant concentration results in decrease in rate. This is generally observed in bimolecular reactions taking place on the micellar surface, where as neutral micelles (triton X-100) caused deceleration on the rate. Applying Berezin's method[15], the second order rate constant, k_2 is given by –

$$k_2 = \frac{k_w + k_m K_A . P_B . C}{(1+K_A C)(1+K_B C)}$$

Where A and B are binding constants of H_2CrO_4 and Co (II) EDTA, respectively with the micelles. In conformity with the Berezin's equation, plot of k_2 (l + K_AC) (1 + K_BC) versus C, {C = ([SDS]-CMC)} is a straight line passing through origin. Thus k_w should be neglected in the numerator of Berezin equation.

The rate of the reaction is decelerated by TX-100. There is a considerable decrease of binding constant of H_2CrO_4 with TX-100 micelles. The value of binding constant of aqueous Cr (VI) with TX-100 micelles is reported[14] to be 54.0 $mol^{-1}dm^3$. Interestingly the interaction of Co (II) EDTA with TX-100 micelles is negligibly small presumably due to the structural difference of SDS and triton X-100 micelles. The reaction, therefore does not take place at the interface but only in the aqueous pseudo phase. As the concentration of triton-X is increased, more and more Co (II) EDTA is removed from the bulk aqueous phase to the micellar phase leading to decrease in rate in the aqueous phase. This accounts for the decelerating effect of Triton X-100 on rate of oxidation of Co (II) EDTA by aqueous Cr (VI).

Test for free radicals

When the reactions were conducted in the presence of acrylonitrile in an evacuated Thunberg tube, no perceptible change was observed and no precipitation of polymer was noticed, indicating the absence of free radical intermediates in the reactions of Co (II) EDTA with Cr (VI).

Kinetic approach

The reaction obeys first order kinetics with respect to each of the reactants Cr (VI), [Co (II) EDTA], under the conditions [Cr (VI)] << [Co (II) EDTA]. The observed pseudo first order rate constants k_l do not vary with change in [Cr (VI)]. The rate constant decreases with the increase in $[H^+]$ and k_l is inversely proportional to $[H^+]$. The inhibition by H^+ ion is presumably due to the effect of H^+ ion on the nature of species of Co (II) EDTA complex. If the protonation of $HCrO_4^-$ is a factor that also determines the rate, which is acceleration in general, this should have countered the inhibition due to the protonation of $CoYH_2O^{2-}$ and the H^+ ion effect should have been zero or a very small magnitude.

Nature of Co (II) EDTA species

Higgionson[16] investigated the nature of cobalt (II)-EDTA complex in aqueous medium and concluded that EDTA in this complex acts as a quinquedentate ligand, the complex having the composition $[MYH_2O]^{2-}$, where EDTA is represented as Y in the tetra negative form. Support for this view comes from the observation that many of this metal-EDTA complexes have nearly the same pK_a value (~3)[17], which pertain to the protonation of free carboxyl rather than involving a metal-carboxyl bond. Wilkins and Yelin[18] reported that the complex exists in the form Co Y^{-2} to an extent of 97% at pH 4-5 or more, whereas at pH $\leq$ 3, the predominant species is the $[CoY\ H_2O]^{2-}$, which are the quinque-coordinated complex of EDTA. Dyke and Higginson have stated that in view of the unfavorable radius of Co^{2+} for a six fold coordination with EDTA, the cobalt (II) EDTA is mainly present in the form $CoY\ H_2O^{2-}$ in equilibrium with CoY^{2-}. Since most of the work was carried out at pH $\leq$ 3. The present authors considers that Co (II) EDTA complex is present predominately in the form $CoYH_2O^{2-}$, which is in equilibrium with the protonated form $CoHY\ H_2O^{1-}$.

The protonated species $CoHY\ H_2O^{1-}$ should be distinctly less reactive than $CoYH_2O^{2-}$, which accounts for the inhibition of the reaction by H^+ ion. To account for the observed kinetics, the author suggests the following scheme of mechanism for Cr (VI) oxidations.

$$CoHYH_2O^{1-} \xrightarrow{K_a} CoYH_2O^{2-} + H^+,\ K_a = 1.0 \times 10^{-3} mol\ dm^{-3}$$

$$CoYH_2O^{2-} + Cr(VI) \xrightarrow{Slow} CoYH_2O^{1-} + Cr(V)$$

$$Cr(V) + CoYH_2O^{2-} \xrightarrow{Fast} CoYH_2O^{1-} + Cr(IV)$$

$$Cr(IV) + CoYH_2O^{1-} \xrightarrow{Fast} CoYH_2O^{2-} + Cr(III)$$

Derivation of rate law

Applying mass balance in the case of oxidation of $[Co\ (II)\ EDTA]_t$ i.e., the total concentration of the complex,

$$[Co^{II}\ EDTA]_t = [CoYH_2O^{2-}] + [CoYH_2O^{1-}] = [CoYH_2O^{2-}] + \frac{[CoYH_2O^{2-}][H^+]}{K_a}$$

$$= \frac{K_a [CoYH_2O^{2-}] + [CoYH_2O^{2-}][H^+]}{K_a}$$

$$[\mathrm{Co^{II}\ EDTA}]_t = \frac{\{K_a + [H^+]\}[\mathrm{CoYH_2O^{2-}}]}{K_a}; [\mathrm{CoYH_2O^{2-}}] = \frac{K_a + [\mathrm{Co^{II}\ EDTA}]_t}{K_a + [H^+]}$$

$$\mathrm{Rate} = \frac{-d}{dt}[\mathrm{CoYH_2O^{2-}}] = k[\mathrm{CoYH_2O^{2-}}][\mathrm{Cr(VI)}] = \frac{kK_a + [\mathrm{Co^{II}\ EDTA}]_t[\mathrm{Cr(VI)}]}{K_a + [H^+]}$$

The pseudo first order rate constant, k_1, is given by:

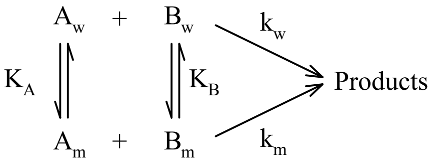
$$k_1 = \frac{kK_a[\mathrm{Co^{II}EDTA}]_t}{K_a + [H^+]}$$

$$\frac{1}{k_1} = \frac{1}{k[\mathrm{Co^{II}EDTA}]_t} + \frac{[H^+]}{kK_a[\mathrm{Co^{II}EDTA}]_t}$$

This equation requires that a plot of $1/k_1$ versus $[H^+]$ should be a straight line with a positive intercept and the same has been realized from the experimental data. The slope of the straight line is equal to $1/k\ K_a\ [\mathrm{Co^{II}\ EDTA}]_t$ and the intercept is equal to $1/k\ [\mathrm{Co^{II}\ EDTA}]_t$.

Micellar effect

To study the micellar effects on the oxidation of Co (II) EDTA by Cr (VI) the scheme of the reaction in micelles with both SDS and TX -100 can be represented as –



For the kinetic analysis of the micellar effects, Berezin's model involving the partition coefficient of the species between the micellar and aqueous pseudo phases has been applied. Under these experimental conditions and in conformity with the Berezin's equation, plot of k_2 (l+K_AC) (1 + K_BC) versus C ([SDS]-CMC) is a straight line passing through origin.

The binding constant of Co (II) EDTA with SDS micelles is 1125 $\mathrm{mol^{-1}dm^3}$ showing that there is some hydrophobicity associated with Co (II) EDTA, that enables the binding of the complex with SDS micelles, in spite of repulsive force. However the oxidation of Co (II) EDTA by Cr (VI) is decelerated by TX-100. Interestingly the interaction of Co (II) EDTA with TX-100 micelles is negligibly small presumably due to the structural difference of SDS and triton X-100 micelles.

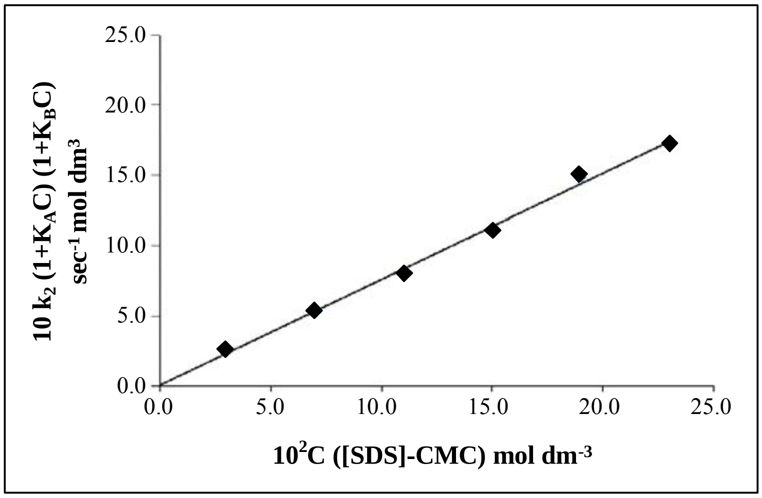


Fig. 4: Plot of ([SDS]-CMC) versus $k_2 (1 + K_AC) (1 + K_BC)$ at [Cr (VI)] = 1.0 x 10^{-4}mol dm^{-3}; [Co (II) EDTA] = 4.0 x 10^{-3}mol dm^{-3}; [H^+] = 0.1 mol dm^{-3}; μ = 0.3 mol dm^{-3}; Temp = 30°C ± 0.1°C

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