J. Chem. Soc. Nigeria, Vol. 41, No. 2, pp 81-86 [2016]

OXIDATION OF ETHYLENEDIAMINETETRAACETATOCOBALTATE(II) COMPLEX BY HYDROGEN PEROXIDE IN AQUEOUS ACIDIC MEDIUM: A KINETIC STUDY

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Accepted:24/08/2016
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Abstract
The oxidation of ethylenediaminetetraacetatocobaltate(II) complex ($[CoEDTA]^{2-}$) by Hydrogen peroxide in aqueous perchloric acidic medium was studied at ionic strength (I) 0.50 mol dm^{-3} ($NaClO_4$), $T = 30\ ^0C$, $[H^+] = 1\times10^{-3}$ mol dm^{-3} and λ_{max} of 510 nm. Stoichiometric determination shows that for two moles of the reductant, one mole of the oxidant was consumed. Kinetics study carried out under pseudo - first order condition gave result that fit into the rate law: $\frac{d[product]}{dt} = k[CoEDTA^{2-}][H_2O_2]^{1/2}$

The study on the effect of $[H^+]$ on the rate of reaction shows that the rate and acid concentration varies inversely and the plot of acid dependent rate constant against $[H^+]^{-1}$ was linear with slope 2.0×10^{-7} $dm^3\ mol^{-1}\ s^{-1}$ and intercept 1.0×10^{-4} s^{-1} . The rate law involving acid concentration is:

$$\frac{d[\Pr oduct]}{dt} = 1.0\times10^{-4} + 2.0\times10^{-7}[H^+]^{-1}[CoEDTA^{2-}][H_2O_2]^{1/2}$$

The reaction displayed negative primary salt effect which suggests the composition of activated complex are oppositely charged reactants ions. The Michaelis – Menten's plot gave significant intercept indicative of presence of intermediate complex. On the basis of available evidence the inner - sphere mechanism is proposed for the reaction.

Keywords: Oxidation, Ethylenediaminetetraacetatocobaltate(II), Complex, Hydrogen Peroxide, Kinetics

Introduction

Hydrogen peroxide, a versatile redox substrate is known for its environmental friendliness and non-toxic reduction end product. It has a wide spectrum of applications which among others include a biocide, a hormonal and sugar regulator as well as energy production in cells[1]. Its applications also extend to the industrial, chemical and environmental processes[2,3,4,5]. It reacts with thiourea under certain conditions to produce powerful reductive bleaching agent very useful in the textile industry[6].The reactions of this substrate have been of interest. An excellent review of its decomposition reactions[5] and its redox reactions with different substrates[7,8,9] have been studied. Equally, kinetics study on the oxidation of tetrahedral Co(II) complexes [10,11,12,13,14] and its octahedral form[9,15,16,17,18], by various oxidizing substrates have been reported. However, literature on the electron transfer reaction of this oxidant and Co(II) complexes is scanty. In furtherance of our interest in the redox reaction of this oxidant, this study is embarked upon. It is hoped that this study will provide additional much needed kinetic data that will shed more light on the pathway of the reaction in terms of Taube's broad inorganic redox reaction mechanistic classification.

Materials and Methods

Ethylenediaminetetraacetatocobaltate(II) complex was prepared by adding Na_2H_2EDTA to $CoCl_2.6H_2O$ in a ratio such that EDTA was in slight excess to ensure complete complexation and characterized by its λ_{max} of 510 nm[18]. Standard solution of perchloric acid (Sigma-Aldrich) was prepared by diluting concentrated perchloric acid (70 %, specific gravity 1.67) using distilled water. The solution was standardized titrimetrically using $B_4O_7Na_2.10H_2O$ as primary standard and methyl red indicator. Standard solution (2 mol dm^{-3}) of $NaClO_4$ (GPR) was prepared by dissolving 61.25 g of salt in 250 cm^3 volumetric flask. A 2 mol dm^{-3} of Lithium perchlorate solution was prepared in 50 cm^3 volumetric flask by neutralizing 6.3 g Lithium carbonate with perchloric acid. Stock solution of sodium ethanaote was prepared by weighing known amount and dissolving in known volume of distilled water.

Stoichiometric Determination

The stoichiometry, under the reaction condition $[CoEDTA^{2-}] = 0.01$ mol dm^{-3}, $[H^+] = 1\times10^{-3}$ mol dm^{-3}, $I = 0.30$ mol dm^{-3}, $[H_2O_2] = (1.0 – 50.0) \times 10^{-3}$ mol dm^{-3} was determined by spectrophotometric titration using the mole ratio approach.

Kinetics Study

The kinetic progress of the reaction was monitored under pseudo first order condition by observing change in absorbance of the reductant on EL UV/Vis digital spectrophotometer at a λ_{max} of 510 nm. The $[H^+]$, temperature and ionic strength were kept constant. The plot of log (A_∞-A_t) versus time using the first order rate equation

$$\log(A_\infty - A_t) = \frac{kt}{2.303} + \log(A_\infty - A_o)$$

was linear up to 70 % of the reaction (Fig. 1). The pseudo-first order rate constant, k_1, of the reaction was determined from the slope of the plot and are presented in Table 1. The log of k_1 versus log $[H_2O_2]$ was plotted. Keeping all other reactions conditions constant as shown on (Tables 2 and 3), the influence of $[H^+]$ (25.00 – 500.00) $\times$ 10^{-4} mol dm^{-3} and ionic strength, 0.10 – 1.00 mol dm^{-3} using $NaClO_4$ was investigated for the reaction.

The Effect of Added acetate ion on the Reaction Rate

The effect of added acetate ion on the reaction was investigated at $[CH_3OO^-]$ = (2.0-8.0) $\times$ 10^{-3} mol dm^{-3} while all other reactants concentration were kept were constant at I = 1.0 mol dm^{-3} ($NaClO_4$).

Free Radical Test

About 5.00 cm^3 of acrylamide solution was added to a partially oxidized reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion. This was followed by addition of a large excess of methanol. The same treatment was applied to solution of oxidant and reductant separately.

Product Analysis

The Co(III) product was identified spectrophometrically by scanning the spectrum of reaction product between wavelength ranges of 350 – 600 nm respectively.

Results and Discussion

The spetrophotometric titration showed reductant-oxidant ratio (2:1) for the system giving overall stoichiometric equation represented by:

$$2[CoEDTA]^{2-} + H_2O_2 + 2H^+ \rightarrow 2[CoEDTA]^- + 2H_2O$$

$[CoEDTA]^{2-}$, a one electron reductant is known to exhibit such stoichiometry to a two electron oxidant like H_2O_2 [7,19]. This fact is supported by the ratio of one mole of $HCrO_4^-$ to two moles of H_2O_2 in the reduction of the latter to give CrO_5 product[20]. The spectrum of the product of reaction gave λ_{max} at 380 and 530 nm characteristic of Co(III)[15,21,22]. The FTIR spectrum of the solution was also taken. Peaks were observed at 445.57 – 459.07 (Co-N), 1398.44 – 1641.48 (Co-COO^-). The product obtained in this reaction further supports the one electron transfer by the reductant.

The pseudo-first order plot was linear for about 70% of the reaction time (Fig. 1). The linearity of the plot confirms first order in the [reductant]. The plot of log k_1 versus log $[H_2O_2]$ gave a slope of 0.53 showing the reaction is half-order in $[H_2O_2]$. $k_{3/2}$ obtained from $\frac{k_1}{[H_2O_2]^{\frac{1}{2}}}$ (Table 1) gave fairly constant values, further confirming order of half with respect to $[H_2O_2]$. Half order reaction as obtained with respect to the concentration of oxidant is known to be occasioned either by molecular dissociation[23] or monomer-polymer equilibria with the monomeric species being the reactive form[20]. Order of one in $[CoHEDTAOH_2]^-$ and $[H_2O_2]$ have been reported for H_2O_2 and $[CoHEDTAOH_2]^-$ reactions[7,16]. Half order in H_2O_2 as obtained for the $[CoEDTA]^{2-}$ - H_2O_2 reaction is uncommon but Rao *et al.*,[24] reported second order in $[H_2O_2]$ in the reduction of thallium(III) by H_2O_2.

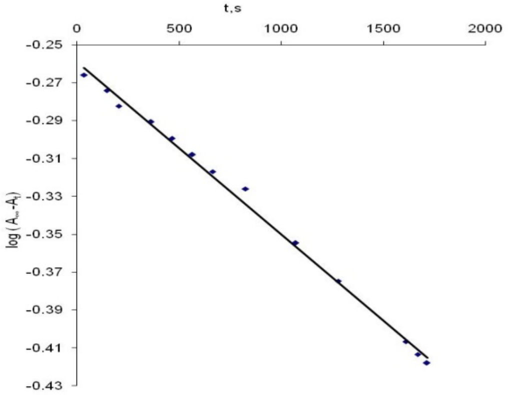

Fig.1: Pseudo - first order plot for the $[CoEDTA]^{2-}$ - H_2O_2 reaction

Table 1: Pseudo - first order and one - half order rate constants for the reaction of $[CoEDTA]^{2-}$ - H_2O_2, at $[CoEDTA^{2-}]$ = 5.0 $\times$ 10^{-3} mol dm^{-3}, T = 30 ^0C, $[H^+]$ = 1.0 $\times$ 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3}($NaClO_4$) and λ_{max} = 510 nm

$[H_2O_2]$, mol dm^{-3}	$10^5 k_1$, s^{-1}	$10^5 k_{3/2}$, $dm^{3/2} mol^{-1/2} s^{-1}$
0.2	11.52	25.75
0.25	13.16	26.31
0.3	13.82	25.23
0.35	14.97	25.31
0.4	16.12	25.49
0.6	20.73	26.76
0.7	21.25	25.40
0.8	23.60	26.39

Acid dependence study shows that the rate of reaction decreased with increase in $[H^+]$ (Table 2) and the plot of the acid dependent rate constant, k_2 versus $[H^+]^{-1}$ was linear with intercept (Fig.2). The implication of this type of acid dependence with a negative order is ascribed to deprotonation pre-equilibrium step and the rate determining reaction involves both the deprotonated and undeprotonated reactant species [20,25]. Inverse acid dependence has been reported for H_2O_2 reactions[7],[24,26].

Table 2: Pseudo - first order and acid dependent rate constants for the reaction of $[CoEDTA]^{2-}$ H_2O_2, at $[CoEDTA^{2-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[H_2O_2]$ = 0.6 mol dm^{-3}, T = 30 ^{0}C,I = 0.5 mol dm^{-3}($NaClO_4$) and λ_{max} = 510 nm

10^4 [H$^+$], mol dm^{-3}	10^5 k_1, s^{-1}	10^5 $k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}
5.0	38.73	50.00
10.0	23.03	29.73
25.0	13.94	18.00
75.0	11.52	14.87
100.0	9.30	12.00
500.0	9.21	11.89

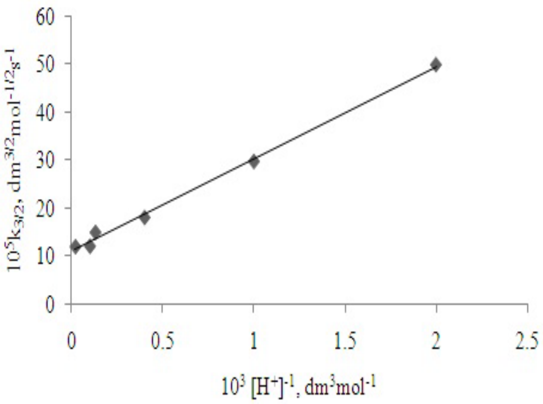

Fig.2. The plot of acid dependent rate constant versus inverse of acid concentration

As the ionic strength of the reaction medium was increased the rate of reaction decreased (Table 3). Plot of $k_{3/2}$ versus √I (Fig.3) gave slope – 0.90. Inverse ionic strength dependence with rate as observed in this reaction indicates involvement of oppositely charged reactant ions [27] at the activated complex. However, given the reactant species, $[CoEDTA]^{2-}$ (reductant) and H_2O_2 (oxidant) in this reaction, to form opposite charges from these substrates to support the negative Bronsted effect observed in this reaction seems unlikely. Also protonation of any of the reactants species is unlikely given the nature of acid dependence of the reaction. The negative Bronsted effect may have been accounted for by other interactions yet to be established by us.

Table 3: Pseudo - first order and Ionic strength dependent rate constants for the reaction of $[CoEDTA]^{2-}$ - H_2O_2, at $[CoEDTA^{2-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, T = 30 ^{0}C, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, and λ_{max} = 510 nm

I, mol dm^{-3}	10^5 k_1, s^{-1}	10^5 $k_{3/2}$, dm$^{3/2}$ mol$^{-1/2}$ s^{-1}
0.1	59.46	59.46
0.3	30.31	39.13
0.5	20.91	27.00
0.7	18.61	24.02
1	10.46	13.50

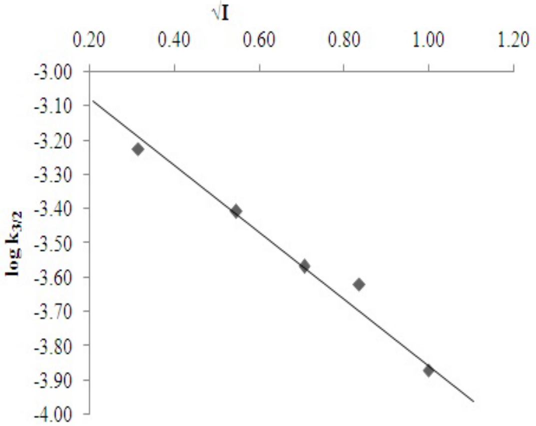

Fig.3. The plot of log $k_{3/2}$ versus √I

Addition of acrylamide solution to a partially oxidized reaction mixture followed by excess methanol gave a negative result. Gelation of the reaction is taken as evidence for the presence of free radicals[28]. The test proved negative for the titled reaction. Banerjee and Pujari[7] however implicated free radical for the reaction of these substrates.

The Michaelis – Menten plot of k_1^{-1} versus $[H_2O_2]^{-1}$ (Fig.4) was linear with an intercept.

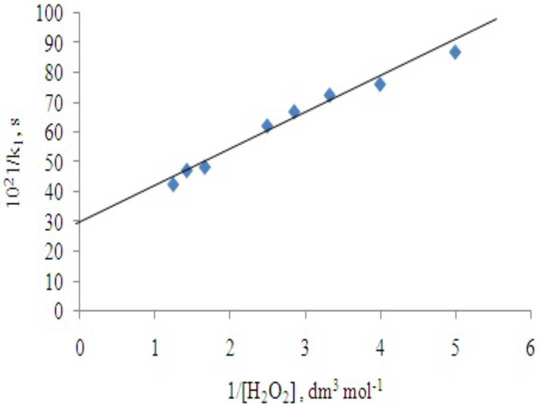

Fig. 4. The plot of k_1^{-1} versus $[H_2O_2]^{-1}$

This observation suggests formation of intermediate complex, a feature known to be associated with reactions occurring by inner - sphere mechanism. The result obtained from this plot support the implication of intermediate complex formation for the oxidation of $[CoEDTA]^{2-}$ by H_2O_2[29]. Added acetate ion unexpectedly accelerated the reaction rate which is contrary to the evidence from the Michaels - Menten plot. Catalysis of reaction by added ion is a feature ascribed to reactions proceeding via the outer-sphere mechanism[30]. The observed effect by the added acetate ion may not be ascribable to the known traditional catalysis of added ions. The observed acceleration of reaction rate by the added acetate ion as earlier observed[18] could have arisen as a result of depletion of $[H^+]$ formed in the pre-equilibrium depronation step (equation 3 in the mechanistic scheme) thereby favoring the forward reaction which leads to the formation of more $[CoEDTAOH]^{3-}$ - a key reactant specie in the reaction. The OH^- group in $[CoEDTAOH]^{3-}$ may have enhanced the intermediate bridge formation as it is known to be an effective bridging group[23]. The experimental data is accounted for by the following mechanistic scheme which is in favour of the inner - sphere reaction.

$$[CoEDTA]^{2-} + H_2O \overset{K_1}{\rightleftharpoons} [CoEDTAOH]^{3-} + H^+ \quad \ldots (3)$$

$$H_2O_2 \overset{K_2}{\rightleftharpoons} H_2O + O \quad \ldots (4)$$

$$[CoEDTA]^{2-} + O \xrightarrow{k_1} [CoEDTA\text{-}O]^{2-} \quad \ldots (5)$$

$$[CoEDTA\text{-}O]^{2-} \xrightarrow[\text{slow}]{k_2} [CoEDTA]^{-} + O^{-} \quad \ldots (6)$$

$$[CoEDTAOH]^{3-} + O \xrightarrow{k_3} [CoEDTAOH\text{-}O]^{3-} \quad \ldots (7)$$

$$[CoEDTAOH\text{-}O]^{3-} \xrightarrow[\text{slow}]{k_4} [CoEDTA]^{-} + HO_2^{2-} \quad \ldots (8)$$

$$O^{-} + HO_2^{2-} + 3H^{+} \xrightarrow{\text{fast}} 2H_2O + O \quad \ldots (9)$$

With equations (6) and (8) being the slow steps, the formation of the product is given by equation (10)

$$\frac{d[CoEDTA^{-}]}{dt} = k_2[CoEDTA-O^{2-}] + k_4[CoEDTAOH-O^{3-}] \quad \ldots(10)$$

$$\frac{d[CoEDTA-O^{2-}]}{dt} = k_1[CoEDTA^{2-}][O] - k_2[CoEDTA-O^{2-}] \approx 0 \quad \ldots(11)$$

$$[CoEDTA-O^{2-}] = \frac{k_1[CoEDTA^{2-}][O]}{k_2} \quad \ldots (12)$$

$$\frac{d[CoEDTAOH-O^{3-}]}{dt} = k_3[CoEDTAOH^{3-}][O] - k_4[CoEDTAOH-O^{3-}] \approx 0 \quad \ldots (13)$$

$$[CoEDTAOH-O^{3-}] = \frac{k_3[CoEDTAOH^{3-}][O]}{k_4} \quad \ldots (14)$$

But

$$[CoEDTAOH^{3-}] = \frac{K_1[CoEDTA^{2-}]}{H^{+}} \quad \ldots (15)$$

then

$$[CoEDTAOH-O^{3-}] = \frac{k_3K_1[CoEDTA^{2-}][O]}{k_4[H^{+}]} \quad \ldots (16)$$

Substituting equations (12) and (16) into (10) gives (17)

$$\frac{d[CoEDTA^-]}{dt} = k_1[CoEDTA^{2-}][O] + \frac{K_1k_3[CoEDTA^{2-}][O]}{H^+} \qquad \dots (17)$$

If $[H_2O_2] = [O] = [O]^2$; $[O]^2 = K_2[H_2O_2]$; $[O] = K_2^{1/2}[H_2O_2]^{1/2}$

$$\frac{d[CoEDTA^-]}{dt} = k_1K_2^{1/2}[CoEDTA^{2-}][H_2O_2]^{1/2} + \frac{K_1k_3K_2^{1/2}[CoEDTA^{2-}][H_2O_2]^{1/2}}{H^+} \qquad \dots (18)$$

$$\frac{d[CoEDTA^-]}{dt} = \left(k_1K_2^{1/2} + \frac{K_1k_3K_2^{1/2}}{H^+}\right)[CoEDTA^{2-}][H_2O_2]^{1/2} \qquad \dots (19)$$

$k_1K_2^{1/2} = 1.0 \times 10^{-4}$ and $K_1k_3K_2^{1/2} = 2.0 \times 10^{-7}$

Conclusion

The Oxidation of ethylene diaminetetraacetato cobaltate(II) complex by Hydrogen peroxide was studied in aqueous perchloric acidic medium. A mole ratio of 2:1 (Complex:Oxidant) was obtained. Analysis of other kinetic data obtained under the pseudo-first order condition gave an overall order of one and half; half order with respect to the concentration of the oxidant and first order with respect to the concentration of the reductant. Rationalizing the evidences obtained in the study favours the inner-sphere mechanism and a plausible mechanistic scheme which explains the kinetic data obtained is proposed.

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