

Kinetics and Mechanism of Oxidation of Catechol by Oxygenated $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]^{5+}$ Complex

Nathaniel Oladunni*, Suleiman Ola Idris, Ameh David Onu, Gideon Adamu Shallangwa

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

Email address:

Nathola2010@gmail.com (N. Oladunni)

*Corresponding author

To cite this article:

Nathaniel Oladunni, Suleiman Ola Idris, Ameh David Onu, Gideon Adamu Shallangwa. Kinetics and Mechanism of Oxidation of Catechol by Oxygenated $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]^{5+}$ Complex. *Science Frontiers*. Vol. 2, No. 1, 2021, pp. 1-7. doi: 10.11648/j.sf.20210201.11

Received: November 25, 2020; Accepted: December 28, 2020; Published: February 10, 2021

Abstract: The kinetics and mechanisms of the redox reaction of Catechol and μ -superoxo-bis[pentaamminecobalt(III)] pentachloridemonohydrate, $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$, hereafter represented as $\text{CoO}_2\text{Co}^{5+}$ was studied in aqueous perchloric acid under pseudo-first-order conditions at $27 \pm 1^\circ\text{C}$, $I = 0.35 \text{ mol dm}^{-3}$ (NaClO_4) and $\lambda_{\text{max}} = 660 \text{ nm}$. μ -superoxo-bis[pentaamminecobalt(III)] pentachloridemonohydrate was used as the oxidant and it was synthesized and characterized according to reported procedure. This study was aimed at generating kinetic data with respect to the oxidation of catechol by μ -superoxo-bridged binuclear cobalt(III) complex of ammine and to propose plausible mechanism that underpin this reaction of interest. Effect of changes in acid concentration, ionic strength, dielectric constant and temperature on the reaction rate was investigated. The reaction was found to be first-order in both reactants, second-order overall, acid dependent and showed a negative Brønsted-Debye salt effect. Decreasing the dielectric constant from 80.1–74.01 ($\text{CH}_3\text{COCH}_3/\text{H}_2\text{O}$) increased the rate of reaction. A large negative value of ΔS^\ddagger ($-224 \text{ J mol}^{-1} \text{ K}^{-1}$) was obtained during the thermodynamic studies and that showed that the activated complex formed is more ordered. This confirmed that the reaction proceeded by associative mechanism. There was evidence for the presence of free radicals during the course of the reaction, but non to validate the formation of an intermediate complex. In overall, the results suggest an outer-sphere mechanism for the reaction. A probable mechanism is proposed.

Keywords: Kinetics, Mechanism, Oxidation, Dioxygen Complex, Observed Rate Constant (k_{obs}), Catechol ($\text{C}_6\text{H}_4(\text{OH})_2$), Ionic Strength (I)

1. Introduction

Electron transfer reactions of metal complexes play very important roles in many biological processes including collagen synthesis, steroid metabolism, the immune response, drug activation, neurotransmitter metabolism, nitrogen fixation, respiration and photosynthesis [1]. The latter two processes are fundamentally significant as they provide most of the energy that is required for the maintenance of life. Oxygen is one of the key factors to sustain higher form of life because; it is the terminal oxidant in respiratory cycle in aerobic organism. The singlet oxygen ($^1\text{O}_2$), present in air is less reactive than its different reduced derivatives[2] like superoxo (O_2^-) and peroxo (O_2^{2-}). These radicals form part of reactive oxygen species (ROS) [3]. In pursuit of understanding the ROS chemistry, numerous metal-bound-oxygen complexes were synthesized, among which cobalt-

bound superoxo complexes are renowned since they are easy to study at ambient conditions [4]. Kinetic studies of 1-methyl-2-thiourea with superoxide coordinated to cobalt(III) showed a first order dependence on oxidant and reductant concentration respectively. The rate of the reaction increases with increase in ionic strength medium [5]. Information on the formation, stability, nature, photochemical decomposition and redox reactions of the μ -superoxobis[pentaamminecobalt(III)] pentachloride monohydrate, $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$ is well documented in the literature [6]. However, the reaction between Catechol and $\text{Co}(\text{O}_2)\text{Co}^{5+}$ is hereby reported for the first time. Catechol, also known as pyrocatechol or 1,2-dihydroxybenzene, is an organic compound with the molecular formula $\text{C}_6\text{H}_4(\text{OH})_2$. It is the *ortho* isomer of the three isomeric benzenediols. This colourless compound occurs naturally in trace amounts. Small amounts of catechol occur naturally in fruits and

vegetables, along with the enzyme catecholase. Upon mixing the enzyme with the substrate and exposure to oxygen (as when a potato is cut and left out), the colorless catechol oxidizes to reddish-brown melanoid pigments, derivatives of benzoquinone [7]. Approximately 50% of synthetic catechol is consumed in the production of pesticides, the remainder being used as a precursor to fine chemicals such as perfumes and pharmaceuticals [8]. It is a common building block in organic synthesis. Several industrially significant flavors and fragrances are prepared starting from catechol. Guaiacol is prepared by methylation of catechol and is then converted to vanillin [9].

This study is aimed at generating kinetic data with respect to the oxidation of catechol by μ -superoxo-bridged binuclear cobalt(III) complex of ammine and to propose plausible mechanism that underpin this reaction of interest. An investigation of this binuclear cobalt (III) species is worthwhile in part because of the possible relevance of the results as a comparative tool. It will also serve as an extension of earlier studies on dioxygen cobalt (III) complex and contribute to the conceptual development of inorganic reaction mechanisms in relation to this type of complexes.

2. Materials and Methods

Analar grade reagents were used in this research. Reaction rates were monitored by following the decrease in absorbance of the reaction mixture at 660 nm on a CORNING colorimeter 253. $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]\text{Cl}_5 \cdot 5\text{H}_2\text{O}$ was used as the oxidant and it was synthesized and characterized according to reported procedure [10]. Catechol, also known as 1,2-dihydroxybenzene (Sigma- Aldrich) was used as the reducing agent, while sodium perchlorate (M&B) was used to maintain the ionic strength of the reaction medium.

The stoichiometry of the reaction was determined by spectrophotometric titration, using the mole ratio method [11] by keeping the concentration of the $\text{Co}(\text{O}_2)\text{Co}^{5+}$ constant at $2 \times 10^{-3} \text{ mol dm}^{-3}$ and varying the concentration of the reductant ($\text{C}_6\text{H}_4(\text{OH})_2$) within the range $(2-16) \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$, $I = 0.35 \text{ mol dm}^{-3}$ (NaClO_4), $\lambda_{\text{max}} = 660 \text{ nm}$ and $T = 27.0 \pm 1.0^\circ\text{C}$.

Kinetic studies were conducted *via* spectrophotometry by monitoring the decrease in absorbance of the reaction mixture at 660 nm which is assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transitions (λ_{max} of aqueous $\text{Co}(\text{O}_2)\text{Co}^{5+}$) as a function of time using Corning Spectrophotometer model 253 [12]. All measurements were made under pseudo-first order conditions with the concentration of catechol ($\text{C}_6\text{H}_4(\text{OH})_2$) at least 10 times greater than that of $\text{Co}(\text{O}_2)\text{Co}^{5+}$ and at constant ionic strength of 0.35 mol dm^{-3} (using NaClO_4), $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$, and temperature of $27.0 \pm 1.0^\circ\text{C}$. Under such conditions, kinetic curves were exponential and rate constants were obtained from logarithmic plots of absorbance differences, $\log (A_t - A_\infty)$ against reaction time. Second order rate constants, k_2 , were derived for each run [13] as represented by equation (1) below

$$k_2 = \frac{k_{\text{obs}}}{[\text{C}_6\text{H}_4(\text{OH})_2]} \quad (1)$$

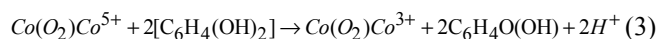
The effect of $[\text{H}^+]$ on the reaction rate was investigated by varying the $[\text{H}^+]$ between $0.08 \times 10^{-1} \leq [\text{H}^+] \leq 0.2 \times 10^{-1} \text{ mol dm}^{-3}$. Kinetic runs were carried out at constant ionic strength of 0.35 mol dm^{-3} (using NaClO_4) and temperature of $27.0 \pm 1.0^\circ\text{C}$, while keeping oxidant's and reductant's concentrations constant at $2 \times 10^{-3} \text{ mol dm}^{-3}$ and $2 \times 10^{-2} \text{ mol dm}^{-3}$ respectively [12]. The effect of varying the ionic strength of the reaction medium on the rate of the reaction was investigated in the range of $0.20 - 0.50 \text{ mol dm}^{-3}$ (using NaClO_4) while the concentrations of the reactants were kept constant at $27 \pm 1^\circ\text{C}$. The effect of added anion and cation on the reaction rates was investigated for $[\text{X}] = (0 - 10) \times 10^{-2} \text{ mol dm}^{-3}$ where X represents sulphate ion (SO_4^{2-}) and Zinc ion (Zn^{2+}) at constant $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$, $[\text{C}_6\text{H}_4(\text{OH})_2]$, ionic strength and temperature [14]. The effect of changes in the dielectric constant (D) of the reaction medium on the rates of reaction of $\text{CoO}_2\text{Co}^{5+}$ and Catechol ($\text{C}_6\text{H}_4(\text{OH})_2$) was investigated at constant $[\text{CoO}_2\text{Co}^{5+}]$, $[\text{C}_6\text{H}_4(\text{OH})_2]$, ionic strength (μ) and temperature of reaction by varying the dielectric constant of the medium using binary mixture of acetone-water (2-10%). The effect of temperature on the reaction rate was studied in the range of 300–340 K. The temperature dependence data were analysed using Eyring plot of $\ln(\frac{k_2}{T})$ versus $\ln(\frac{1}{T})$ (eq. 2) and thermodynamic parameters were determined at constant $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$, $[\text{C}_6\text{H}_4(\text{OH})_2]$ and ionic strength.

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} - \left[\frac{1}{T}\right] \quad (2)$$

Electronic spectra of partially reacted reaction's mixture at wavelength interval of 400nm-700nm was carried out. Similar run was made for the oxidant separately and the two results were compared. Michaelis–Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{C}_6\text{H}_4(\text{OH})_2]$ was also carried out to detect the presence or absence of intermediate complex formation. Test for free radicals was carried out by adding about 5cm^3 of $0.015 \text{ mol dm}^{-3}$ of acrylamide to a partially oxidised reaction mixture. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of $[\text{H}^+]$, ionic strength (I) and temperature [14-16].

3. Results and Discussion

Plot of absorbance at completion of reaction *versus* $[\text{C}_6\text{H}_4(\text{OH})_2] / [\text{CoO}_2\text{Co}^{5+}]$ gave a breaking point at 2. (Figure 1). This result indicates a stoichiometry of two mole of $\text{C}_6\text{H}_4(\text{OH})_2$ reacting with one moles of $\text{CoO}_2\text{Co}^{5+}$ as represented with eqn. 3.



This result is the inverse of the finding of Singh *et al.*, (2013) where the stoichiometry of the reaction of

$\text{Co}(\text{O}_2)\text{Co}^{5+}$ with acetaminophen was found to be ratio 2:1 respectively [17] while a stoichiometry of 1:1 was reported in the reaction of $\text{CoO}_2\text{Co}^{5+}$ with thiourea [5].

In the kinetic analysis, the pseudo-first order plot of $\log(A_t - A_\infty)$ (where A_t and A_∞ are absorbances at time 't' and at infinity, respectively) against time was linear to more than 80% extent of reaction, indicating that the reaction is first order with respect to $[\text{CoO}_2\text{Co}^{5+}]$ under the experimental conditions (Figure 2). This is further supported by the values of second order rate constant, k_2 , which were fairly constant (Table 1). The order of the reaction with respect to $[\text{C}_6\text{H}_4(\text{OH})_2]$ was found by plotting $\log k_{\text{obs}}$ against $\log[\text{C}_6\text{H}_4(\text{OH})_2]$. The plot of $\log k_{\text{obs}}$ against

$\log[\text{C}_6\text{H}_4(\text{OH})_2]$ was linear with a slope of 0.96 (approx. 1) (Figure 3). This suggests that the order of reaction with respect to $[\text{C}_6\text{H}_4(\text{OH})_2]$ is first order. Therefore, the rate equation for the reaction is represented by equation 4;

$$-d \frac{[\text{Co}(\text{O}_2)\text{Co}^{5+}]}{dt} = k_2 [\text{Co}(\text{O}_2)\text{Co}^{5+}] [\text{C}_6\text{H}_4(\text{OH})_2] \quad (4)$$

Where $k_2 = (0.87 \pm 0.02) \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

This finding is similar to the one observed by Osunlaja *et al.*, (2013) in the reduction of this complex with thiourea [5].

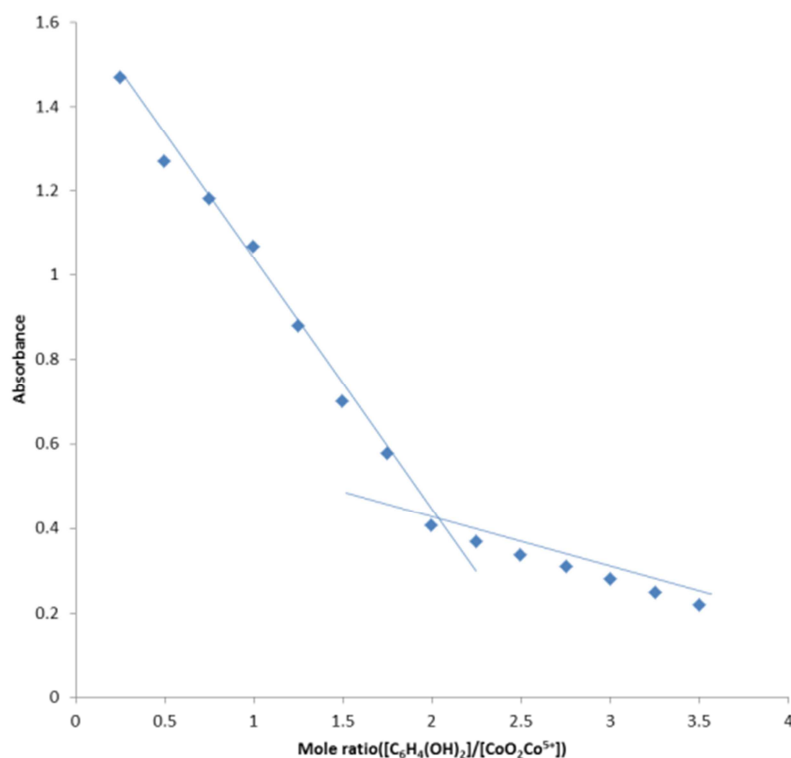


Figure 1. Stoichiometry of the oxidation of $[\text{C}_6\text{H}_4(\text{OH})_2]$ by $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = (0.5 - 7.0) \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.35 \text{ mol dm}^{-3}$ (NaClO_4), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

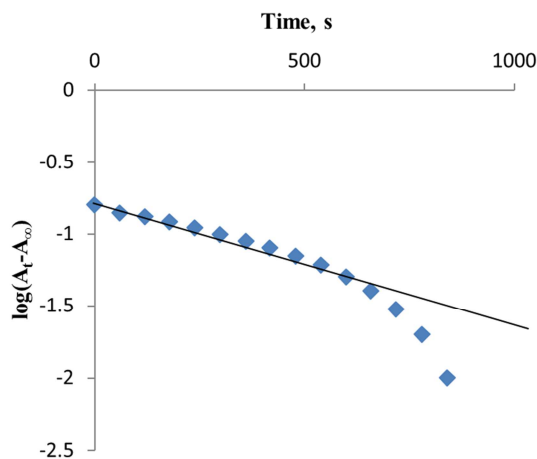


Figure 2. Typical Pseudo-first order plot for the oxidation of $[\text{C}_6\text{H}_4(\text{OH})_2]$ by $[\text{CoO}_2\text{Co}^{5+}]$ at $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = 4 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$, $I = 0.35 \text{ mol dm}^{-3}$ (NaClO_4), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

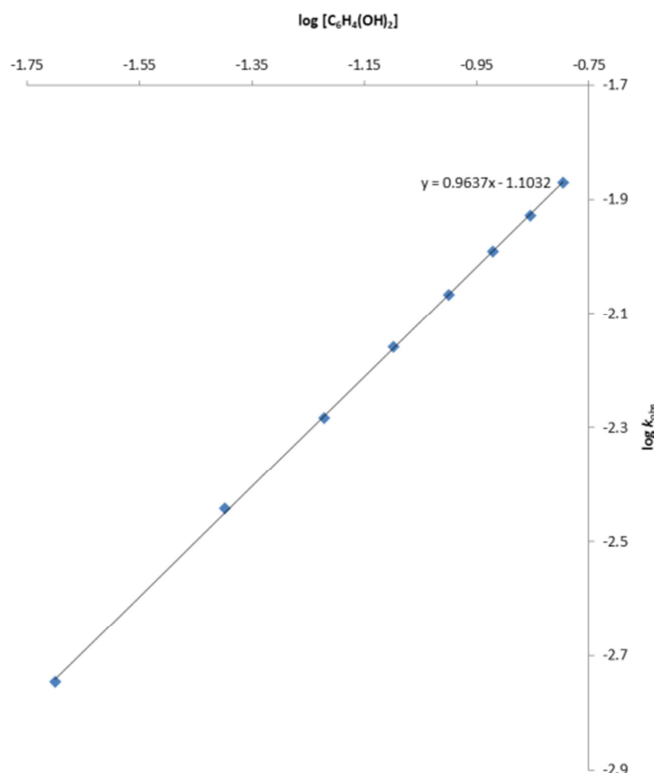


Figure 3. Plot of $\log k_{\text{obs}}$ versus $\log [\text{C}_6\text{H}_4(\text{OH})_2]$ for the oxidation of $\text{C}_6\text{H}_4(\text{OH})_2$ by $\text{Co}(\text{O}_2)\text{Co}^{5+}$ at $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = (2-16) \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$, $I = 0.35 \text{ mol dm}^{-3}$ (NaClO_4), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

Table 1. Pseudo-first order and second order rate constants for the oxidation of $\text{C}_6\text{H}_4(\text{OH})_2$ by $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ at $T = 27.0 \pm 1.0^\circ\text{C}$, $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

$10^2 [\text{C}_6\text{H}_4(\text{OH})_2]$ (mol dm^{-3})	$10^1 [\text{H}^+]$ (mol dm^{-3})	I (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})	$10^1 k_2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
2	0.2	0.35	1.82	0.91
4	0.2	0.35	3.62	0.90
6	0.2	0.35	5.21	0.87
8	0.2	0.35	6.96	0.87
10	0.2	0.35	8.57	0.86
12	0.2	0.35	10.20	0.85
14	0.2	0.35	11.91	0.85
16	0.2	0.35	13.61	0.85
2	0.08	0.35	4.74	2.37
2	0.1	0.35	3.80	1.90
2	0.12	0.35	3.22	1.61
2	0.14	0.35	2.76	1.38
2	0.16	0.35	2.26	1.13
2	0.18	0.35	2.26	1.13
2	0.2	0.35	1.82	0.91
2	0.2	0.20	7.97	3.89
2	0.2	0.25	4.84	2.52
2	0.2	0.30	2.94	1.46
2	0.2	0.35	1.79	0.91
2	0.2	0.40	1.09	0.53
2	0.2	0.45	0.66	0.34
2	0.2	0.50	0.40	0.22

In order to investigate the effect of $[\text{H}^+]$ on the reaction

rate, $[\text{H}^+]$ was varied within the range of $0.08 \times 10^{-1} \leq [\text{H}^+] \leq 0.2 \times 10^{-1} \text{ mol dm}^{-3}$ at constant ionic strength (I), while keeping $[\text{CoO}_2\text{Co}^{5+}]$ and $[\text{C}_6\text{H}_4(\text{OH})_2]$ constant. Inverse acid dependence was observed for this reaction at $I = 0.35 \text{ mol dm}^{-3}$ (using NaClO_4), and $T = 27 \pm 1^\circ\text{C}$. The pseudo-first order and second order rate constants at increasing $[\text{H}^+]$, but constant $[\text{CoO}_2\text{Co}^{5+}]$, $[\text{C}_6\text{H}_4(\text{OH})_2]$, I and T are presented in Tables 1. The plots of $k_2([\text{H}^+])$ versus $[\text{H}^+]$ is linear (Figure 4). The dependence of rate constants on $[\text{H}^+]$ can be represented by Equation (5). This result is similar to the finding of Singh *et al.*, (2015) for the reaction of $[(\text{NH}_3)_4\text{Co}^{\text{III}}(\mu\text{-NH}_2, \mu\text{-O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_4]^{4+}$ with $\text{S}_2\text{O}_3^{2-}$ [18].

$$k_2 = \frac{k_3 K_4}{[\text{H}^+]} \quad (5)$$

The effect of ionic strength on the rate of the reaction is shown in Table 1. It depicts that the rate constants decreased with increase in ionic strength of reaction medium, from 0.20 – 0.50 mol dm^{-3} (using NaClO_4), indicating a negative Brønsted-Debye salt effect. A plot of $\log k_2$ versus \sqrt{I} gave a slope of -4.91 (Figure 5). This is an indication of unlike charges operating at the rate determining step. The result is in concomitance with the findings of Singh and his co-workers for the reaction of $[(\text{NH}_3)_4\text{Co}^{\text{III}}(\mu\text{-NH}_2, \mu\text{-O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_4]^{4+}$ with $\text{S}_2\text{O}_3^{2-}$ [18].

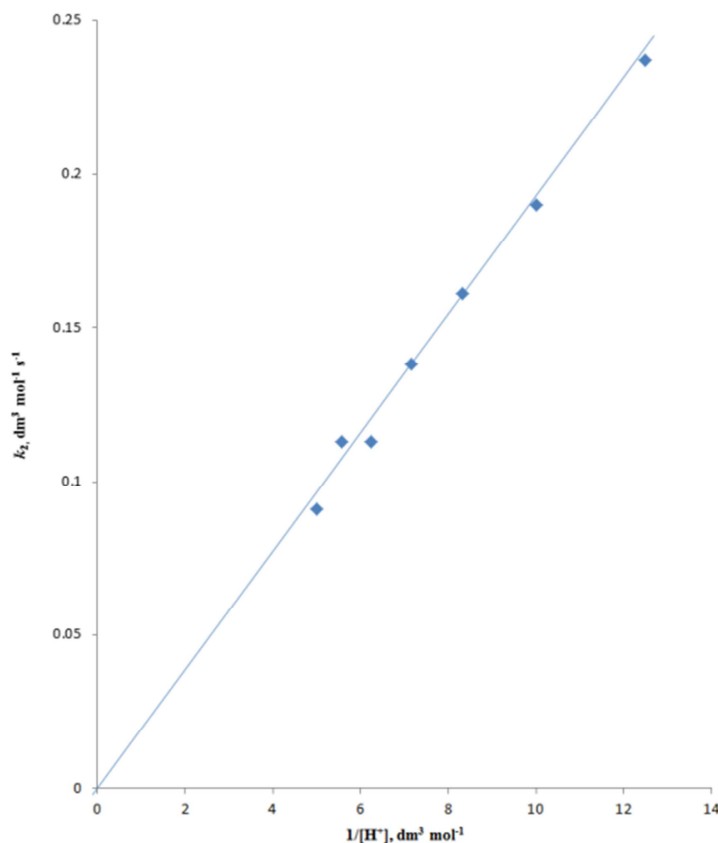


Figure 4. Plot of $\log k_1$ versus $1/[H^+]$ for the oxidation of $C_6H_4(OH)_2$ by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = (0.08-0.2) \times 10^{-1} \text{ mol dm}^{-3}$, $[C_6H_4(OH)_2] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.35 \text{ mol dm}^{-3}$ ($NaClO_4$), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

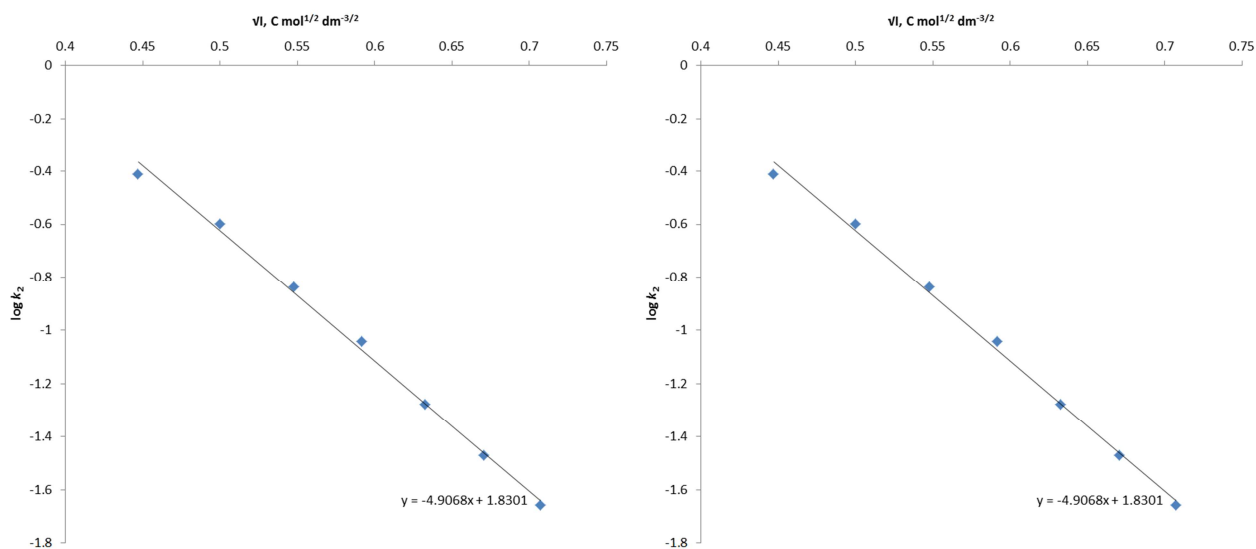


Figure 5. Plot of $\log k_2$ versus \sqrt{I} for the oxidation of $C_6H_4(OH)_2$ by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[C_6H_4(OH)_2] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = (2.0-5.0) \times 10^{-1} \text{ mol dm}^{-3}$ ($NaClO_4$), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

The reaction rate was inhibited as $[SO_4^{2-}]$ and $[Zn^{2+}]$ increases (Table 2). The anion's and cation's inhibition of this reaction hints that this reaction most likely proceeds by the outer-sphere mechanism [19].

Decreasing the dielectric constant from 80.1–74.01 (CH_3COCH_3/H_2O) increases the rate of reaction (Table 3). According to electron transfer theory, changes in

dielectric properties are expected to affect reorganization of a solvent molecule around the reactants and the activated complex [19]. This observation is in support of the influence the ionic strength had on the rate of this reaction. The plot of absorbance against wavelength showed that there was no significant shift in the λ_{max} of the reaction mixtures compared to that of $[Co(O_2)Co]^{5+}$ (Figure 6). Also, Michaelis-Menten

plot of $1/k_{\text{obs}}$ versus $1/[\text{C}_6\text{H}_4(\text{OH})_2]$ was linear with no intercept (Figure 7). These suggest that, there is no formation of stable intermediate preceding the electron transfer step [19]. The absence of intermediate complex is an evidence that the reaction proceeded by an outer-sphere redox mechanism.

The presence of free radicals were indicated by gel formation on addition of acrylamide (a known radicals scavenger) to partially oxidized mixture of the reactants in excess methanol.

The plot of $\ln(k_2/T)$ against $(1/T)$ is shown in Figure 8 and the results of temperature dependence of the rate constants and activation parameters for the reaction are presented in Table 4. A large negative value of ΔS^\ddagger ($-224\text{Jmol}^{-1}\text{K}^{-1}$) is obtained and that shows that the activated complex formed is more ordered. This further confirms that the reaction proceeded by associative mechanism.

In the end of the reaction, KSCN solution in excess acetone was added to the final reaction mixture of $[\text{CoO}_2\text{Co}]^{5+}$ and $\text{C}_6\text{H}_4(\text{OH})_2$. A blue colour was obtained which is a qualitative confirmatory test for the presence of Co^{2+} as a product for the reaction under investigation. Furthermore, organic qualitative test on the product confirmed the presence of Alkanone ($\text{C}=\text{O}$) and hydroxyl ($-\text{OH}$) functional group.

Table 2. Table of effect of added ions on $\text{CoO}_2\text{Co}^{5+}$ - $\text{C}_6\text{H}_4(\text{OH})_2$ reaction.

X	$10^2 [\text{X}] (\text{mol. dm}^{-3})$	$10^3 k_{\text{obs}} (\text{s}^{-1})$	$10^1 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
SO_4^{2-}	0	1.84	0.92
	2	1.70	0.85
	4	1.57	0.78
	6	1.43	0.71
	8	1.34	0.67
	10	1.24	0.62
Zn^{2+}	0	1.82	0.91
	2	1.54	0.77
	4	1.31	0.66
	6	1.11	0.55
	8	0.85	0.43
	10	0.69	0.35

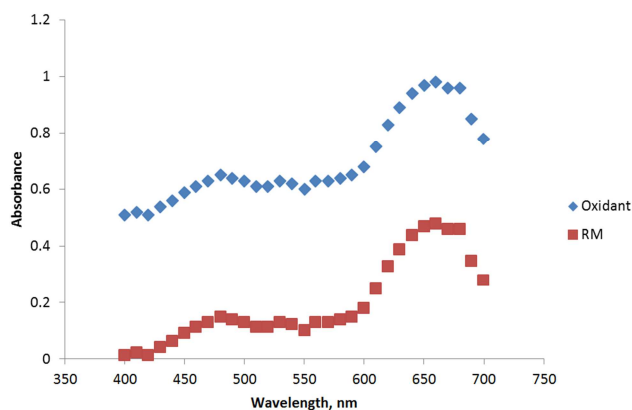


Figure 6. Spectra of $\text{CoO}_2\text{Co}^{5+}$ and that of reaction mixture (Oxidant= $\text{CoO}_2\text{Co}^{5+}$ and RM=reaction mixture).

Table 3. Table of effect of dielectric constant on $[\text{Co}(\text{O}_2)\text{Co}]^{5+}$ - $\text{C}_6\text{H}_4(\text{OH})_2$ reaction.

D	$10^2/D(\text{mol dm}^{-3})$	$10^3 k_{\text{obs}} (\text{s}^{-1})$	$10^1 k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
80.10	1.25	1.82	0.91
78.88	1.27	2.26	1.13
77.67	1.29	2.74	1.37
76.45	1.31	3.41	1.70
75.23	1.33	4.15	2.07
74.01	1.35	5.27	2.64

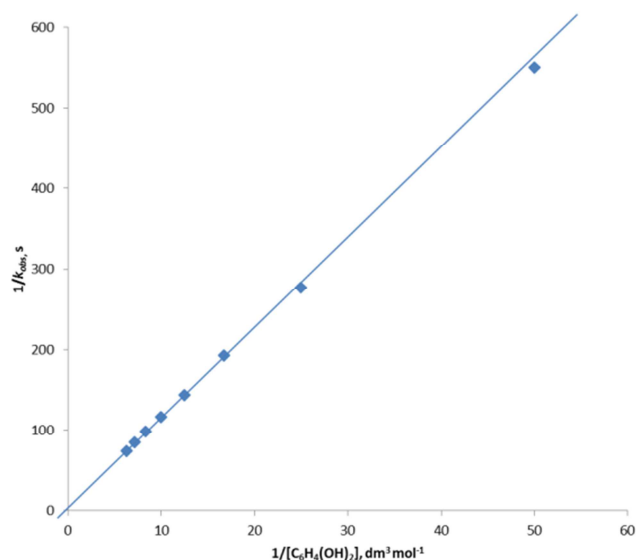


Figure 7. Michaelis Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{C}_6\text{H}_4(\text{OH})_2]$ for the oxidation of $[\text{C}_6\text{H}_4(\text{OH})_2]$ by $\text{CoO}_2\text{Co}^{5+}$ at $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = 2 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{H}^+] = 2 \times 10^{-2} \text{mol dm}^{-3}$, $I = 0.35 \text{mol dm}^{-3}$ (NaClO_4), $T = 27.0 \pm 1.0^\circ \text{C}$ and $\lambda_{\text{max}} = 660 \text{nm}$.

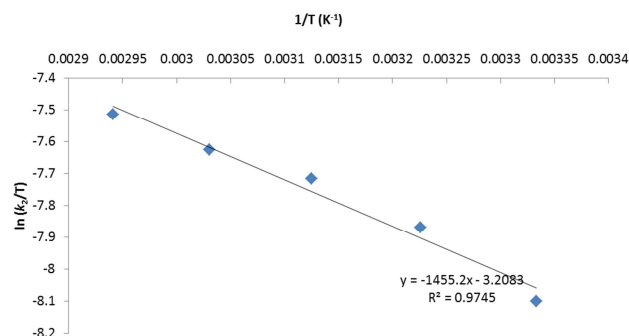


Figure 8. The plot of $\ln(k_2/T)$ versus $1/T$ for the reaction of $\text{C}_6\text{H}_4(\text{OH})_2$ with $\text{CoO}_2\text{Co}^{5+}$ at $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = 2 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{H}^+] = 2 \times 10^{-2} \text{mol dm}^{-3}$, $I = 0.35 \text{mol dm}^{-3}$ (NaClO_4), $T = 27.0 \pm 1.0^\circ \text{C}$ and $\lambda_{\text{max}} = 660 \text{nm}$.

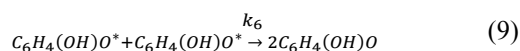
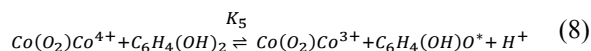
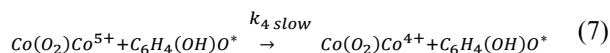
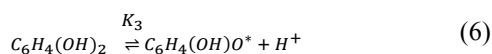
Table 4. Temperature dependence of the rate constants and activation parameters for the reaction of $[\text{CoO}_2\text{Co}^{5+}]$ with $[\text{C}_6\text{H}_4(\text{OH})_2]$ at $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = 2 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{H}^+] = 2 \times 10^{-2} \text{mol dm}^{-3}$, $I = 0.35 \text{mol dm}^{-3}$, (NaClO_4) and $\lambda_{\text{max}} = 660 \text{nm}$

T, K	$10^3 k_{\text{obs}}, \text{s}^{-1}$	$10 k_2, (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
300	1.82	0.91
310	2.37	1.19
320	2.86	1.43
330	3.22	1.61
340	3.71	1.85

$$\Delta H^\ddagger = +12 \text{kJmol}^{-1}, \Delta S^\ddagger = -224 \text{Jmol}^{-1}\text{K}^{-1}, \Delta G^\ddagger = +79 \text{kJmol}^{-1}.$$

$$E_a = +15 \text{ KJ mol}^{-1}, E_a = +15 \text{ KJ mol}^{-1}$$

Based on the results obtained from this investigation, the following reaction mechanism is proposed for this reaction:



$$Rate = k_4 [Co(O_2)Co^{5+}] [C_6H_4(OH)O^*] \quad (10)$$

From equation (6), we have

$$K_3 = \frac{[C_6H_4(OH)O^*][H^+]}{[C_6H_4(OH)_2]} \quad (11)$$

Substituting equation (12) into (10), we have

$$[C_6H_4(OH)O^*] = \frac{K_3 [C_6H_4(OH)_2]}{[H^+]} \quad (12)$$

$$Rate = \frac{K_3 k_4 [Co(O_2)Co^{5+}] [C_6H_4(OH)_2]}{[H^+]} \quad (13)$$

Equation (13) is analogous to equation (4) where

$$k_2 = \frac{k_3 K_4}{[H^+]} = (0.87 \pm 0.02) \times 10 dm^3 mol^{-1} s^{-1}$$

4. Conclusion

The redox reaction of μ -superoxo-bis[pentaamminecobalt(III)]pentachloridemonohydrate complex with catechol in aqueous medium showed a stoichiometry of 1:2. The reaction is second-order overall and showed negative Brønsted-Debye salt effect. The reaction rate changes with varying acid concentration, temperature and dielectric constant. Both spectroscopic and kinetic studies showed no proof of intermediate complex formation. The major redox products of this reaction are cobalt complex(CoO_2Co^{3+}) in its +2 oxidation state and 1,8-dihydroxynaphthalene-2,7(1H,6H)-dione. In general, the results suggest an outer-sphere mechanism as the plausible pathway for the reaction.

References

- [1] Prince, R. C. and George, G. N. (1990). Tryptophan Radicals. Trends in Biochemical Sciences. 15: 170-172.
- [2] Cheeseman, K. H. Slater, T. F. (1993). Br. Med. Bull. 49: 481.
- [3] Kehrer, J. P, Smith, C. V. (1994). Free Radicals in Biology: Sources, Reactivity and Roles in the Etiology of Human Diseases in Natural Antioxidants in Health and Disease, Academic Press, London.
- [4] Steinbrecher, U. P. Zhang, H. Loughheed, M. (1991). J. Free Radical Biol. Med. 9: 155.
- [5] Osunlaja A. A., Idris S. O. and Iyun J. F. (2013). Kinetics and mechanism of thiourea oxidation by oxygenated $[Co_2(O_2)(NH_3)_10]^{5+}$ complex. Journal of Chemical and Pharmaceutical Research, 5 (2): 328-336.
- [6] Sykes, A. G. and Weil J. A. (1970). Progress in Inorganic Chemistry. 13: 1-56.
- [7] Charrouf, Z.; Guillaume, D.(2007)."Phenols and Polyphenols from Arganiaspinosa". American Journal of Food Technology. 2 (7): 679–683.
- [8] Barner, B. A. (2004) "Catechol" in Encyclopedia of Reagents for Organic Synthesis (Ed: LPaquette), J. Wiley & Sons, New York.
- [9] Fiegel, Helmut *et. al.*, (2002) "Phenol Derivatives" in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH: Weinheim.
- [10] Robert W. P. (1970). Inorganic synthesis. *University of Utah, Salt Lake City, Utah. McGraw-Hill book Company, New York* 12: 199-201.
- [11] Onu D. A. Idris S. O. and Iyun J. F. (2015). Kinetics and Stoichiometry of the Reduction of Hydrogen Peroxide by an Amino carboxylacetocobaltate (II) Complex in Aqueous Medium. *Open Journal of Inorganic Chemistry* 05 (04): 75-82.
- [12] Idris S. O., Samson V. O. and Myek B. (2015). Kinetics of the Oxidation of Bromopyrogallol Red by Nitrite Ion in aqueous Acidic Medium. *International Frontier Science Letters*. 3: 32-38.
- [13] Ukoha, P. O. and Iyun, J. F. (2001). Kinetics of reduction of an Iron(III) complex ion by mercaptoethanol and mercaptoethylamine in perchloric acid medium. *Journal of the Chemical Society of Nigeria*, 26 (2): 163-168.
- [14] Ukoha, P. O. and Ibrahim, E. (2004). Mechanism of the oxidation of β -mercaptoacetic acid by trioxiodate (V) in aqueous acid medium. *Chemclass Journal*, 138-141.
- [15] Iyun, J. F. and Adebite, A. (1990). Kinetics and mechanism of the reduction of dichlorotetrakis (2,2'-bipyridine)- μ -oxodirutheniumionbyTi(III)-EDTA in aqueous Acidic Medium. *Bulletin of Chemical Society of Ethiopia*, 4: 27-31.
- [16] Vaidya, V. K., Pitlia, R. L., Kabra, B. V., Mali, S. L. and Ameta, S. C. (1991). Dye-sensitized photo-oxidation of thiourea by singlet oxygen. *Journal of Photochemistry and Photobiology A*, 60 (1): 47-50.
- [17] Singh B., Das R. S., Banerjee R., Mukhopadhyay S. (2013). Superoxo radical scavenging action by common analgesic drug paracetamol: A model kinetic study. *Inorganica Chimica Acta* 406: 266–271.
- [18] Singh B., Das R. S., Banerjee R., Mukhopadhyay S. (2015). Kinetics and Mechanism of Oxidation of $S_2O_3^{2-}$ by a Co-Bound μ -Amido- μ -Superoxo Complex. Wiley Online Library.
- [19] Iyun, J. F., Ayoko, G. A. and Lawal, H. M. (1992). Transition Met. Chem., 17: 63-65.