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Electron transfer mechanism for the oxidation of ternary N-(2-Acetamido) iminodiacetatocobaltate (II) complexes involving glycine with benzoyl peroxide

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Abstract

The kinetics of oxidation of the Co(II) complexes, $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ by benzoyl peroxide (BPO) to Co(III) has been followed spectrophotometrically where, [ADA=N-(2-Acetamido imino-diacetato), Gly=Glycinate] over 30-50ºC and a variety pH 7.9-8.8 range. The reaction of oxidation of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ by benzoyl peroxide was studied under pseudo-order kinetic conditions with respect to complex and it obeys the following rate law:

Rate$=\{(k_3+k_4[H^+])/[H^+])+([H^+]/(k_5+k_6[H^+]))\}[Co^{II}(ADA)(Gly)(H_2O)_3]^-[Gly]$

In the oxidation of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ the rate-determining obeys substitution of one coordinated water molecule by glycinate. The thermodynamic activation parameters have been calculated.

Keywords: Benzoyl peroxide; Oxidation; Cobalt(II); Glycine; N-(2-Acetamido imino-diacetato).

1. Introduction

Benzoyl peroxide (BPO) has been used widely as a highly powerful oxidizing agent oxidant [1,2] . In chemical industry catastrophes, many thermal runaway incidents are caused by benzoyl peroxides due to its thermal instability. Its thermal instability is caused by weak oxygen-to-oxygen bonds, which lead to a tendency towards more stable substances [3,4]. Because of its versatile properties, BPO has been widely employed as a polymerization intiator [5] or hardening or bridge formation [6,7]. Benzoyl peroxide (BPO) widely employed in the pharmaceutical industry as antibacterial agent to treat acne [8,9] , as antimicrobial agents [10], in the plastic and rubber industries [11,12], in the food industry, as a bleaching agent [13]; and in the medical area [14,15].

Cobalt is essential to all animals. It is a key constituent of cobalamin, also known as vitamin B₁₂ [16]. Cobalt(II) oxide was used as pigments for paintings because of its superior stability [17,18] and in Batteries [19].

N-(2-acetamido)iminodiacetate (ADA) is a zwitterionic buffer used in biochemistry and molecular biology. The useful range of ADA buffer in aqueous solution is 6.0-7.2, and the effect of ADA on the activity of dog kidney (Na$^+$ + K$^+$)-ATPase activity has been investigated [20,21]. Oxidations of binary Co(II) complexes have been studied [21]. Ternary metal complexes might appear in biological fluids creating specific structure [22-24], most frequently manifesting themselves as enzyme-metal ion-substrate complexes [24-27]. This explain why ternary system has recently received increasing attention. In this study, the kinetics of oxidation of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ where, [ADA = N-(2-Acetamido imino-diacetato), Gly = Glycinate] was studied .

Choice of these ternary complexes was attributed to two considerations. Firstly, in order to study the effect of complex formation of the binary and ternary complexes on the rate parameters for oxidation of these Co(II) complexes. Secondaly, because transition metal ternary complexes have received particular focus and have been employed in mapping protein surfaces as probes for biological redox centers and in protein capture for both purification and study. BPO has little attention in oxidation of inorganic compounds, thus the kinetics of oxidation of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ by BPO is reported here for the first time.

2. Materials and methods
Instrumentation.

A jenway 6300 spectrophotometer equipped with temperature cell-holder connected to a thermostat-circulating water bath was used to measure the

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oxidation rates of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ with [BPO].

A double beam JASCO UV-530 spectrophotometer equipped with a thermostated cell holder was used to measure the UV-Vis absorbtion spectra of the oxidation product of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ by BPO.

Potentiometric measurements were performed with a Metrohm 702 SM titrino.

The titroprocessor was equipped with a 728 dosimat (Switzerland-Hereaus). The titroprocessor and electrode were calibrated with standard buffer solution [28].

Calculations were performed using MINIQUAD-75 loaded on an IBM-550 computer.

Cyclic voltammetric measurements were performed on a potentiostat/Galvanostat (EG&G model 273A) with a single-compartment voltammetric cell equipped with a platinum working electrode (area = 0.5 cm^2), a platinum wire counter electrode, and Ag/AgCl (3mol dm^{-3} KCl) as reference electrode. M270 research electrochemistry software from EG&G Princeton Applied Research was used.

A Chertsey Surrey 7065 pH meter was used in pH measurements of the reaction mixture.

Methodology

All compounds used were of reagent grade or analar chemicals (BDH, Aldrich, Sigma). $Co(NO_3)_2$ (BDH) solutions were standardized volumetrically with EDTA [29]. Commercial benzoyl peroxide was purified by dissolving about 75 g. in 1 liter of acetone at room temperature, precipitating by the addition of 2 liters of distilled water with stirring, filtering and thoroughly drying the product in air stream. The purified material assayed 99.5-99.7% by iodometric titration. Fresh solution of benzoyl peroxide was prepared by dissolving the calculated accurate weight in ethanol/water mixture and this is due to that BPO is slightly soluble in water [30,31,32]. The stability of benzoyl peroxide solution in water/ethanol mixture was checked, no decomposition was observed during the time taken and the experimental conditions used for the kinetic measurements.

NaOH/Glycine buffers of known pH were used, and the ionic strength was adjusted with KNO_3. Doubly distilled H_2O was used in all kinetic runs.

Kinetic procedures

All the reactants except BPO were thermostated at required temperature to reach thermal equilibrium. The required amount of separately thermostated BPO stock solution was then added, and after rapid mixing, recording the absorbance changes with time. Reactions of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ complex by BPO were carried out under Pseudo order conditions in all runs by the presence of large (more than 10 fold) excess of Co^{II}-

complex over Benzoyl Peroxide, because of the low solubility of BPO in aqueous solutions [30,31,32]. The ionic strength was kept constant by addition of KNO_3 solution. The pH of the reaction mixture was found to be always constant during the reaction run. The error limits for results are calculated using Microcal ^{TM} Origin (Version 6.0).

2. *Results and discussion*
Characterization of Na [Co^{II}(ADA)(Gly)(H$_2$O)$_3$]

$[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ was prepared using the same procedure as for the preparation of $[Co^{II}(ADA)(H_2O)_3]$ Confirmation of the complex formula was obtained from IR spectrum, thermal gravimetric analysis (TGA), and UV-Vis absorption spectrum. The elemental analysis data of the oxidation products of $Na[Co^{II}(ADA)(Gly)(H_2O)_3]$ is found: C, 22.4; H, 4.49; m N, 8.28. $[Co^{II}(C_8H_{10}N_3O_{10})]$, Calcd: C, 21.23; H, 5.31; N, 9.29. To confirm the formula of the complex, IR spectrum and TGA data were carried out.

In $Na[Co^{II}(ADA)(Gly)(H_2O)_3]$ the infrared spectrum, bands in the (3415-3363) cm^{-1} region, were attributed to $\upsilon(OH)$ of the water molecules. The OH of the carboxylic group disappeared and a new (υCOO^-) appeared in the region (1509-1615) cm^{-1} indicating the that the carboxylic group of the ligands participates in the coordination with the metal ion through deprotonation.

The thermogram of the complex $Na[Co^{II}(ADA)(Gly)(H_2O)_3]$ shows that weight loss (56.46%) begins at 373 °C corresponding to the loss of three coordinated water molecules (calcd. 58.9 %). The elemental and thermal analysis of $Na[Co^{II}(ADA)(Gly)(H_2O)_3]$ complex agree with the formula $Na[Co^{II}(C_8H_{10}N_3O_{10})]$. The structure of the complex has been resolved is given in Fig. 1.
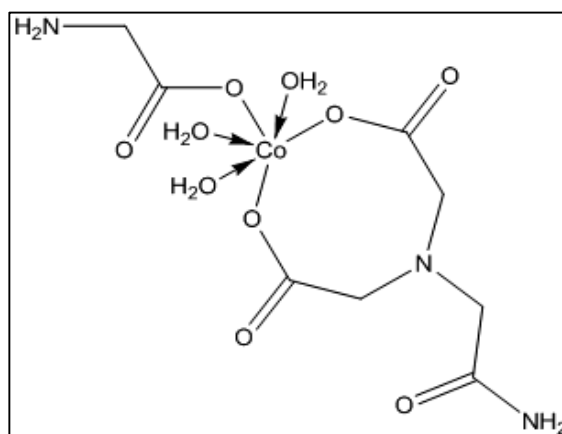
Figure 1. Suggested structure for $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$.

Oxidation product

The UV-V absorption spectra of the oxidation products of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ is shown in Fig. 2.   The function of time over the 350-700 nm range on a JASCO UV-530 spectrophotometer. From Fig. 2, it is clear that the final cobalt(III) product was formed. the final products was violet. The maxima and molar absorptivity coefficients of the final cobalt(III) product at pH =8.8 of oxidation of Glycinate ternary complex were $\varepsilon_{max}^{312} = 166.77$ and $\varepsilon_{max}^{508} = 25.19$ dm³ mol⁻¹cm⁻¹.
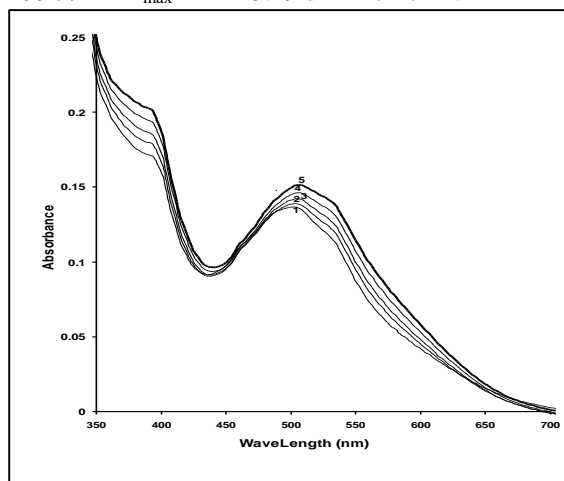

Figure 2. Change in absorbance as a function of time. Curves (1-5) were recorded at 40, 90, 120, 180 and 240 min, respectively from the time of initiation of the reaction; curve (5) represents the final product. [complex]=6.0 × 10⁻³M, BPO=1.0×10⁻⁴ mol dm⁻³, I=0.15 mol dm⁻³, pH=8.8, and Temp=30ºC.

Kinetics of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$/BPO reaction

Oxidation of $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ by BPO was studied over BPO concentration range (1.0-5.0) ×10⁻⁴ mol dm⁻³ at constant $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ concentration of 5.0×10^{-3} mol dm⁻³ at 35ºC, pH =8.8 and I= 0.15 mol dm⁻³.

Plots of A_t *versus* time were linear up to 85 % of reaction where A_t is absorbance at time t . The rate of the reaction is constant i.e. independent of BPO concentration and which is in agreement with zero order dependence on the concentration of BPO. This behavior is represented by zero-order equation (1):

$$d[Co^{III}]/dt = k_{obs} [BPO]^0 \qquad (1)$$

At constant [H⁺] and ionic strength, plotting of k_{obs} against $[Co^{II}(ADA)(Gly)(H_2O)_3^-]$, was found to be linear without intercept as shown in Fig. 3 The dependence of k_{obs} on [Complex] is thus described by Equation (2) :

$$k_{obs}=k_1[Co^{II}(ADA)(Gly)(H_2O)_3^-] \qquad (2)$$
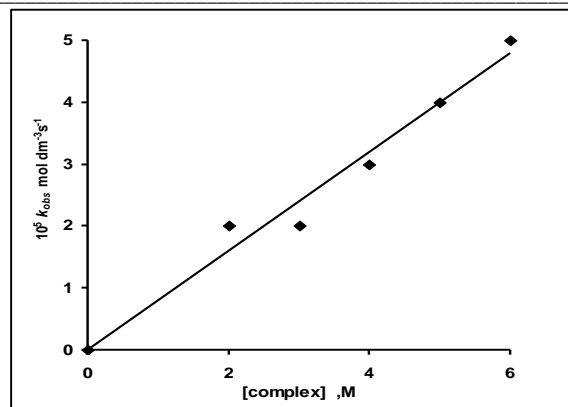
Figure 3. Dependence of k_{obs} (mol dm⁻³ s⁻¹) on $[Co^{II}(ADA)(Gly)(H_2O)_3^-]$ at [BPO]=1.0×10⁻⁴ mol dm⁻³, pH=8.8, I= 0.15 mol dm⁻³ and T= 40ºC.

Effect of glycine on rate of reaction was examined under constant condition of pH, I, $[Co^{II}(ADA)(Gly)(H_2O)_3^-]$ and over[glycine] range of 1.0-5.0 × 10⁻² mol dm⁻³. Rate of reaction increases with increasing glycine concentration as shown in table (1). Plotting of k_1 against **[Gly],** was found to be linear without intercept as shown in supplemental Figure 1.

Table 1. Variation of k_1 with [Gly] concentrations at$[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ = 4.0 ×10⁻³ mol-dm⁻³, [BPO]=1.0 ×10⁻⁴ mol dm⁻³ ,T =40 ºC , I=0.15mol dm⁻³ and pH=8.8.

10^2 [Glycine] (mol dm⁻³)	$10^5 k_{obs}$ (mol dm⁻³ s⁻¹)	k_1 (s⁻¹)
1.0	3.0 ± 0.02	7.0
1.5	5.23 ± 0.03	13.08
2.0	6.37 ± 0.02	15.93
3.0	10.00 ± 0.06	25.00
4.0	14.12 ± 0.02	35.30
5.0	10.90 ± 0.03	42.25
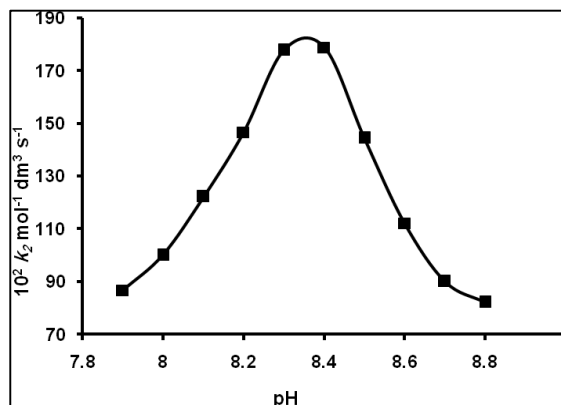
Figure 4. Variation of k_2 with pH in range (7.9-8.8) at $[Co^{II}(ADA)(Gly)(H_2O)_3^-]$=6.0 ×10⁻³ mol dm⁻³, [BPO]= 1.0 ×10⁻⁴ mol dm⁻³, I= 0.15 mol dm⁻³ and T=35ºC.

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The dependence of k_1 on [Gly] is represented by the following equation:-

$$k_1 = k_2[\text{Gly}] \qquad (3)$$

The variation of k_2 with pH was studied over pH range of (7.9 – 8.8) is graphically represented in figure. 4, and summarized in table (2). From Fig .4 it is found that k_2 increases and then decreases with increasing pH in the used range. Plots of k_2 against 1/[H⁺] in the pH range (7.9-8.3) and 1/k_2 against 1/[H⁺] in the range of (8.4-8.8) are listed in table (2).

Table 2. Variation of k_2 and $1/k_2$ with 1/[H⁺] at T = 35°C ,I=0.15 mol dm⁻³, [Co^{II}(ADA)(Gly)(H$_2$O)$_3$⁻] =6.0 ×10⁻³ mol dm⁻³ , [BPO] =1.0 ×10⁻⁴ mol dm⁻³,[Gly] =1.5 ×10⁻² mol dm⁻³ and pH range (7.9 - 8.8).

pH	10⁻⁸1/[H⁺]	10⁵ k_{obs} (mol dm⁻³ s⁻¹)	10³ k_1 (s⁻¹)	10² k_2 (mo⁻¹dm³s⁻¹)	10² 1/k_2 (mol dm⁻³ s)
7.9	0.79	7.8± 03	13.00	86.67	
8.0	1.00	9.01± 04	15.02	100.11	
8.1	1.26	11.0± 01	18.33	122.22	
8.2	1.58	13.2± 01	22.00	146.67	
8.3	1.99	16.0± 07	26.67	177.78	
8.4	2.51	16.1± 02	26.83		55.90
8.5	3.16	13.0± 04	21.67		69.23
8.6	3.98	10.1± 03	16.83		89.10
8.7	5.01	8.1± 05	13.50		111.11
8.8	6.31	7.4± 01	12.33		121.62
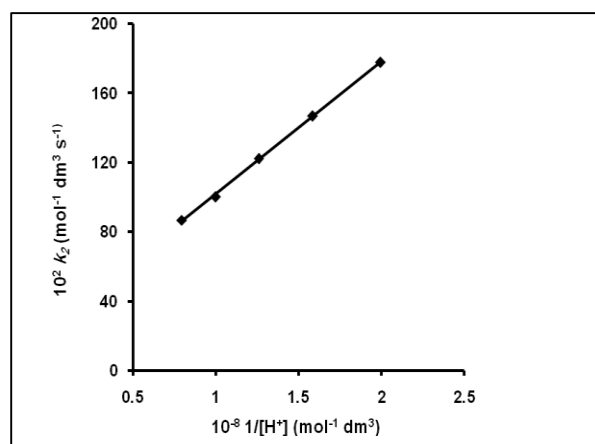
Figure 5. Plot of k_2 versus 1/[H⁺] at pH range (7.9-8.3), T=35°C, I=0.15 mol dm⁻³ , [BPO] = 1.0 × 10⁻⁴

mol dm⁻³, [Gly] = 1.5 ×10⁻² mol dm⁻³ and [Co^{II}(ADA)(Gly)(H$_2$O)$_3$] = 6.0 ×10⁻³ mol dm⁻³.

From Fig. 5, variations of k_2 with 1/[H⁺] at T = 35°C can be described by Eq. (4). k_2 is linearly varied with 1/[H⁺] with intercept:-

$$k_2 = k_3/[\text{H}^+] + k_4 \qquad (4)$$

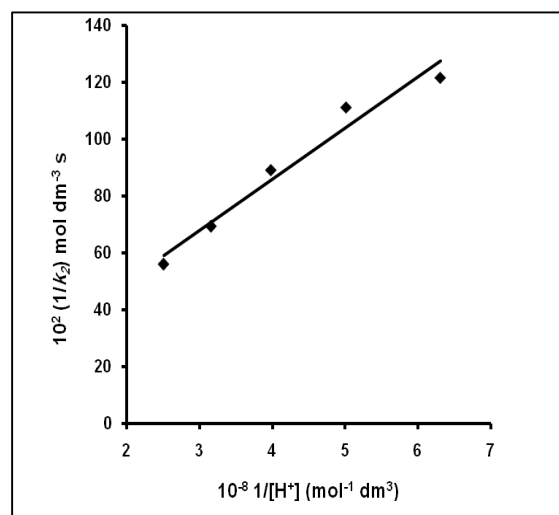**Figure 6.** Plot of 1/ k_2 versus 1/[H⁺] at pH range (8.4.-8.8), T=35°C, I=0.15 mol dm⁻³, [BPO]=1.0 ×10⁻⁴ mol dm⁻³,[Gly] =1.5 ×10⁻² mol dm⁻³and [Co^{II}(ADA)(Gly)(H$_2$O)$_3$]⁻=6.0 ×10⁻³ mol dm⁻³.

From Fig. 6, variations of 1/k_2 with 1/[H⁺] at T =35°C are given by Eq. (5). Plot of (1/k_2) versus 1/[H⁺] is linear with intercept .

$$1/k_2 = k_5/[\text{H}^+] + k_6 \qquad (5)$$

From equations (1-5) the following experimental rate law is formulated:

$$d[\text{Co}^{III}]/dt = \{(k_3/[\text{H}^+] + k_4) + ([\text{H}^+]/k_5 + 1/k_6)\}[\text{Co}^{II}(\text{ADA})(\text{Gly})(\text{H}_2\text{O})_3^-][\text{Gly}] \quad (6)$$

On the rearrangement:-

$$d[\text{Co}^{III}]/dt = \{(k_3+k_4[\text{H}^+])/[\text{H}^+]) + ([\text{H}^+]/(k_5+k_6[\text{H}^+]))\}[\text{Co}^{II}(\text{ADA})(\text{Gly})(\text{H}_2\text{O})_3^-][\text{Gly}] \quad (7)$$

Table 3. Variation of k_{obs} with temperature at different [Co^{II}(ADA)(Gly)(H$_2$O)$_3$⁻], pH=8.8 ,I=0.15 mol dm⁻³ ,[BPO]=1.0 ×10⁻⁴ mol dm⁻³.

10³ [Co^{II}(ADA)(Gly)(H$_2$O)$_3$] mol dm⁻³	10⁶ k_{obs} (mol dm⁻³ s⁻¹)				
	T=30°C	T=35°C	T=40°C	T=45°C	T=50°C
2.0	5.10±02	7.03±03	22.1±02	60.1±04	100.0±05
3.0	6.02±03	7.10±01	20.1±01	70.0±01	100.0±01
4.0	6.01±01	8.01±05	30.1±04	80.1±03	200.0±0.1
5.0	7.13±01	8.00±03	42.0±07	80.0±02	200.0±0.1
6.0	8.01±04	10.0±01	51.1±03	90.0±05	300.0±0.3

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Results in Table (3) represent variation of k_{obs} with $[Co^{II}(ADA)(Gly)(H_2O)_3^-]$ at different temperatures in range of 30-50 °C. From these results, thermodynamic activation parameter were calculated using the transition state theory equation. The enthalpy of activation, ΔH^* have been calculated as 148.74 kJ mol^{-1}. The corresponding entropy of activation, ΔS^* is equal to 189.34 JK^{-1}mol^{-1}. The effect of ionic strength was studied under conditions of pH= 8.2, [BPO]= 1.0×10^{-4} mol dm^{-3}, T= 35°C and complex concentration of (2.0-6.0) $\times 10^{-3}$ mol -dm^{-3}. The obtained 10^2 k_{obs} values were 1.02 ± 001, 1.01 ± 0.05, 1.03 ± 0.03, 1.01 ± 0.03 and 1.05 ± 0.02 mol dm^{-3} s^{-1} at I= 0.1, 0.15, 0.2, 0.25 and 0.3 mol dm^{-3} indicates that the rate of the reaction is unaffected by increasing ionic strength, and this is in agreement with the fact that the reaction takes place between charged and uncharged species.

3. Discussion

Free radicals are produced purposefully by the decomposition of benzoyl peroxide. Once free radicals are formed, they react in a chain according to the following equations [33].

$$C_6H_5COO-OOCC_6H_5 \rightarrow 2C_6H_5COO\bullet \quad (8)$$

$$2C_6H_5COO- + C_6H_5COO-OOC\ C_6H_5 \rightarrow CO_2 + C_6H_5COOC_6H_5 + C_6H_5COO\bullet \quad (9)$$
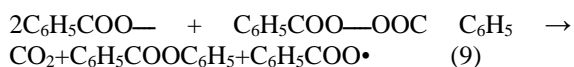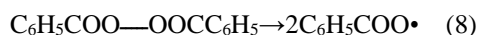
The decomposition of BPO initiated by the one-electron reduction of peroxidic bond by Co^{II} complex and oxy free radicals [33,34], this is represented by the following equations :
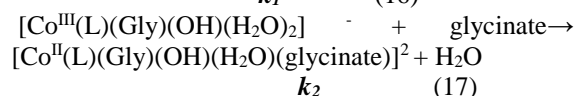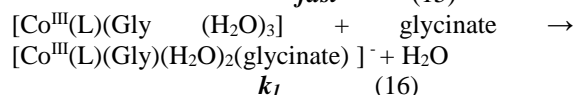
$$[Co^{II}(L)] + PhCOO-OOCPh \rightarrow [Co^{III}(L)] + Ph\bullet$$

$$Ph\bullet + PhCOO-OOCPh \rightarrow CO_2 + C_6H_5COO\ C_6H_5 + Ph\bullet \quad (10)$$
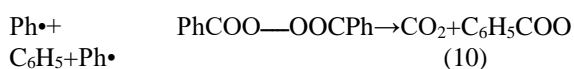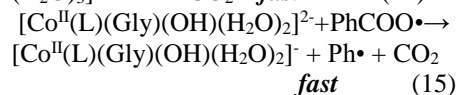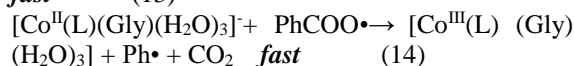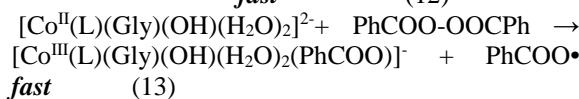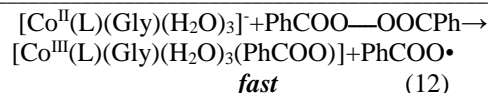
BPO is capable of acting as a ligand, as evidenced from its coordination to Co(II) through the carbonyl group [6, 7].
In aqueous medium the $[Co^{II}(ADA)(Gly)(H_2O)_3]^-$ complex is in equilibrium:

$$[Co^{II}(ADA)(Gly)(H_2O)_3]^- \rightleftharpoons$$
$$[Co^{II}(ADA)(Gly)(H_2O)_2(OH)]^{2-} + H^+$$
$$(K_1) \quad (11)$$
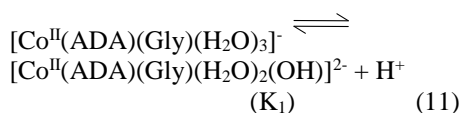
K_1 is determined potentiometrically as 8.63×10^{-6}, it is observed from value of K_1 at the employed pH range (7.9 -8.8) that this equilibrium is prevailing. The reaction sequence (Eqs. 12-17) may describe the mechanism of oxidation of $[Co^{II}(L)(Gly)(H_2O)_3]^-$, [where L= (ADA)].

$$[Co^{II}(L)(Gly)(H_2O)_3]^- + PhCOO-OOCPh \rightarrow$$
$$[Co^{III}(L)(Gly)(H_2O)_3(PhCOO)] + PhCOO\bullet$$
$$\textit{fast} \quad (12)$$
$$[Co^{II}(L)(Gly)(OH)(H_2O)_2]^{2-} + PhCOO-OOCPh \rightarrow$$
$$[Co^{III}(L)(Gly)(OH)(H_2O)_2(PhCOO)]^- + PhCOO\bullet$$
$$\textit{fast} \quad (13)$$
$$[Co^{II}(L)(Gly)(H_2O)_3]^- + PhCOO\bullet \rightarrow [Co^{III}(L)(Gly)(H_2O)_3] + Ph\bullet + CO_2 \quad \textit{fast} \quad (14)$$
$$[Co^{II}(L)(Gly)(OH)(H_2O)_2]^{2-} + PhCOO\bullet \rightarrow$$
$$[Co^{II}(L)(Gly)(OH)(H_2O)_2]^- + Ph\bullet + CO_2$$
$$\textit{fast} \quad (15)$$
$$[Co^{III}(L)(Gly\ (H_2O)_3] + glycinate \rightarrow$$
$$[Co^{III}(L)(Gly)(H_2O)_2(glycinate)]^- + H_2O$$
$$k_1 \quad (16)$$
$$[Co^{III}(L)(Gly)(OH)(H_2O)_2]^- + glycinate \rightarrow$$
$$[Co^{II}(L)(Gly)(OH)(H_2O)(glycinate)]^{2-} + H_2O$$
$$k_2 \quad (17)$$

From the above mechanism, we can derive the rate of reaction :-

$$d[Co^{III}]/dt = k_1\ [Co^{III}(L)(Gly)(H_2O)_3]\ [Gly] + k_2\ [Co^{III}(L)(Gly)(OH)(H_2O)_2]\ [Gly] \quad (18)$$

Since; The total Co(II) can be described by equation (19):-

$$[Co^{III}]_T = [Co^{III}(L)(Gly)(H_2O)_3^-] + [Co^{III}(L)(Gly)(OH)(H_2O)_2^-] \quad (19)$$

From equation (11)
$$[Co^{III}]_T = [Co^{III}(L)(Gly)(H_2O)_3] + \{K_1/[H^+]\} [Co^{III}(L)(Gly)(H_2O)_3] \quad (20)$$
$$= [Co^{III}(L)(Gly)(H_2O)_3]\{1 + (K_1/[H^+])\} \quad (21)$$

$$[Co^{III}(L)(Gly)(H_2O)_3] = [Co^{III}]_T\ /\ [1 + (K_1/[H^+])] \quad (22)$$

$$[Co^{III}]_T = [Co^{III}(L)(Gly)(OH)(H_2O)_2^-]\ [H^+]/K_1 + [Co^{III}(L)(Gly)(OH)(H_2O)_2^-] \quad (23)$$

$$= [Co^{III}(L)(Gly)(OH)(H_2O)_2^-]\ \{([H^+]/K_1) + 1\} \quad (24)$$

$$[Co^{III}(L)(Gly)(OH)(H_2O)_2^-] = [Co^{III}]_T\ /\ \{([H^+]/K_1) + 1\} \quad (25)$$

Substitution from equations (22) and (25) into (18) we obtain (26):-
$$d[Co^{III}]/dt = (k_1[1/\ \{1 + (K_1/[H^+])\}] + k_2[1/\{1 + ([H^+]/K_1)\}])\ [Co^{III}]_T[Gly] \quad (26)$$

Which is identical to the experimental rate law given by equation (7) and therefore,

$$k_{obs} = (k_1[1/\ \{1 + (K_1/[H^+])\}] + k_2[1/\{1 + ([H^+]/K_1)\}])\ [Co^{III}]_T[Gly] \quad (27)$$

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Since the kinetics of this reaction showed zero-order dependence in benzoyl peroxide and the rate of reaction increases with glycine concentration, substitution of glycinate forming the more reactive species $[Co^{III}(L) (Gly)(H_2O)_2(glycinate)]^-$ in the rate-determining step.

Comparison equation (27) and (2) gives;

$$k_1 = (k_1[1/ \{1+(K_1/[H^+])\}] + k_2[1/\{1+ ([H^+]/ K_1)\}]) [Gly] \qquad (28)$$

And;

$$k_2 = (k_1[1/ \{1+(K_1/[H^+])\}] + k_2[1/\{1+ ([H^+]/K_1)\}]) \qquad (29)$$

In the range of $[H^+] = (1.26 \times 10^{-8} : 5.01 \times 10^{-9})$ mol dm^{-3}, the reaction is represented by:

$$k_2 = k_2 [1/\{1+([H^+]/K_1)\}] \qquad (30)$$
$$= k_2 [K_1 / (K_1+[H+])] \qquad (31)$$
$$= k_2 K_1 /(K_1+[H^+]) \qquad (32)$$

And in the range of $[H^+] = (3.98 \times 10^{-9}: 1.58 \times 10^{-9})$ mol dm^{-3}, the reaction represented by :

$$1/k_2 = 1 / \{ k_1 [1/(1+ (K_1/[H^+]))]\} \qquad (33)$$
$$= 1 / \{ k_1 [[H^+]/([H^+]+K_1)] \} \qquad (34)$$
$$= 1 / \{ k_1 [H^+] / ([H^+] + K_1 \qquad (35)$$
$$= ([H^+]+K_1)/ k_1 [H^+] \qquad (36)$$

The derived equations (32) and (36) are consistent with our kinetic results.

According to the value of the enthalpy of activation, ΔH^*; the substitution of glycinate in the rate-determining step is an endothermic process. Steric hindrance of the coordinated ligands may be determined in the rate- determining steps and this idea can be accommodated by a dissociative substitution type of mechanism. Marked topological change can be expected leading to the positive ΔS^* value.

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