

Studies on the Oxygen Atom Transfer Reactions of Peroxomonosulfate: Oxidation of Glycolic Acid

S. SHAILAJA, M. S. RAMACHANDRAN

School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

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ABSTRACT: The kinetics of oxidation of glycolic acid, an α -hydroxy acid, by peroxomonosulfate (PMS) was studied in the presence of Ni(II) and Cu(II) ions and in acidic pH range 4.05–5.89. The metal glycolate, not the glycolic acid (GLYCA), is oxidized by PMS. The rate is first order in [PMS] and metal ion concentrations. The oxidation of nickel glycolate is zero-order in [GLYCA] and inverse first order in $[H^+]$. The increase of [GLYCA] decreases the rate in copper glycolate, and the rate constants initially increase and then remain constant with pH. The results suggest that the metal glycolate ML^+ reacts with PMS through a metal-peroxide intermediate, which transforms slowly into a hydroperoxide intermediate by the oxygen atom transfer to hydroxyl group of the chelated GLYCA. The effect of hydrogen ion concentrations on k_{obs} suggests that the structure of the metal-peroxide intermediates may be different in Ni(II) and Cu(II) glycolates. © 2008 Wiley Periodicals, Inc. *Int J Chem Kinet* 41: 160–167, 2009

INTRODUCTION

Glycolic acid (GLYCA) is a member of the α -hydroxy acids family, which is used in cosmetic products, such as exfoliants, moisturizers, and emollients, to correct skin disorders, to improve/increase skin hydration, and to improve some of the visible effects of ageing [1,2]. GLYCA is one of the most active and beneficial ingredients in skin care formulations/products, since it can easily penetrate skin barrier. Because of the practical importance, the oxidations of aliphatic α -hydroxy acids have been studied extensively. The presence of hydroxyl group at α -position to carboxyl group makes the oxidation reaction to proceed by many possible routes. The mechanism with two-electron oxidants is

either by transfer of α -hydrogen or by concerted decarboxylation [3], involving cleavage of a C–C bond. Therefore, the kinetics of oxidation of α -hydroxy acids is an active field of interest.

Peroxomonosulfate (PMS) is a potential two-electron oxidant that decomposes spontaneously in aqueous alkaline solution [4] to give oxygen and sulfate ions. The self-decomposition of PMS is catalyzed by transition metal ions in which a redox process is operative, resulting in a more reactive radical intermediate $SO_4^{\bullet-}$. Anipsitakis and Dionysiou [5] have investigated the efficiency of various transition metal ions in the activation of PMS and observed that Co(II) ion is the most effective and Ni(II) ion is least among the various transition metals studied. The Co(II)/PMS system is an emerging radical generated advanced oxidation process/technology in environmental and wastewater treatment [6–9]. The lower reactivity of Ni(II) is due to the formation of caged or bound to the metal ion

Correspondence to: M. S. Ramachandran; e-mail: ramachandran_mku@yahoo.co.in.

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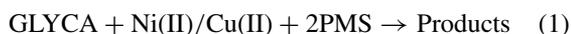
radical [5] as $[\text{Ni}^{\text{III}}\text{SO}_4^{\bullet}]^{2+}$. The redox potential of Ni(III)/Ni(II) couple is ~ 2.3 V, and this may be the reason for the low efficiency of radical formation with PMS. It is expected that complexation of Ni(II) with organic ligands may lower the redox potential and PMS (1.8 V) may be strong enough to oxidize Ni(II) to Ni(III), along with the formation of radical intermediates. But still caged sulfate ion radical is reported in nickel complexes/PMS system [10–14]. However, results from this laboratory show that Ni(II) ion catalyzed decomposition of PMS in acidic pH [15] proceeds through the oxygen atom transfer mechanism with nickel peroxide intermediate instead of redox mechanism. The oxidation of Ni-glycylglycine by PMS also involves an oxygen atom transfer mechanism [16]. Therefore, in continuation of exploring the possibility of Ni(II)–PMS system without redox process, we have studied the reaction of GLYCA with PMS in the presence of Ni(II) and Cu(II) and the results are reported.

EXPERIMENTAL

Potassium PMS, with a trade name OXONE[®] and supplied by FlukaChemie (Buchs, Switzerland), is a triple salt of the composition $\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$. The oxidant was used as received. The GLYCA was from AlfaAesar (Oxford, UK). The stock solution of GLYCA was prepared afresh daily and estimated by titrimetry with standardized alkali. Ni(II) ions in the form of nitrate and Cu(II) sulfate were from Merck (Darmstadt, Germany). All other chemicals used in this study were of highest purity available.

The reaction was followed by monitoring the concentration of PMS at various times by iodometry. The hydrogen ion concentration of the reaction mixture was kept constant using sodium acetate/acetic acid buffer. The pH value, ranging from 4.05 to 5.89, was maintained at the predetermined values by adjusting the concentration of HOAc while keeping $[\text{OAc}^-]$ constant, usually at 0.32 M. The regression analyses were carried out using SigmaPlot for Windows (Version 9.0, Systat Software, Inc., Chicago, IL, USA).

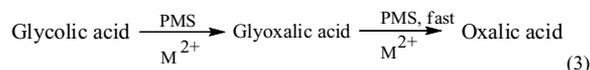
The stoichiometry of the reaction was determined at pH 4.75 in the presence of metal ions Ni(II)/Cu(II). In a typical experimental setup, a large excess of PMS (0.08 M) over GLYCA (0.025 M) and Ni(II) (0.005M)/Cu(II) (0.01 M) was allowed to stand for 24 h, and the unreacted [PMS] was determined. After applying corrections for thermal decomposition of PMS the observed stoichiometry can be represented as in Eq. (1).



The product of oxidation was identified as oxalic acid by aniline blue test [17] and was estimated. The product analysis was also carried out under the condition $[\text{GLYCA}] \gg [\text{PMS}]$. The oxidation product was the oxalic acid. Thus, under kinetic condition the reaction can be expressed as in Eq. (2).



The studies on the oxidation of glyoxalic acid were also performed under identical conditions. The reaction was very fast to be measured by the conventional method. Therefore, the reaction between GLYCA and PMS can be represented as in Eq. (3), and we are monitoring the kinetics of the first part.



RESULTS AND DISCUSSION

In the pH range from 4.05 to 5.89, the reaction between GLYCA and PMS was very slow and, even after 24 h, the conversion of [PMS] was only $\sim 4.0\%$ – 5.0% . The oxidation reaction proceeds at a reasonable speed only in the presence of Ni(II) and Cu(II) ions. The concentrations of Ni(II) used were from 5.0×10^{-4} M to 1.0×10^{-2} M, and the pH range was 4.05–5.20. However, higher concentrations (0.01 M–0.02 M) and higher pH (4.75–5.89) ranges were necessary for Cu(II). The reactions were monitored up to 50% conversion of PMS. The decrease of [PMS] followed first-order kinetics with respect to [PMS], as evidenced by the following facts: (i) linear plots of $\log[\text{PMS}]$ versus time (with very high correlation coefficients), (ii) the close agreement between initial concentrations of PMS from the first-order plot and the analytical values, and (iii) independence of first-order rate constant (k_{obs}) values on the initial concentration of PMS.

The k_{obs} values are calculated at different sulfate ion concentrations and the values are found to be independent of $[\text{SO}_4^{2-}]$ in both Ni(II) and Cu(II) ion-catalyzed reactions. The k_{obs} values increase with the metal ion concentrations and the plots k_{obs} versus $[\text{Ni(II)}]$ and k_{obs} versus $[\text{Cu(II)}]$ are straight lines passing through origin (Figs. 1 and 2). The effect of GLYCA concentrations on the kinetic constants is calculated at different pH and temperatures. In Ni(II)-catalyzed reaction, the k_{obs} values are independent of the substrate concentrations at all conditions. But in the presence of Cu(II) ions, the k_{obs} values decrease with increase in GLYCA concentration and the plots of k_{obs}^{-1} versus $[\text{GLYCA}]$ are approximately straight lines with positive intercept

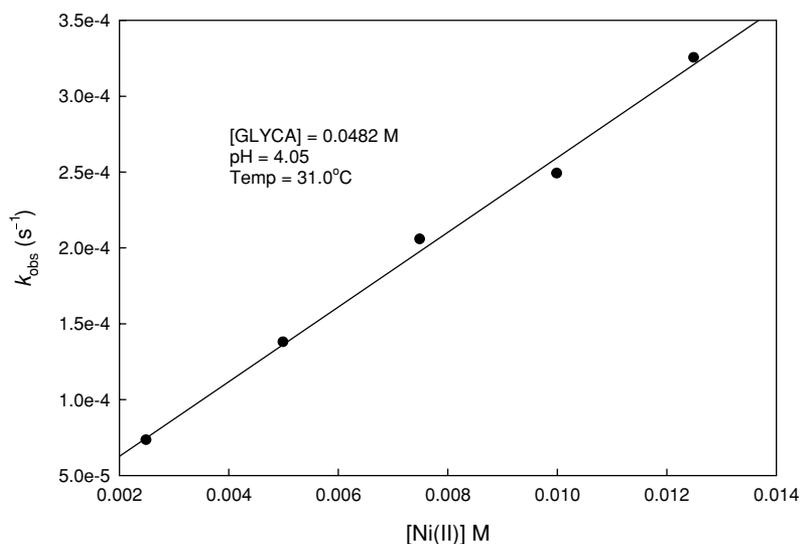


Figure 1 Plot of k_{obs} versus $[\text{Ni(II)}]$.

(Fig. 3). This inverse effect is observed at all pH and temperatures.

The influence of $[\text{H}^+]$ on the rate of the reaction is studied from the plots k_{obs} versus $[\text{metal ion}]$ and also from the effect of $[\text{GLYCA}]$ on the rate. Perusal of the results suggests that the slope (k'_1) of the plots k_{obs} versus $[\text{M(II)}]$ increases with pH. In Ni(II) ion-catalyzed reactions (Table I), the plots $\log(k'_1)$ versus pH are straight lines with a slope ~ 1.0 and also the plots k'_1 versus $[\text{H}^+]^{-1}$ are straight lines passing through origin (Fig. 4). But in the presence of Cu(II) ion the slope initially increases with pH and then remains almost constant. The effect of base, that is, acetate ion on the

reaction is also studied at pH 4.05 in Ni(II) and 4.7 in Cu(II). The results show that the rate of the reaction is not at all influenced by the acetate ion concentration in the range 0.08–0.32 M. The reactions are also carried out in the presence of aliphatic alcohols such as ethanol or *tert*-butanol to identify the radical intermediates, if any. A concentration range of 0.025–0.05 M is used in the quenching studies. The speed of the reaction is not at all affected by the added alcohols.

The oxidant PMS exists as a mixture of HSO_5^- and SO_5^{2-} due to the equilibrium (4). The dissociation constant, K_d , value is reported as 4.0×10^{-10} M at 25°C [4]. The kinetics described in this report was carried

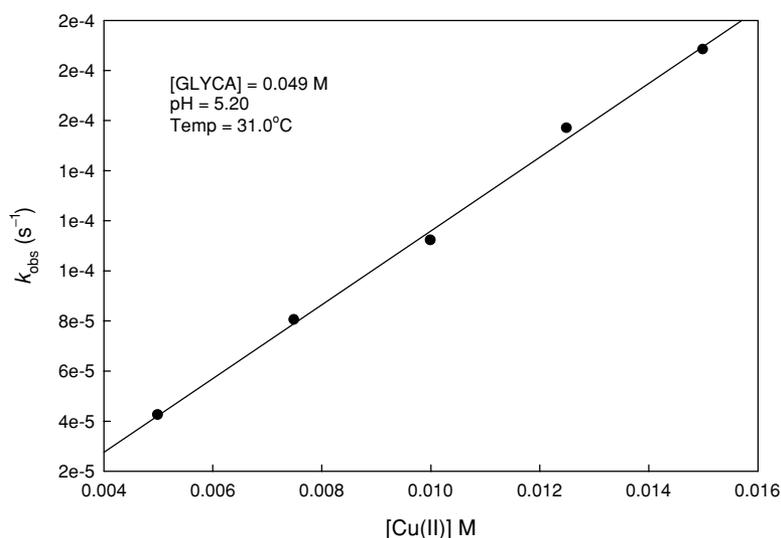


Figure 2 Plot of k_{obs} versus $[\text{Cu(II)}]$.

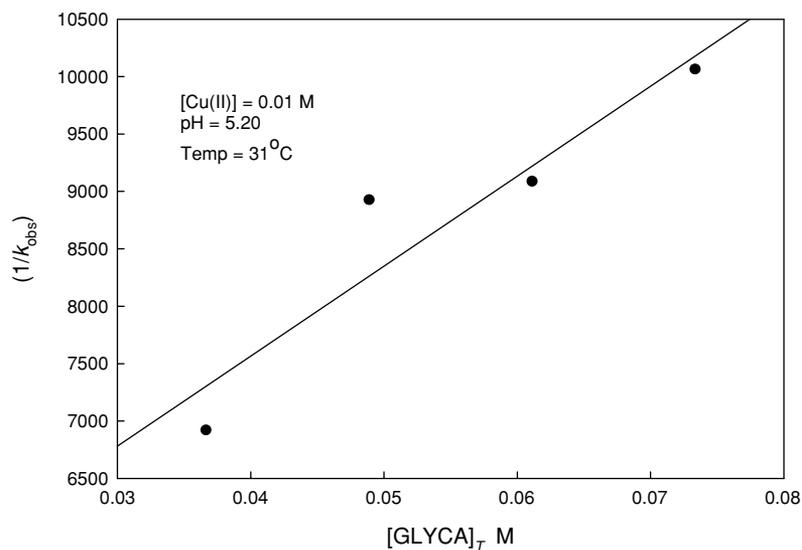
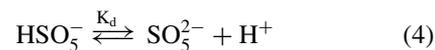


Figure 3 Plot of $1/k_{\text{obs}}$ versus $[\text{GLYCA}]_T$.

Table I The k_1' Values for Nickel Glycolate

Temperature	$10^2 \times k_1' \text{ (M}^{-1} \text{ s}^{-1}\text{)}$		
	25°C	31°C	38°C
pH			
4.05	1.49	2.46	4.71
4.75	5.55	6.92	18.00
5.20	16.30	28.03	55.29
$10^7 \times k_1 K_d$	10.13	17.92	34.71
		ΔH^\ddagger	69.54 kJ mol ⁻¹
		ΔS^\ddagger	-126.40 J K ⁻¹ mol ⁻¹

out in the pH range 4.05–5.89.



Under this experimental conditions, $K_d/[\text{H}^+]$ is $\sim 10^{-4}$ or even smaller, and hence we can approximate that all PMS exists as the mono anion HSO_5^- .

Glycolic acid is an α -hydroxy monobasic acid with a $\text{p}K_a$ value of 3.586 at 25°C [18]. In our experimental conditions $\sim 75\%$ – 99.5% of GLYCA will be in the

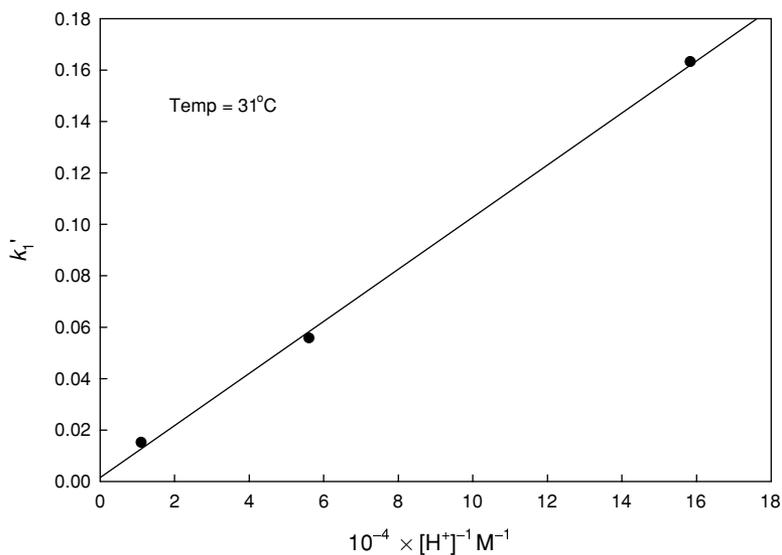
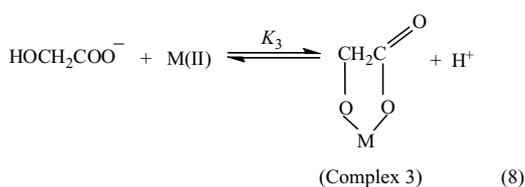
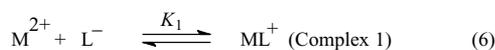


Figure 4 Plot of k_1' versus $[\text{H}^+]^{-1}$.

form of glycolate anion.

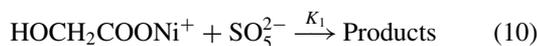
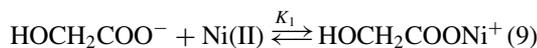


Glycolate ion (L^-) forms chelate compounds with metal ions and the complex equilibria can be represented as in Eqs. (6)–(8).



Equilibrium (8) represents the chelate formation through the deprotonation of α -hydroxyl group. Earlier researchers reported that Ni(II) ion forms a chelate without deprotonation of α -OH group [19–22]. Stability constant determinations show that Complex 2 (reaction 7) is not observed, and we have used K_1 (183 at 25°C) value from Evans and Monk [20] in our calculations. All three equilibria are observed in Cu(II) ions. The equilibrium constant values [18] used in this report are $K_1 = 208.9$, $K_2 = 5370.3$, and $K_3 = 1.29 \times 10^{-4}$. Perusal of the K values suggests that the concentration of Complex 3 is negligible at lower pH.

As already mentioned, the reaction proceeds only in the presence of metal ions such as Ni(II) and Cu(II) ions and this clearly suggests that the metal glycolate is the active form of the GLYCA. From the experimental observations, we can write the kinetic schemes (8) and (9) for the oxidation of nickel glycolate by PMS.



The rate equation for the kinetic scheme can be written as in Eq. (11).

$$\frac{-d[\text{PMS}]}{dt} = k_1 K_d \cdot [\text{HOCH}_2\text{COONi}^+] \cdot [\text{PMS}]/[\text{H}^+] \quad (11)$$

$$\therefore k_{\text{obs}} = k_1 K_d \cdot [\text{HOCH}_2\text{COONi}^+]/[\text{H}^+] \quad (12)$$

The equilibrium constant K_1 value suggests that, even at the lowest pH (4.05) used in this study, all the Ni(II) ions will be chelated. Since nickel forms Complex 1 (reaction 6) only, the nickel glycolate concentration in Eq. (12) can be approximated to the metal ion concentration itself. The experimental observation, the rate is zero order with respect to GLYCA concentration, also supports this approximation. Therefore, Eq. (12) can be approximated as in expression (13), and this equation explains the observed kinetics.

$$k_{\text{obs}} = k_1 K_d \cdot [\text{Ni(II)}]/[\text{H}^+] \quad (13)$$

The values of $k'_1 = (k_1 K_d/[\text{H}^+])$ calculated from the plots of k_{obs} versus $[\text{Ni(II)}]$ at different pH values are shown in Table I. The thermodynamic parameters for the reactions of PMS with Ni-glycolate are also calculated (Table I). Perusal of the rate expressions in Eq. (12) shows that the observed enthalpy of activation for nickel glycolate can be expressed as $\Delta H^\ddagger = \Delta H^0 + \Delta H_{10}^\ddagger$, where ΔH^0 denotes the enthalpy of dissociation for equilibrium (4) and ΔH_{10}^\ddagger is the enthalpy of activation for the bimolecular process represented by Eq. 10. Similarly, the entropy of activation can be represented by $\Delta S^\ddagger = \Delta S^0 + \Delta S_{10}^\ddagger$. The heat of dissociation ΔH^0 for the reaction (4) was estimated as 20.93 kJ mol⁻¹ [4]. Therefore, ΔH_{10}^\ddagger , the enthalpy of activation for the oxidation of nickel glycolate, is 48.6 kJ mol⁻¹. Similarly, the entropy for the dissociation of PMS (reaction (4)) is 108.0 J K⁻¹ mol⁻¹ [4]. This suggests that the entropy of activation for the bimolecular process (10) is 18.4 J K⁻¹ mol⁻¹. As expected for a bimolecular reaction, the entropy of activation is a negative quantity. But the magnitude is small and this may be due to the following reason. The water loss from the inner shell of the metal ion during the activated complex formation (reaction scheme in Fig. 5) may contribute positively to the entropy change. This positive contribution may offset the negative entropy of activation for the bimolecular process (10).

The rates are not at all affected by the added radical quenchers ethanol and *tert*-butanol [23], and this suggests that alcohol quenchable radical intermediates such as OH^\bullet and $\text{SO}_4^{\bullet-}$ are not involved in the reaction. Similar results were observed in the decomposition of PMS in the presence of Ni(II) at acidic pH [15] as well as in the oxidation of Ni-glycylglycine [16]. By analogy with the earlier studies we can assume the oxidation of glycolates proceeds through a molecular mechanism. Usually, the two-electron oxidation by PMS proceeds through the oxygen atom transfer from the terminal peroxide following a nucleophilic attack at the peroxide by the substrate [24]. It is the nickel glycolate, not glycolate or GLYCA, that gets oxidized

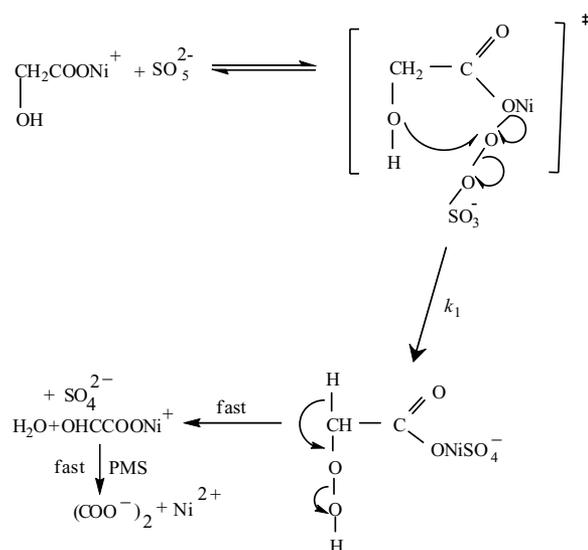
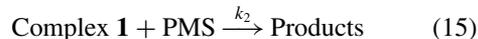
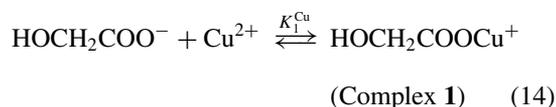


Figure 5 Mechanistic scheme for the oxidation of Ni-glycolate.

by PMS and therefore the positively charged metal ion plays an important role in this reaction. The kinetic mechanism on the oxidation of copper glycolate (*vide infra*) also supports this conclusion. The first step is the formation of nickel peroxide intermediate similar to the one in Ni(II)-catalyzed decomposition of PMS [15]. The peroxide oxygen may become more electrophilic because of the bond formation with (ligand)Ni⁺. The detailed mechanistic scheme is shown in Fig. 5. Peroxy anions can react with α -hydroxy acids through the hydroxyl or carboxyl group. Alcohols give hydroperoxide with hydroperoxy anions [25]. The formation of hydroperoxide intermediate in the oxidation of GLYCA by hydrogen peroxide was reported [26]. The syntheses of peroxy carboxylic acid by the reaction with peroxide have been increasingly reported. Formation of peroxy carboxylic acid from α -hydroxy

down of the intermediate should result in the formation of formaldehyde. But the observed oxidation product is oxalic acid probably through glyoxalic acid. The results from this laboratory show that formaldehyde (even about 10% of [PMS]₀) acts as a catalyst in the oxidation of nickel glycolate and therefore the kinetics would not be as simple as we have observed. Therefore, the reaction should proceed through the oxygen atom transfer from SO₅²⁻ to the hydroxyl group of the GLYCA.

Calculations on the concentrations of copper glycolate ([GLYCA] = 0.05 M) show that ~1.5% [Cu(II)] will exist as Complex **3** at pH 4.75, which increases to ~17% at pH 5.89. The slope of the plots k_{obs} versus [Cu(II)] over this pH range increases by a factor ~2.5. This suggests that contribution of Complex **3** to the reaction may be negligible. Based on the experimental results, the kinetic scheme for the copper ion-catalyzed oxidation may be formulated as in Eqs. (14) and (15).



The rate equation is

$$k_{\text{obs}} = k_2 * [\text{Complex } \mathbf{1}]. \quad (16)$$

The pK_a value suggests that at pH 4.75, 95% of GLYCA will exist as glycolate ion and the concentration will increase slightly with pH. Therefore, as a first approximation, the analytical concentration of GLYCA can be used in the place of glycolate ion while calculating the [Complex **1**]. Substituting for the concentrations of Complex **1**, from reactions (6) to (8), in equation (16) we get expression (17).

$$k_{\text{obs}} = \frac{k_2 K_1^{\text{Cu}} \cdot [\text{Cu(II)}]_T \cdot [\text{GLYCA}]_T}{1 + K_1^{\text{Cu}} \cdot [\text{GLYCA}]_T + (K_3^{\text{Cu}}/[\text{H}^+]) \cdot [\text{GLYCA}]_T + K_2^{\text{Cu}} \cdot [\text{GLYCA}]_T^2} \quad (17)$$

acids, such as citric acid, with hydrogen peroxide has been reported [27]. Therefore, the oxidation of nickel glycolate can proceed through either peroxy acid intermediate or hydroperoxide intermediate. The formation of peroxy acid intermediate through the interaction of PMS with the carboxylate group can be ruled out on the basis of the following facts. The concerted break-

Equation (17) is valid under the condition [GLYCA]_T ≫ [Cu(II)]_T. But the correlations k_{obs} versus [Cu(II)] were carried out with [GLYCA]_T/[Cu(II)] ratio in the range from ~3 (at maximum [Cu(II)]) to ~10 (at minimum [Cu(II)]). Let us assume Eq. (17) is still applicable under our experimental conditions. The equilibrium constant

values [18] suggest that the term unity in the denominator can be neglected. Therefore, Eq. (17) can be simplified as Eq. (18).

$$k_{\text{obs}} = \frac{k_2 K_1^{\text{Cu}} \cdot [\text{Cu(II)}]}{K_1^{\text{Cu}} + (K_3^{\text{Cu}}/[\text{H}^+]) + K_2^{\text{Cu}}[\text{GLYCA}]_T} \quad (18)$$

Eq. (18) explains the observations that the plots k_{obs} versus $[\text{Cu(II)}]$ are straight lines passing through origin (Fig. 2) and the plots k_{obs}^{-1} versus $[\text{GLYCA}]$ are straight lines with positive intercepts (Fig. 3). The value of $K_3^{\text{Cu}}/[\text{H}^+]$ at pH 4.75 and 5.20 is negligible as compared to the value of K_1^{Cu} and hence can be omitted in Eq. (18). Therefore, from the slope and intercepts of the plots of the type in Fig. 3 we can calculate the ratio $K_2^{\text{Cu}}/K_1^{\text{Cu}}$. The values at 25°C are 16.2, 16.8, and 21.7, and these are close to the literature value 25.7 [18]. This clearly shows that the 1:1 complex of copper glycolate is reacting with PMS. From the plots k_{obs} versus $[\text{Cu(II)}]$ and using the literature values of the formation constants, the rate constant k_2 values are calculated at 25°C and the results shown in Table II.

Perusal of the rate constant values in Table II shows that k_2 values seem to initially increase with pH and then remain almost constant. The k_2 values at other temperatures could not be calculated since the formation constants are not available. However, the slopes of k_{obs} versus $[\text{Cu(II)}]$ show the same trend as observed at 25°C. Thus, the effect of $[\text{H}^+]$ on k_{obs} in Cu-glycolate-

Table II The Rate Constant Values for Copper Glycolate at 25°C

pH	$10^3 \times k_2 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$
4.75	6.63
5.20	18.48
5.89	19.20

PMS is not due to the interaction with SO_5^{2-} as proposed in Ni-glycolate-PMS system. Studies on the decomposition of PMS in the acidic pH [15] show that Ni(II) catalyzes the reaction while Cu(II) is nonreactive. This clearly shows that the mode of interaction of these two metal ions with PMS may be different and Cu(II) may form an intermediate with PMS through the oxygen atom of the sulfate ion. The possible reaction mechanism is shown in Fig. 6. Similar to the mechanism of decomposition of PMS in strong acidic medium [28] the (ligand)Cu-peroxide intermediate may undergo hydrolysis to a less reactive hydrogen peroxide. This may be the reason for the inhibitory effect of H^+ ion at low pH.

In summary, GLYCA is oxidized by PMS only when it is complexed with Ni(II) and Cu(II) of the type (ligand) M^+ . The Ni(II) in the presence of oxidizable organic ligands catalyzes the reaction between the ligand and PMS rather than the decomposition of peroxide.

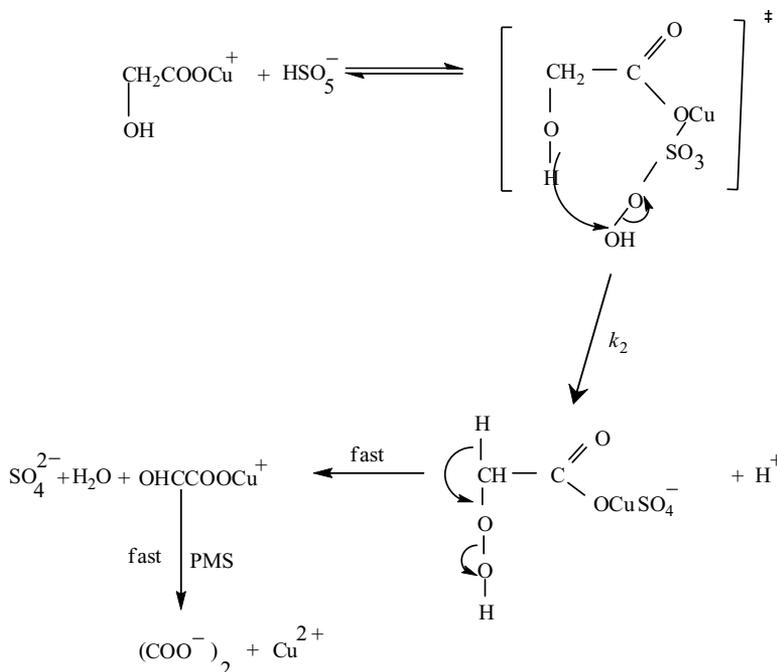


Figure 6 Mechanistic scheme for the oxidation of Cu-glycolate.

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