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Studies on Catalytic Oxidation of Glycolic Acid by PMS

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The Standard Fireworks Rajaratnam College for Women, Sivakasi, Tamil Nadu, India**Abstract:**

The kinetics of the reaction between peroxomonosulphate with glycolic acid was studied in the presence of Mn (II) in the pH range 4.05 to 4.75 at 304K. The reaction followed first order with respect to peroxomonosulphate. The rate of the reaction increases with the [Mn (II)] and independent with respect glycolic acid. A plot of k_{obs} vs $1/[H^+]$ is a straight line passing through origin. Based on the results a rate equation, kinetic scheme and a most probable mechanism has been predicted.

Keywords: Alphahydroxy acid, glycolic acid, peroxomonosulphate, manganese (II)

1. Introduction

Glycolic acid (GA), an hydroxy acetic acid is the smallest alpha hydroxy acid with the IUPAC name 2-hydroxy ethanoic acid. It appears as a colorless, odorless and hygroscopic crystalline solid that is highly soluble in water and related solvents. GA is derived from sugar cane [1], sugar beets, pineapple, cantaloupe and unripe grapes. So it can be considered as a natural product. GA makes up a major portion of the organic content of (troposphere) atmospheric aerosols in part due to its strong tendency towards intermolecular H-bonding (eg. with water) [2]. GA finds applications in skin care products, most often as a chemical peel. GA is believed to be the most effective in the skin care products because it has the smallest molecular size, which helps it to penetrate the stratum corneum easily [3].

PMS (HSO_5^-), the anion of caro's acid (H_2SO_5) is considered as an inexpensive and environmentally friendly oxidant in different applications [4-12]. Commercial peroxomonosulphate (PMS) is a triple salt of composition $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. The active component of Oxone is Potassium monopersulfate ($KHSO_5$, Potassium peroxomonosulphate). The peroxosulfate ion, SO_5^{2-} , is a sulfur oxoanion. Thermal decomposition of PMS is catalyzed by various transition metal ions in aqueous, acidic or weakly alkaline medium [13-24].

Manganese finds its application in number of enzymes [25-27] and found as soluble Mn^{2+} ions in aqueous solutions. It is quite interesting to see that GA has multifunctional groups. It contains a hydroxy group alpha to the carboxyl group. Both the functional groups present in the compound of study can be easily oxidized. So the Struggle between these two functional groups to get oxidized first makes the study of this simplest compound fascinating. Though it has been realized that the oxidation of this candidate can proceed by many possible routes, most of the literature available focus on the one electron oxidation [28-32] rather than ionic mechanism. The two electron oxidation can either occur by transfer of an α - hydrogen [33-43] or by concerted oxidative decarboxylation involving the cleavage of a C-C bond [44-50]. So, in continuation of the above works we are interested in exploring the mechanism of the reaction of GA with PMS in the presence of transition metal ion catalysts (Mn^{2+}). Therefore the kinetics was carried out in detail and the results of the reactions are reported in this paper and a probable mechanism has been proposed for this oxidation reaction.

2. Experimental

Stock solution (0.5M) of glycolic acid (supplied by Alpha Aesar Landcaster (UK)) was prepared and standardized by alkalimetric titrations. Oxone (PMS) supplied by Fluke Chemie (Switzerland) was prepared afresh daily and standardized iodometrically. Concentration of $[H^+]$ in the reaction mixture was maintained by using acetic acid–sodium acetate buffer. The reaction was studied in the pH range 4.05 to 4.75. Concentration of [GA] is maintained high ($[GA] \gg [Mn(II)]$ & $[GA] \gg [PMS]$) through out the course of

the reaction. The kinetics of the reaction was followed by estimation of unreacted [PMS] iodometrically using starch as indicator. Product analysis was carried out under the condition $[GA] \gg [PMS]$ and the reaction mixture was allowed to stand for 48 hours to ensure completion of the reaction. The products obtained were sulphate ion, oxygen, oxalic acid and Mn^{2+} ion. The presence of sulphate ion was confirmed by adding barium chloride to form barium sulphate [51]. The evolution of oxygen was confirmed by sodium dithionite test [52]. Presence of oxalic acid was confirmed by aniline blue test [53].

3. Results

The reaction between GA and PMS was found to be very slow and even after the completion of 24 hours only ~4% of PMS was reacted. Upon addition of a small amount of Mn(II) the reaction proceeded with a measurable speed and the rate of the reaction is studied by measuring the concentration of the unreacted PMS as a function of time. The kinetics of Mn(II) catalyzed oxidation of glycolic acid by peroxomonosulphate has been studied under three pH at 304K. The kinetics were carried out always under pseudo first order conditions ($[substrate] \gg [oxidant]$). The kinetic runs were carried out by adding required volume of aqueous solutions of acetic acid, sodium acetate, hydroxy acid and metal ion solutions (in order). The reaction mixture was diluted with water to 90ml and thermostated. 10 ml of PMS solution, thermostated separately, was pipetted out into the mixture and the timer was started. An aliquot of the reaction mixture was taken out at various time intervals and then added into KI -sulphuric acid mixture. The liberated iodine was titrated with sodium thiosulphate using starch indicator. Linear Regression analysis was used to calculate the slope and intercept in all these linear plots. The statistical software "Sigmaplot 10.0" was used and the linear regression analysis was performed on Windows XP operating system.

3.1. Effect of [PMS]

The reaction followed first order kinetics which is evidenced by the linear plot of $\ln [PMS]$ versus time as given in Fig.1. The first order rate constant (k_{obs}) is found to be independent of the initial concentration of the PMS.

3.2. Effect of $[SO_4^{2-}]$ on k_{obs}

Sulphate ion is one of the products obtained in most of the reactions involving PMS [54]. So it is necessary to study the effect of sulphate ion during the course of the reaction. The k_{obs} values are calculated at a different sulphate ion concentration by maintaining the concentration of all other constituents of the reaction mixture a constant. The rate of the reaction was found to be independent of the sulphate ion concentration.

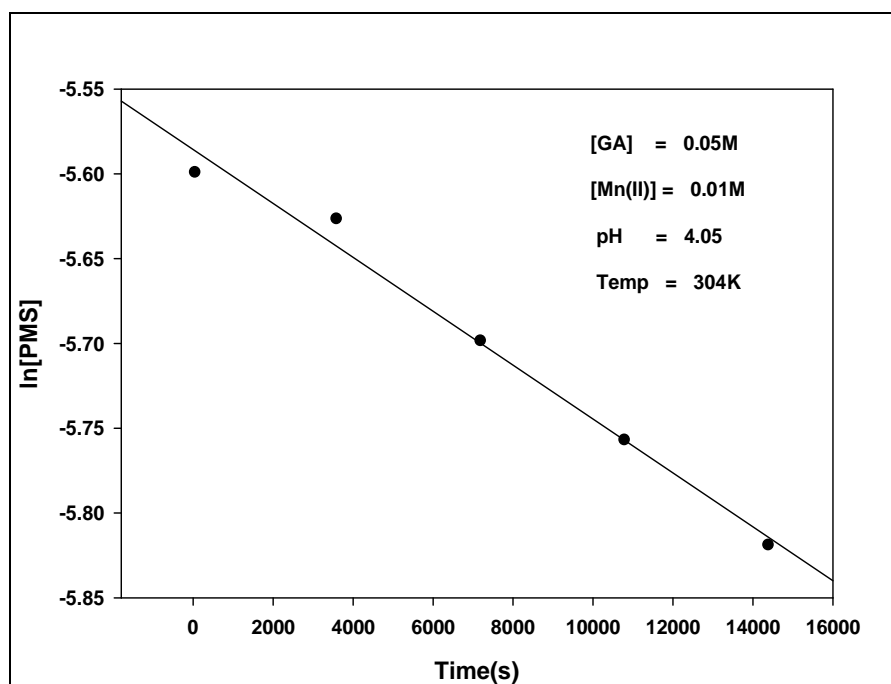


Figure 1: Plot of $\ln[PMS]$ vs time

3.3. Effect of Mn(II) on k_{obs}

The effect of the metal ion is determined at all the pH by varying the metal ion concentration and keeping the concentration of glycolic acid and PMS constant. The plot of Mn(II) versus k_{obs} (Fig 2) is a straight line with a positive intercept which revealed that the reaction proceeded through more than one step.

3.4. Effect of [GA] on k_{obs}

Effect of the substrate on the rate of the reaction is studied by varying the concentration of glycolic acid and maintaining the concentration of all other constituents a constant. The rate of the reaction was found to be independent of [GA].

3.5. Effect of $[OAc^-]$ Concentration on k_{obs}

It is necessary to study the effect of acetate ion because acetate ion used for maintaining the pH can act as a nucleophile. Though the rate of the reaction was found to be independent of the acetate ion concentration the kinetic studies were carried out by maintaining the concentration of the acetate ion constant usually at 0.32M.

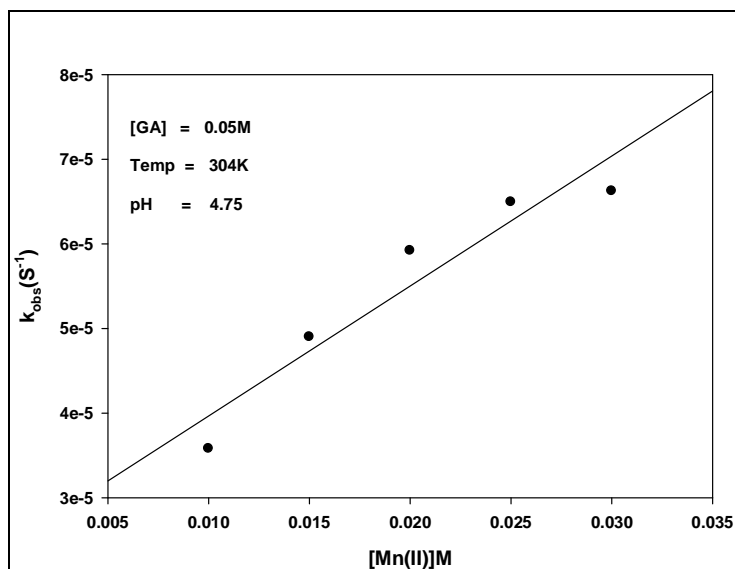


Figure 2: Plot of k_{obs} vs $[Mn(II)]$

3.6. Effect of Radical Quenchers

As discussed in the beginning the oxidation reaction may be due to one electron oxidation [28-32] quenching studies were carried out in order to determine any radical intermediates formed during the course of the reaction. The rate of the reaction was unaffected by the added radical quenchers like ethanol and t-butanol.

3.7. Effect of pH

Effect of hydrogen ion concentration on the rate of the reaction is studied by varying the pH and maintaining the concentration of all other constituents of the reaction mixture a constant. The rate of the reaction was found to increase with increase in concentration of hydrogen ion. A plot of k_{obs} vs $[H^+]^{-1}$ is a straight line passing through the origin.

4. Discussion

Glycolic acid dissociates to form glycolate ion as shown below in Equation (1). The dissociation constant K_a is reported [55] as 1.49×10^{-4} at 25°C. From mass balance equations, the total concentration of glycolic acid is equal to the sum of equilibrium concentrations of glycolic acid and glycolate anion. Calculation of glycolate anion concentration reveals that under the experimental pH of the study almost all the glycolic acid exist as glycolate anion. The reaction between glycolic acid and PMS was studied in the absence of Mn(II), but the reaction was found to be very slow and when a small amount of Mn(II) in the concentration range (3×10^{-5} to 8×10^{-5} M) was added into the reaction mixture the reaction proceeded with a reasonable speed which was followed by using iodometry. This indicates that glycolic acid-Mn⁺ is the active species involved in the reaction.

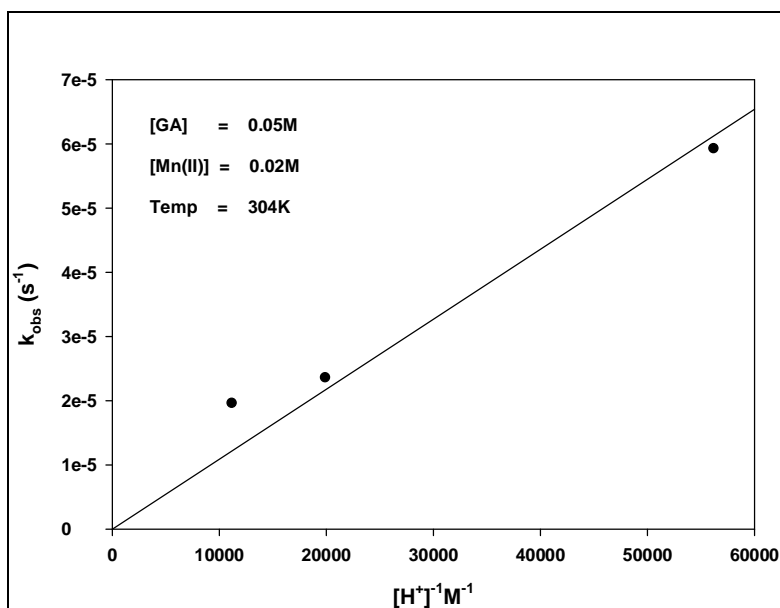
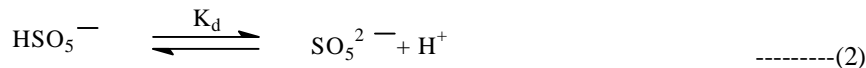
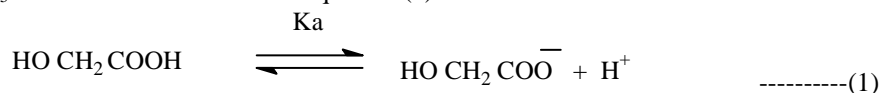
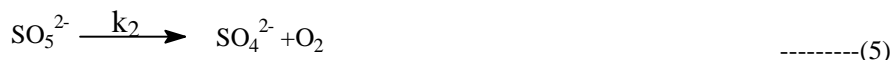
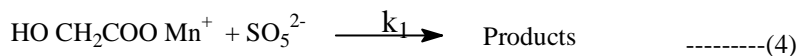
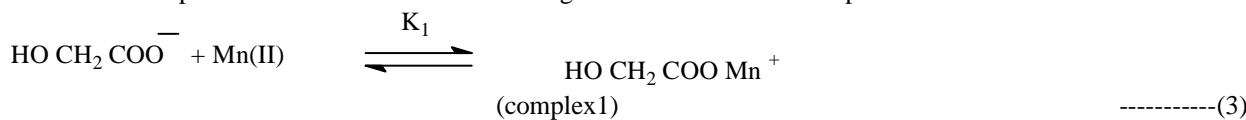


Figure 3: Plot of k_{obs} vs $[H^+]^{-1}$

Glycolate anion forms chelate compounds with metal ions and it is reported in the literature [56] that glycolic acid- Mn^+ is the only complex formed as shown in Equation (3). As almost all the glycolic acid exist as glycolate anion and complexes with $Mn(II)$, the concentration of the glycolic acid- Mn^+ complex can be approximated to the concentration of $Mn(II)$ itself. PMS exist as both HSO_5^- and SO_5^{2-} anion as shown below in Equation (2)



Based on the experimental observation the following kinetic scheme has been predicted.



The rate equation for the above mentioned scheme is derived as follows

$$-\frac{d[PMS]}{dt} = k_1 [SO_5^{2-}] [HOCH_2COO Mn^+] + k_2 [SO_5^{2-}] \quad \text{-----(6)}$$

$$K_d = \frac{[SO_5^{2-}] [H^+]}{[HSO_5^-]} \quad \text{-----(7)}$$

$$-\frac{d[PMS]}{dt} = \frac{k_1 K_d [PMS] [HOCH_2COO Mn^+]}{[H^+]} + \frac{k_2 [HSO_5^-]}{[H^+]} \quad \text{-----(8)}$$

As mentioned above the concentration of the glycolic acid- Mn^+ complex can be approximated to the concentration of $Mn(II)$ itself.

$$k_{obs} = \frac{1}{[H^+]} \left\{ k_1 K_d [Mn(II)] + k_2 \right\} \quad \text{-----(9)}$$

$$k_{\text{obs}} = - \frac{1}{[\text{PMS}]} \frac{d[\text{PMS}]}{dt}$$

. Now this equation explains all the experimental observations that (i) plot of k_{obs} vs Mn(II) is a straight line with a positive intercept (ii) plot of k_{obs} vs $[\text{H}^+]^{-1}$ is a straight line passing through the origin and (iii) zero order dependence of glycolic acid variation. The value of the rate constants k_1 and k_2 are calculated from the plots and reported. At pH 4.75 and , the value of $k_1 = 1.832 \times 10^{-5} \text{ s}^{-1}$ and $k_2 = 4.325 \times 10^{-10} \text{ s}^{-1}$.

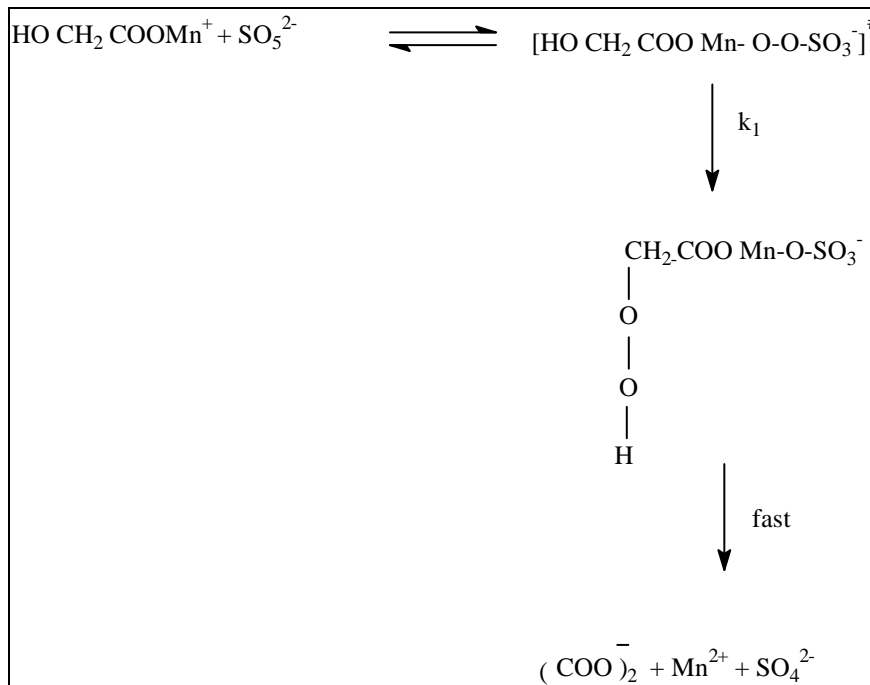


Figure 4: Mechanism of oxidation of glycolic acid by PMS

The effect of the radical quenchers had no effect on the reaction indicating the absence of radicals during the course of the reaction. Literature evidences are also available for the molecular mechanism [54]. So based on all the above discussion a probable mechanism has been proposed as given in Figure (4).

5. Conclusion

The kinetics of the reaction between glycolic acid and PMS is found to be very slow to be measured by conventional method. When a small quantity of Mn(II) catalyst was added into the reaction mixture the rate of the reaction proceed with a measurable speed. The reaction of glycolic acid-Mn(II)-PMS system was studied in the pH range 4.05 to 4.75 at 304K. The reaction was found to follow first order kinetics. The rate of the reaction was found to increase with the increase in concentration of [Mn(II)] and independent of glycolic acid concentration. The rate of the reaction was also affected by the variation in the pH and the plot of k_{obs} versus $[\text{H}^+]^{-1}$ is a straight line passing through the origin. A probable mechanism and kinetic scheme has been proposed based on the above results.

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