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Research Article

KINETICS OF CATALYTIC OXIDATION OF GLYCOLIC ACID BY PMS

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ABSTRACT

The kinetics of the reaction between peroxomonosulphate with glycolic acid was studied in the presence of Mn²⁺ in alkaline pH at three different temperatures (298K, 305K & 311K). The reaction followed first order with respect to peroxomonosulphate. The rate of the reaction increases with the Mn²⁺ and independent of glycolic acid, sulphate ion and hydroxide ion. Thermodynamics parameters were calculated and reported. Based on the results a rate equation, kinetic scheme and a most probable mechanism has been predicted.

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INTRODUCTION

Manganese is available abundantly in the earth crust (Goel *et al*, 1996) and also in number of enzymes (Glasby *et al*, 1984). Glycolic acid is the simplest α -hydroxyacid which can be considered as a naturally product as it is available in sugar cane (Shorey *et al*, 1899), sugar beets, pineapple, cantaloupe and unripe grapes. Glycolic acid is used in skin care products, most often as a chemical peel in cosmetics. Peroxomonosulphate (PMS), also called as oxone, is an anion of caro's acid (H₂SO₅)(DuPont data sheet for oxone, 2001). It is considered as an inexpensive and environmentally accepted oxidant (Antipsitakis, 2003; Lente & Epenon, 2005; Rivas, 2003; Desai *et al*, 2006; Wong *et al*, 2006). Perusal of the literature evidences reveals that the oxidation reaction of glycolic acid has been carried out by various transition metal ions under different experimental conditions. In the continuation of the above work oxidation of glycolic acid has been targeted using Mn (II) as catalyst and PMS as the oxidant in alkaline pH which has not been reported earlier.

MATERIALS AND METHODS

Stock solution (0.5M) of Glycolic acid supplied by Alpha Aeaser, Lancaster (U.K) was prepared afresh and standardized by alkalimetry. Sodium hydroxide solution was standardized by using oxalic acid and phenolphthalein indicator. Manganese sulphate supplied by Merck (India) Ltd. was prepared daily

afresh before the commencement of the experiment. PMS was supplied by SIGMA-ALDRICH- CHEMIE GmbH. Purity of the sample was tested by cerimetry using ferroin indicator. Sodium thio sulphate as pentahydrate was purchased from Merck, India and standardized by using potassium dichromate. The kinetic studies were carried out always under the condition [substrate] >> [oxidant]. The reaction mixture was prepared by adding required volume of aqueous solutions of glycolic acid, metal ion and sodium hydroxide solutions (in this order).

The reaction mixture was diluted with water to 90ml and thermostated. Ten ml of PMS solution, thermostated separately, was pipette out into the reaction mixture and the timer was started. An aliquot (10ml) of the reaction mixture was taken out at various time intervals and then added into KI solution and H₂SO₄ mixture. Unreacted PMS in the reaction mixture reacts with I⁻ and I₂ is liberated. The liberated iodine was estimated by titrating against sodium thiosulphate solution using starch as an indicator. Stoichiometry of the reaction was determined by taking large excess of [PMS] over [GA] and [Mn(II)]. The unreacted PMS was estimated after 24 hours. The product analysis was carried out under the conditions [GA] >> [PMS] and oxalic acid was identified by aniline blue test (Feigel, 1956). The statistical software "Sigma plot 10.0" was used and the linear regression analysis was performed on Windows XP operating system.

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RESULTS

Kinetics of Mn (II) catalysed oxidation of glycolic has been studied in the alkaline medium by iodometry using PMS as the catalyst and the reaction was followed by calculating the concentration of the unreacted peroxomonosulphate in all the kinetic runs. The disappearance of [PMS] followed first order kinetics which is given by the plot of \ln [PMS] versus time in (Fig 1) with high correlation coefficient. All the further discussion in this paper is based on the pseudo first order kinetics.

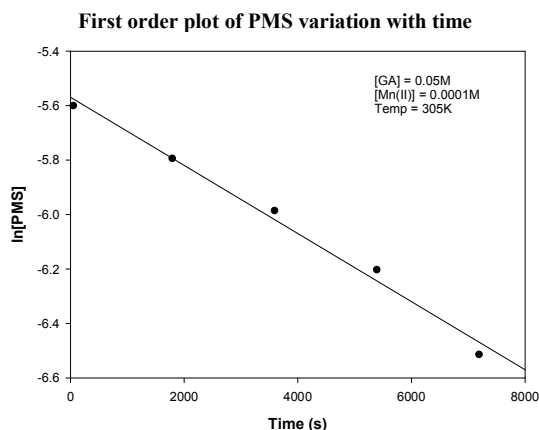


Fig 1 Plot of \ln [PMS] vs Time

Effect of Mn^{2+}

The effect of Mn^{2+} on the rate of the reaction was studied by varying the concentration of the Mn^{2+} and keeping the concentration of all other reactants in the mixture constant. The concentration of the Mn^{2+} used is in the range $2 \times 10^{-4} M$ to $3 \times 10^{-3} M$. The value of k_{obs} increased with the metal ion concentration. The plot of k_{obs} versus $[Mn(II)]$ is a straight line passing through origin (Fig 2).

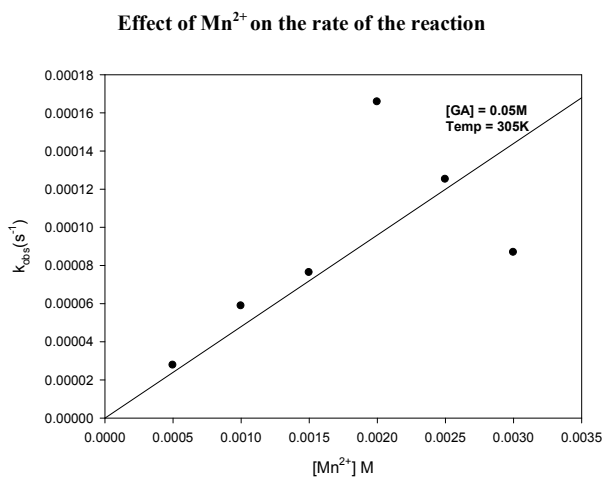


Fig 2 Plot of k_{obs} vs $[Mn^{2+}]$

Effect of glycolic acid

As glycolic acid is the substrate used, it is necessary to study the effect of glycolic acid on the rate of the reaction. The concentration of the glycolic acid is varied by maintaining the concentration of all other reactants in the reaction mixture a constant. The rate of the reaction was found to be independent of glycolic acid.

Effect of [sulphate ion]

As sulphate ion is one of the products formed generally in the reaction involving PMS, it is necessary to study the effect of sulphate ion on the rate of the reaction. Sodium sulphate is used to vary the sulphate ion concentration. The reaction was found to be independent of sulphate ion concentration.

Effect of temperature on the rate

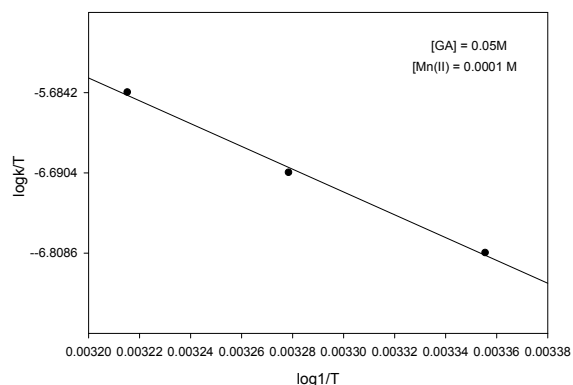


Figure 3 Plot of $\log k/T$ vs $1/T$

Effect of $[OH^-]$

Alkaline pH is maintained by using sodium hydroxide. The effect of hydroxide ion concentrations on the rate of oxidation was studied by calculating the kinetic constants at various hydroxide ion concentrations (0.05 to 0.1M). The k_{obs} values show a zero order dependence on $[OH^-]$ at all temperatures of study.

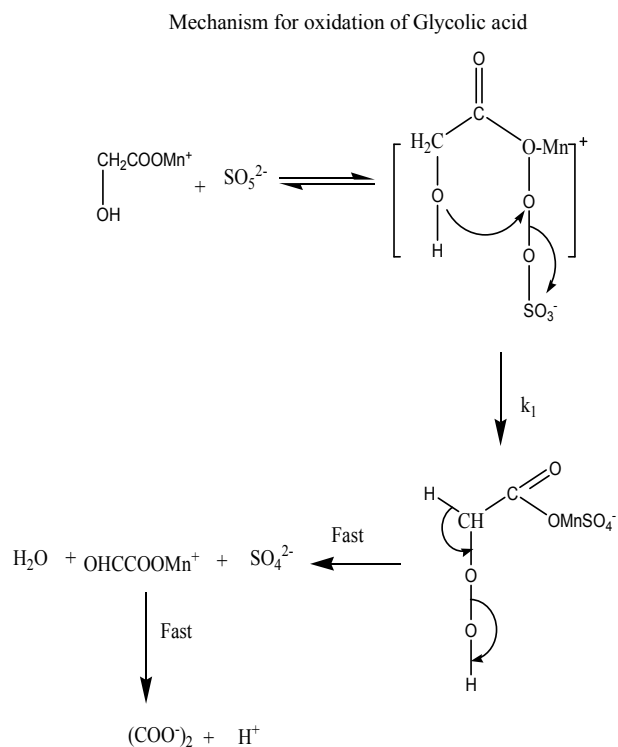


Fig 4 Mechanism of oxidation of glycolic acid

Effect of radical quenchers

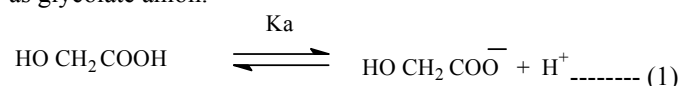
Perusal of the literature reveals that most of the reaction involving peroxides follows radical mechanism. So it is necessary to find out whether any radical intermediates are produced during the course of the reaction. For this study radical quenchers like t-butanol and ethanol were used. It has been found out that radical quenchers had no effect on the rate of the reaction. From this result the formation of radical intermediates in the reaction mixture can be ruled out.

Effect of temperature

The reaction was carried out at three different temperatures (298K, 305K & 311K) in order to calculate the thermodynamic parameters like activation energy, enthalpy, entropy etc and the results are reported. It was found that the rate of the reaction increased with increase in temperature.

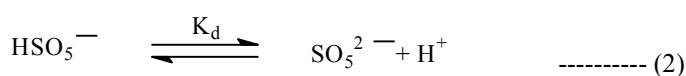
DISCUSSION

Oxidation of glycolic acid was carried out using peroxomonosulphate in the presence of Mn^{2+} . Glycolic acid is the simplest alpha hydroxy acid with one hydroxy and one carboxyl acid group. So the oxidation can take place either through the hydroxy or carboxyl group. Literature evidences are also available for the one electron oxidation (Kabir-ud-Din *et al.*, 2001) and molecular mechanism (Tinsay, 2011) of glycolic acid. The reaction between glycolic acid and peroxomonosulphate in alkaline medium was very slow and could not be studied under our experimental conditions. When a small amount of Mn^{2+} in the form of manganese sulphate was introduced in the reaction mixture the reaction proceeded with a measurable speed. This shows that Glycolic acid- Mn^{2+} is the active species in this reaction. The rate of the reaction is found to be first order with respect to $[Mn(II)]$ at all the temperatures of study. Glycolic acid is an alpha hydroxy acid with pKa value of 3.586 at 25C (Piispanen, 1995). Calculation of glycolate anion concentration reveals that under the experimental pH of the study almost all the glycolic acid exist as glycolate anion.

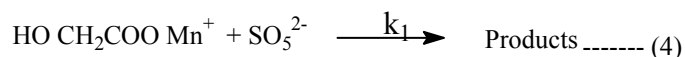
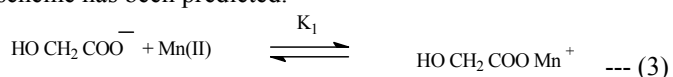


Earlier researchers have reported that glycolic acid forms MnL^+ complex only and have reported the equilibrium constant values (Robert Harreld Karraker, 1961). As almost all the glycolic acid exist as glycolate anion and complexes with Mn^{2+} , it can be approximated that the concentration of the complex is equal to the $[Mn^{2+}]$.

PMS exist as HSO_5^- and SO_5^{2-} in aqueous solution. The dissociation constant K_d is reported to be $4 \times 10^{-10} M$ at 25 C (Ball & Edwards, 1956). So under the experimental pH values all PMS will exist as SO_5^{2-} .



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



The rate equation for the above mentioned scheme is

$$-d[PMS]/dt = k_1 [SO_5^{2-}] [HOCH_2COO Mn^+] \text{----- (5)}$$

As mentioned above the concentration of the [Glycolic acid- Mn^{2+}] complex can be approximated to the concentration of Mn (II) itself.

$$k_{obs} = k_1 [HOCH_2COO Mn^+] \text{----- (6)}$$

A probable mechanism has also been proposed for the above mentioned oxidation reaction (Fig 4). The effect of the radical quenchers had no effect on the reaction indicating the absence of radicals during the course of the reaction. By analogy with earlier studies (Thendral *et al.*, 2009; Murugavel *et al.*, 2009; March & J.O. Edwards, 1989) we assume that oxidation of glycolate proceeds through a molecular mechanism. The thermodynamic parameters were calculated by using Eyring equation (Eqn 7). From the plot of $\log(k/T)$ Vs $(1/T)$ the change in entropy (ΔS) & enthalpy (ΔH) is calculated. The H & S values are found and reported as $-1085.379 \text{ KJ mol}^{-1}$ and $266.034 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

$$\ln(k/T) = \ln(k_B/h) - (\Delta H - T\Delta S/RT) \text{----- (7)}$$

CONCLUSION

Reaction between glycolic acid and PMS is found to be very slow. But in the presence of a small amount Mn (II) the reaction proceeded with a reasonable speed. The kinetics of the above reaction was studied in the alkaline pH at three different temperatures 298K, 305K & 311K by iodometry. The reaction followed first order with respect to peroxomonosulphate. The rate of the reaction increases with the $[Mn(II)]$ and independent of glycolic acid. A plot of k_{obs} Vs $[Mn(II)]$ is a straight line passing through origin. Based on the results a rate equation, kinetic scheme and a most probable mechanism has been predicted. Thermodynamic parameters are also calculated. A mechanism based on the oxygen atom transfer has been proposed.

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