Kinetic Studies of Glycolic Acid –PMS System In the Presence Of Fe (II)

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Abstract: *The kinetics of the reaction between peroxomonosulphate with glycolic acid was studied in the presence of Fe(II) in the pH range 4.05 to 5.2 at 304K. The reaction followed second order with respect to peroxomonosulphate. The rate of the reaction increases with the [Fe(II)] and independent with respect glycolic acid. A plot of k_{2obs} 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: *Glycolic acid, Peroxomonosulphate, Kinetics, Alphahydroxy acid, Catalyst*

I.   Introduction

Peroxomonosulphate (PMS) is a versatile oxidant used widely in research owing to its high reactivity and oxidation potential[1-4]. The high reactivity and the tendency of spontaneous decomposition may be attributed to the relatively weak oxygen-oxygen linkage with bond dissociation energy 20-40Kcal mol^{-1}[5-13]. In the presence of transition metal ions, PMS produces more reactive radical intermediates. Due to this PMS is used in advanced oxidation technologies for waste water treatment [14-19]

Glycolic acid (GA) is the simplest member of alpha hydroxy acid which has two functional groups (carboxyl and hydroxyl) and finds its application extensively in skin care products [20-25]. Oxidation of glycolic acid is fascinating because of the competition between the functional groups to get involved in the reaction and the formation of intra and intermolecular hydrogen bonds [26-31]. Though it has been realized that the reaction of glycolic acid can proceed by many possible routes most of the literature focuses on one electron oxidation [32-36] rather than ionic mechanism. Oxidation of glycolic acid by Ni(II) & Cu(II) [37] has been reported to follow oxygen atom transfer mechanism. So in continuation of the above works in order to explore the mechanism of reaction between glycolic acid by PMS in the presence of Fe(II), this study was undertaken in the pH range 4.75 to 5.2 at 304K.

II.   Experimental

Glycolic acid was supplied by Alpha Aesar Landcaster (UK). The stock solution (0.5M) was prepared daily before the start of the experiments and standardized by alkalimetric titrations. PMS was supplied by Fluke Chemie (Switzerland) under the trade name Oxone. The purity was tested iodometrically. PMS was prepared daily afresh and standardized iodometrically. The kinetics of the reaction between glycolic acid and Fe(II) in the presence of PMS was studied in the pH range 4.74 to 5.2. pH of the reaction mixture was maintained by using acetic acid /sodium acetate buffer solution by varying the concentration of acetic acid and keeping the concentration of [NaOAc$^-$] constant. The reaction was studied under the condition [GA] >> [Fe(II)] & [GA] >> [PMS]. The reaction was followed by estimation of unreacted PMS as a function of time by iodometry in the pH range 4.75 to 5.2 at 304K. The liberated iodine was titrated against sodium thiosulphate using starch indicator. The stoichiometry of the reaction was determined at pH 4.75 by taking large excess of [PMS] over [GA] and [Fe(II)]. The unreacted PMS was estimated after 24 hours. The stoichiometry observed is represented as follows.

$$GA + 2\,PMS \longrightarrow Products$$

The product analysis was carried out under the conditions [GA] >> [PMS] and evolution of oxygen was identified by the colour change with alkaline solution of sodium dithionite activated with indigocarmine [38]. Traces of oxalic acid was also identified by aniline blue test. [39]

III.   Results

The rate of disappearance of [PMS] follows second order kinetics with respect to [PMS] which is evidenced by the linear plot of $[PMS]^{-1}$ versus time (Fig.1) with high correlation coefficient. Therefore the results reported in this paper in based on the second order conditions.
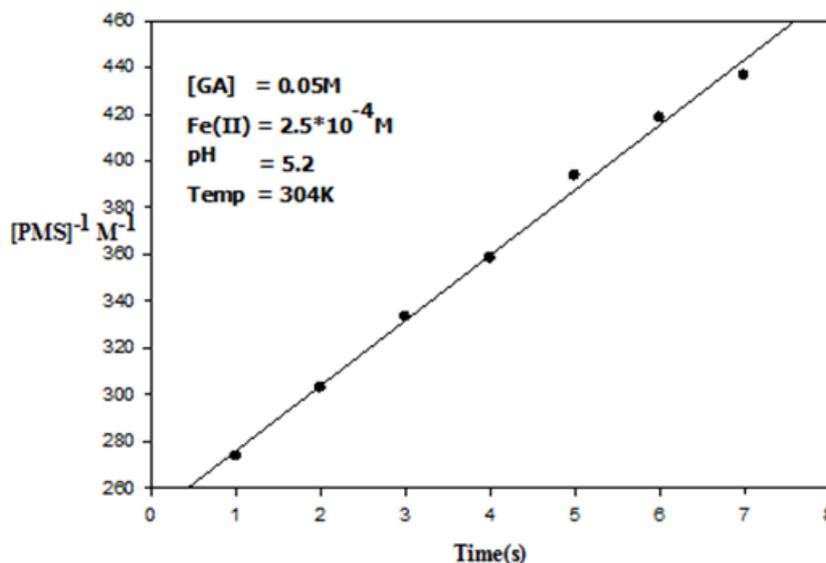
Figure 1. Plot of $[PMS]^{-1}$ versus Time

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

Sulphate ion is one of the probable products in most of the PMS systems [40]. So it is necessary to study the effect of sulphate ion during the course of the reaction. The k_{2obs} values are calculated at 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.

Effect of Fe(II) on k_{2obs}

The effect of the metal ion in all the three pH are determined by varying the metal ion concentration and keeping the concentration of glycolic acid and oxidant constant. The concentration of Fe(II) used in this study is in the range $5x10^{-5}$M to $3x10^{-4}$ M. It is observed that the k_{2obs} values increased with the metal ion concentrations and the results are given in Fig 2. The plot of k_{2obs} versus Fe(II) are straight lines passing through origin or with a small intercept which can be statistically approximated as origin. The same trend is observed in all the pH.
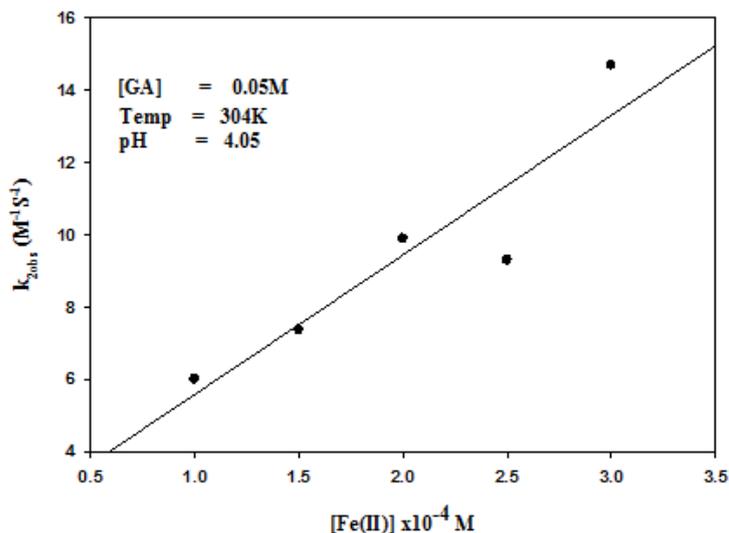
Figure 2. Plot of k_{2obs} versus [Fe(II)]

Effect of glycolic acid concentration on k_{2obs}

Effect of glycolic acid concentration on the rate of the reaction was studied by varying the [GA] and keeping the concentration of metal ions and oxidant constant at all pH. k_{2obs} values are found to be independent of the alpha hydroxy acid concentration.

Effect of acetate ion concentration on k_{2obs}

Acetic-acid-sodium acetate buffer was used to maintain the hydrogen ion concentration through out the course of the reaction. As the acetate ion can act as a nucleophile, it was necessary to test the effect of the acetate ion on the rate of the reaction. The effect of base, that is, acetate ion on the reaction was studied at all pH. But it was found that the rate of the reaction was not affected by the acetate ion in the concentration range 0.08 – 0.32M of acetate ion. However the different pH of the kinetic studies were maintained at a predetermined value by adjusting the concentration of acetic acid while keeping the acetate ion concentration constant, usually at 0.32M.

Effect of radical quenchers

Quenching studies were carried out inorder to determine any radical intermediates formed during the course of the reaction. Ethanol and t-butanol were used as radical quenchers. The rate of the reaction was unaffected by the added radical quenchers.

Effect of pH

The influence of $[H^+]$ on the rate of the reaction is found by varying the pH and maintaining the concentration of all other parameters constant. The plot of k_{2obs} versus pH are straight lines passing through origin.

The observed rate equation based on the experimental result is given below in equation (1)

$$k_{2obs} = k_2 [Fe(II)] /[H^+] \qquad \text{------------ (1)}$$
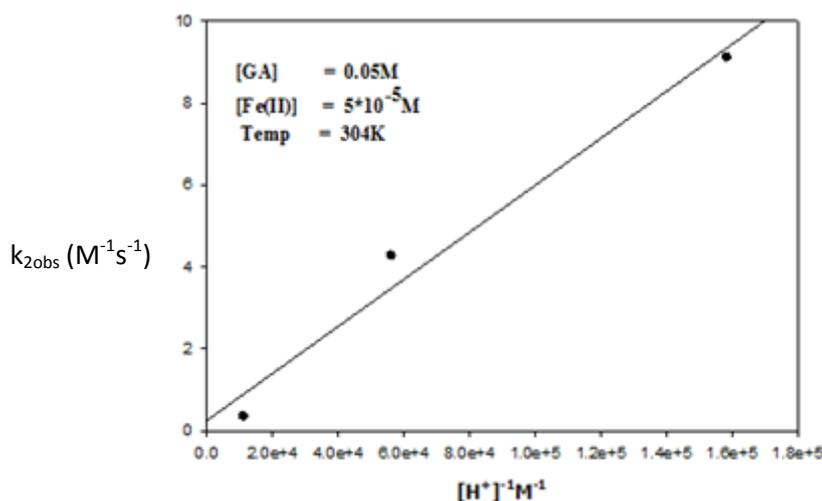
Figure 3. Plot of k_{2obs} vs $[H^+]^{-1}$

IV.   Discussion

Glycolic acid is an alpha hydroxy acid with pKa value of 3.586 at 25°C .[41]

$$HOCH_2COOH \xrightleftharpoons{K a} HOCH_2COO^- + H^+ \qquad \text{---------- (2)}$$
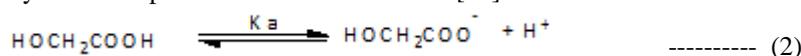
Calculations reveal that under experimental conditions almost all the acid exist as glycolate anion. Alphahydroxy acid can act as both as monodendte ligand by complexing with metal ion at the carboxyl group or bidentate ligand in which the additional bonding is through the oxide of the hydroxyl group. Earlier researchers have shown that Fe(II) ion form FeL^+ complex only [42]. The high equilibrium value suggests that even at low pH used in our study, about 80% of Fe(II) will be chelated to FeL^+. Therefore as and first approximation we can approximate that the concentration of FeL^+ complex is equal to Fe(II) itself. The reaction between GA & PMS was found to be very slow even after the completion of 24 hours. It was interesting to see that the reaction proceeded with a reasonable speed upon addition of small amount of catalyst Fe(II). This shows clearly shows that Glycolic acid-Fe(II) complex is the active species in our reaction.

$$[HO\ CH_2\ COO]^- + Fe(II) \xrightleftharpoons{K_1} HO\ CH_2\ COO\ Fe^+ \qquad \text{---------- (3)}$$

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[43]. Under the experimental pH values all PMS will exist as HSO_5^- and therefore these two terms caused interchangeably.

$$HSO_5^- \underset{}{\overset{K_d}{\rightleftharpoons}} SO_5^{2-} + H^+ \qquad \text{------------ (4)}$$

Based on the experimental results, we can propose the following kinetic scheme for the reaction of PMS with iron glycolate system.

The kinetic scheme for the reaction is given as follows:

$$HO\,CH_2\,COO\,Fe^+ + HSO_5^- \overset{K_2}{\rightleftharpoons} HO\,CH_2\,COO\,Fe\text{-}SO_5^- + H^+ \qquad \text{----------- (5)}$$

$$HO\,CH_2\,COO\,Fe\text{-}SO_5^- + HSO_5^- \overset{k_2}{\longrightarrow} \quad Pdt \qquad \text{------------ (6)}$$
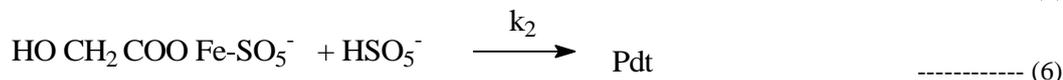
$$-\frac{d[PMS]}{dt} = k_2\,[HSO_5^-]\,[HO\,CH_2\,COO\,Fe\,SO_5^-] \qquad \text{------------ (7)}$$

$$= k_2\,[HSO_5^-]\,\underline{[HO\,CH_2\,COO\,Fe^+]\,[HSO_5^-]} \qquad \text{------------ (8)}$$
$$[H^+]$$

$$k_{2obs} = k_2\,\frac{[HOCH_2COO\,Fe^+]}{[H^+]} \qquad \text{------------ (9)}$$

$$k_{2obs} = k_2\,\frac{[Fe(II)]}{[H^+]} \qquad \text{---------- (10)}$$

This expression explains all the experimental findings that (i) the rate is zero order with respect to glycolic acid, (ii) plot of k_{2obs} vs [Fe(II)] is a straight line passing through origin and (iii) plot of k_{2obs} vs $1/[H^+]$ is also a straight line passing through origin. The value of rate constant k_2 calculated individually from the plot of k_{2obs} vs [Fe(II)] and k_{2obs} vs $1/[H^+]$ should agree with each other. This is found to be true. The value of rate constant k_2 calculated individually from the plot of k_{2obs} vs [Fe(II)] and k_{2obs} vs $1/[H^+]$ are 0.748 M^{-1} s^{-1} and 1.11 M^{-1} s^{-1} respectively . The good agreement of the values of k_2 suggest that the proposed kinetic scheme is a correct one. As already mentioned the rates are not affected by the added radical quenchers and this clearly shows that the free radicals are not involved in the reaction and the kinetics follow molecular mechanism. Edwards and Marsh [44] suggested that the oxidation reaction with HSO_5^- may proceed by the nucleophilic attack at the peroxide by the substrate resulting in an oxygen atom transfer, usually the terminal peroxide oxygen. Similar observation is reported in the oxidation of lactic acid and tartaric acid by PMS in the presence of Ni(II)[45, 46]. Therefore the oxidation of Fe-glycolate by PMS may proceed through the same mechanism. The probable mechanistic scheme for the oxidation of Fe-glycolate by PMS is shown in Fig. 4.
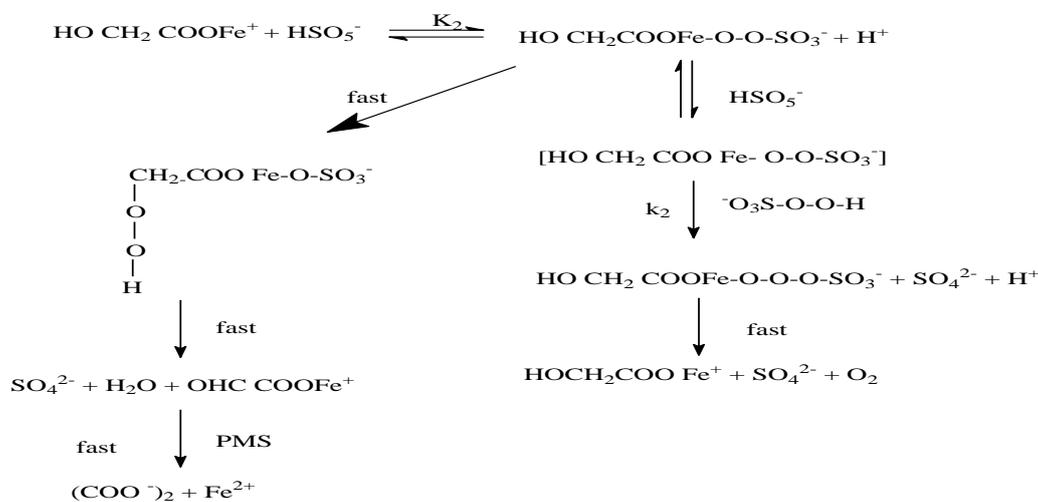
Figure 4. Mechanism of reaction between GA and PMS

V. Conclusion

Reaction between glycolic acid and PMS is very slow. But in the presence of transition metal ions like Fe(II), the reaction proceeded with a reasonable speed.. The kinetics of the reaction between peroxomonosulphate with glycolic acid was studied in the presence of Fe(II) in the pH range 4.05 to 5.2 at 304K. The reaction followed second order with respect to peroxomonosulphate. The rate of the reaction increases with the [Fe(II)] and independent with respect glycolic acid. A plot of k_{2obs} 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. A mechanism based on the oxygen atom transfer has been proposed.

Acknowledgements

References

[1]. Dupont data sheet for Oxone. www.dupont.com/oxone/applications/index.html2001
[2]. J.O. Edwards & E. Marsh, Prog. React. Kinet., 15, 1989, 35.
[3]. M.D. Johnson & R.J. Balahura, Inorg. Chem., 27,1987, 3104.
[4]. N. Trost & D. Curban, Tetrahedron Lett, 22, 1981, 1287.
[5]. G.P. Anipsitakis & D.D. Dionysiou, *Environ. Sci. Technol.,* 37, 2003, 4790-4797.
[6]. G. Lente & J.H. Espenson., *Green Chem.,* 7, 2005, 28-34.
[7]. M.K. Wong, T.C. Chan, et al, *Environ. Sci. Technol.,* 40, 2006, 625-630.
[8]. F.J. Rivas, F.J. Beltrn, F. Carvalho & P.M. Alvarez., *Ind. Eng. Chem. Res*., 44, 2005, 749-758.
[9]. L.V. Desai, H.A. Malik & M.S. Sanfora, *Org. Lett.,* 8, 2006, 1141-1144.
[10]. C.A. Delcomyn, K.E. Bushway & M.V. Henley, *Environ. Sci. Technol.,* 40, 2006, 2759-2764.
[11]. R. Gandhari, P.P. Massukuri & T.K. Vinod, *J. Chem. Edu.,* 84, 2007, 852-854.
[12]. A. Rastogi, S.R. Al-Abed & D.D. Dionysiou, *Appl. Catal. B: Environ.,* 85, 2009, 171-179.
[13]. M.C. Marcotuillio, F. Epifano & M. Curini, *Trends Org. Chem.,* 10, 2003, 21-34.
[14]. G.P. Anipsitakis, D.D. Dionysiou, Environ. Sci. Technol. 38, 2004, 3705.
[15]. G.P. Anipsitakis, D.D. Dionysiou, Environ. Sci. Technol. 37, 2003, 4790.
[16]. G.P. Anipsitakis, D.D. Dionysiou, Appl. Catal. B: Environ. 54, 2004, 155.
[17]. G.P.Anipsitakis,D.D.Dionysiou,M.A.Gonzalez,Environ.Sci.Technol.40, 2006, 1000.
[18]. E.R. Bandala, M.A. Pelaez, et al, J.Photochem. Photobiol. A: Chem. 186, 2007, 357.
[19]. G.P. Anipsitakis, T.P. Tufano, D.D. Dionysiou, Water Res. 42 (2008) 2899.
[20]. E.A. Dutra, M.I.M. Santoro et al., *J. Pharmaceut . Biomed. Anal.,* 40, 2006, 242-248.
[21]. Federal register 67, 2002, 71577-71578. http://www.fda.gov/ohrms/dockets/98fr/02-30340.pdf.
[22]. Z.D. Draelos., *Dermatol. Ther.*, 13, 2000, 154-158.
[23]. C. Howard, R.L.Sams II, D.A. Dennis & W.G. Wamer, *J. Food Drug Anal.,* 10, 2002, 258-261.
[24]. G.S. Habn., *Drug cosmet. Ind.,* 162, 1998, 18-22.
[25]. F.A. Anderson, *Int. J. Toxicol.,* 17, 1998, 241.
[26]. A.J. Thakkar, N.E.B. Kassimi & S. Hu, *Chem. Phy. Lett.,* 387, 2004, 142-148.
[27]. D. Harvey & K.J. Feierabent, *J. Phy. Chem. A,* 110, 2006, 6439-6446.
[28]. R.D. Ellison , C.K. Johnson & H.A. Levy, *Act. Cryst.*, B27, 1971, 333.
[29]. W.P. Pijper, *Acta. Cryst.,* B27, 1944, 344.
[30]. N.E.B. Kassimi, E.F. Atvhibonh & A.J. Thakkar, *J. Mol. Struct. (Theochem)*, 591, 2002, 189.
[31]. G. Cassanas, M. Morssli, E.F. Fabreque & L. Bardet, *J. Raman Spectrosc.,* 22, 1991, 11.
[32]. W.C. Vasudeva, M.R. Suliman & A. Hossaoy, *J. Inor. Nucl. Chem.*, 40, 1978, 1705-1707.
[33]. S. Prasad & J. Choudhary, *Indian J. Chem*., 17A, 1979, 167-169.
[34]. N. Datt, R.R. Nagori & R.N. Mehrotra, *Can. J. Chem*., 64, 1986, 19.
[35]. Kabir-ud- Din, K. Hartani & Z. Khan, *Int. J. Chem. Kinet.*, 33, 2001, 377-386.
[36]. P. Levesley & W.A. Waters, *J. Chem. Soc*., 1955,217-221.
[37]. S. Shailaja, M. S. Ramachandran, Int. J. Of Chem. Kinet., 41, 2009, 160-167.
[38]. Vogel A. I , A Text Book of Quantitative Inorganic Analysis, ELBS and Longman, London, 194 p-1081.
[39]. Feigl.F Spot Tests in Organic Analysis, Elsevier, New York 1956, 335
[40]. M. Spiro Electrochim. Acts, 24, 1979, 313-314.
[41]. J. Piispanen & L.H. Lajunen, Acta.Chem. Scand., 49,1995, 241.
[42]. Rotertoportanova et al , Pure Appl. Chem., 75(4), 2003, 495-540.
[43]. Ball D.L, Edwards J.O, J.Am. Chem.Soc. 78, 1956, 1125
[44]. J.O Edwards & C. Marsh, Prog. React. Kinet., 15, 1989, 35.
[45]. M. Murugavelu, P. Andal, S. Shailaja & M.S Ramachandran, J. Mol.. A: Chem., 306, 2009, 1-5.
[46]. S. Shailaja, M.S. Ramachandran, *Int. J. Chem. Kinet.*, 3, 2011, 620-630.