ORIGINAL RESEARCH PAPER Volume-6 | Issue-9 | September-2017 | ISSN No 2277 - 8179 | IF : 4.176 | IC Value : 78.46

INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

KINETIC AND MECHANISTIC STUDY OF THE OXIDATION OF GLYCOLIC ACID BY QDC IN NON- AQUEOUS MEDIUM

Chemistry

Shikha Soni Research scholar, Department of chemistry, Pacific University, Udaipur

B.K. Dangarh Asstt. Prof. Of Chemistry, Govt. P.g. College, Neemuch, M.P.

ABSTRACT

The oxidation of Glycolic acid by QDC carried out in the presence of PTSA (P-toluene sulfonic acid) in DMSO (Dimethyl sulfoxide) as solvent at 303 K spectrophotometrically (λ_{max}= 460nm). The reaction is first order with respect to QDC, $[H^+]$ and substrate. Michaelis-Menten type kinetics was observed. The reaction rate increases with increasing volume percentage of DMSO in reaction mixture, suggesting the involvement of an ion in the rate determining step. The reaction rates were studied at different temperature and the activation parameters has been computed. The reaction proceeds through formation of cyclic chromate-ester between protonated QDC and α-hydroxy acid.

KEYWORDS

Glycolic acid, QDC, Oxidation, DMSO

Introduction:-

Oxidation of organic compounds under non-aqueous condition is an important reaction in synthetic organic chemistry[1-5]. Different chromium(VI) derivatives have been reported as oxidant[6-9]. Quinolinium dichromate (QDC) is found to be a mild reagent for the oxidation of organic compounds. The mildness of QDC was demonstrated effectively in the oxidation of diols[10] ,where a single hydroxyl group was oxidized to give hydroxy carbonyl compound as the product. Oxidation of alpha-hydroxy acids by QDC was carried out by Chimatader *et al.*[11] and Aruna et al.[12] in various organic solvents. The formation of ketoacids by the C-H cleavage of the alpha-hydroxy acids was reported with many chromium (VI) oxidants[13]. Anandaratchangan *et al.* studied the oxidation of pentaamminecobalt (III) perchlorate complexes of alpha-hydroxy acids by quinolinium dichromate (QDC)[14].

Hiran et al.[15] studied the oxidation of lactic and mandelic acid by quinolinium dichromate in aqueous acetic acid medium. The reaction is first order in each reactant. Dangarh *et al*[16]. studied the kinetics of oxidation of lactic acid by PDC in perchloric acid medium. Active oxidizing species involved was protonated PDC.

Material and Method:-

Quinolinium dichromate was prepared according to the procedure describe by Balasubramanian et al.[17]. The alpha-hydroxy acids (A.R) supplied by Sigma-Aldrich and used as such. The purity of the compound was checked by spectral analysis IR (KBr) exhibited band at 3250,1660,1500,1340,110,950,870,770 cm-1. DMSO was purified by distillation. All other reagents used were of "AnalaR" grade. All the solutions for the experiments were maintained at the specified temperature.

The reaction progress was followed by monitoring the decreasing concentration of QDC spectrophotometrically at 460 nm for up to 80% of the reaction.

Result and discussion:-

Stoichiometry and product analysis

The stoichiometry of the rectionwas found to correspond to the equation.

$CH_2(OH)COOH + QHCrO_4 \rightarrow$ HCHO + Cr(III) + H_2O + CO_2 + Q

[Glycolic acid] [QDC] [Formaldehyde]

Effect of oxidant:-

When Glycolic acid were in excess, the disappearance of QDC followed the first-order rate law. The first-order rate constants are independent of the initial concentration of the QDC. [Table 1]

Effect of Substrate:-

At constant [QDC], the rate constants for oxidation calculated at different initial concentration of substrates found to increase linearly ($2x10^{-2}$M to $6x10^{-2}$M). The results of the effect of substrate concentration on the rate constant are summarized in (Table - 1). A plot of log k_1 against log [substrate] gives a straight line (fig-1). This revealed that the rate of oxidation is first order with respect to the acid.

It has been found that plot of [1/k_1] versus (1/[substrate]) is straight line with an intercept on the rate ordinate, indicating the oxidation of Glycolic acid follows Michaelis–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the substrate.

Effect of H^+ Ion Concentration:-

To the study effect of hydrogen ion p-toluenesulphonic acid [PTSA] was used. The rate of oxidation was studied from $[H^+] = 1x10^{-3}$ to $5x10^{-3}$M. It was observed that rate increases with increase in hydrogen ion concentration. log k_{obs} v/s log $[H^+]$ is a stright line in all the cases and the slopes are near to one. The results are summarized in Table-1.

Effect of Solvent composition:-

Effect of solvent was studied by changing proportion of DMSO and water; varied from 30 to 70% water v/v. The reaction rate decreases with an increase in the percentage of water, suggesting that a low dielectric medium favors the oxidation (Table-1). A plot of log k_1 against 1/D (dielectric constant) is linear with a positive slope for the acids under study. This indicates an ion–dipole type of interaction in the rate-determining step[18-20]. Wieberg and Evans [21] have made a similar approximation with regard to the same binary solvent system.

Effect of Temperature:-

Rate of oxidation increases with increase in temperature. Rate of reactions were determined at different temperature (298 to 323 K). In all the cases, a plot of log k_{obs} versus 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid for this oxidation. The energy of activation is 45.24 kJ mol^{-1}. The entropy value is negative, suggesting that the transition state is more rigid and extensively solvated than the reactants. The negative entropy also suggests the formation of cyclic intermediate from acyclic species. (Table 2 &3)

Conclusion:-

Oxidative transformation of Glycolic acid is first order with respect to oxidant and $[H^+]$. Glasston [22] has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast, but if it is negative, the reaction is slow. In our case, the negative value of entropy of activation suggests slow reaction and formation of cyclic structure from non-cyclic structure. Thus the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product.

TABLE NO. 1

Effect of [Substrate], [H+] and Solvent

[QDC]=2 x 10^{-3}M T = 303K

[Subs] x10-2 M	[PTSA] $x10^{-3}$ M	Water in DMSO% v/v	kobs X 10^5 Sec-1
2	1	0	10.17
3	1	0	15.31
4	1	0	18.76

5	1	0	21.49
6	1	0	23.52
2	1	0	7.21
2	2	0	10.17
2	3	0	17.00
2	4	0	22.30
2	5	0	24.68
2	1	0	10.17
2	1	30	4.10
2	1	50	3.00
2	1	70	2.65

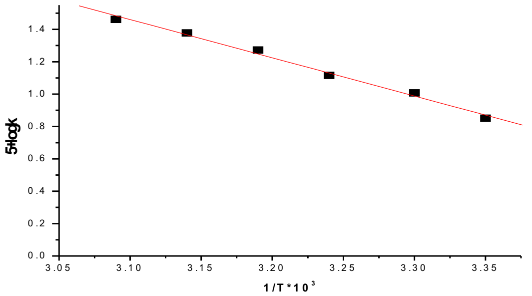
TABLE NO. 2
[SUBSTRATE] = 2 X 10^{-2} M [PTSA] =1 X 10^{-3}M [QDC] = 2 X 10^{-3}M [DMSO]=100% v/v

Temperature In K	kobs X 10^{5} Sec-1
298	7.10
303	10.17
308	13.05
313	18.73
318	23.91
323	28.97

TABLE NO. 3
THERMODYNAMIC PARAMETERS
[SUBSTRATE] = 2 X 10^{-2} M [PTSA] =1 X 10^{-3}M [QDC] = 2 X 10^{-3}M
[DMSO]=100% v/v T = 303K

α-Hydroxy Acid	log A	$Ea^{\#}$ kJ mol^{-1}	$S^{\#}$ J $mol^{-1}K^{-1}$	$H^{\#\#}\triangle$ kJ mol^{-1}	$G^{\#}\triangle$ kJ mol^{-1}
Glycolic acid	8.50	45.24	-86.04	42.72	68.79

Figure :-1
VARIATION OF RATE WITH TEMPERATURE OF DL-ALANINE
log k Vs 1/T



References:-

1. Mehrotra, R. N. Eur. Chem. Bull., (2013), 2(10), 758.
2. Banerji, J., Banerji, K. K.; Kotai, L., Sharma, D., Sharma, P. K., J. Ind. Chem. Soc., (2011), 88(12), 1879.
3. Kotai, L., Gacs, I., Sajo, I.E.; Sharma, P. K.; Banerji, K. K., Trends Inorg. Chem., (2009), 11, 25.
4. Purohit, T., Banerji, J., Kotai, L., Sajo, I., Banerji, K.K., Sharma, P. K., J.Ind .Chem. Soc., (2012), 89, 1045.
5. Meena,.A. K., Daiya, A., Sharma, A., Banerji, J., Sajó, I. E., Kotai, L.,Sharma, V., Int. J. Chem. (Mumbai) (2012), 1, 55.
6. Corey, E. J., Suggs, W. J. Tetrahedron Lett., (1975), 2647.
7. Panchariya, P., Purohit, T., Swami, P., Malani, N.,Kotai, L., Prakash, O.,Sharma, P. K. Int. J. Chem. Sci., (2012), 10, 557.
8. Ashgar, B. M., Mansoor, S. S., Malik, V. S., Eur.Chem., Bull., (2013). 2(8),538- 544.
9. Panchariya, P., Vadera,K., Malani, N., Prasadrao, P., Kotai, L., Sharma, P.K., J.Chem. Asia, (2011), 2(4), 225.
10. B. Kuotsu, E. Tiewsoh, A. Debroy and M. K. Mahant, J. Org. Chem., 61, 8875 (1996).
11. A. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, Oxid. Commun., 27, 81 (2004).
12. K. Aruna, P. Manikyamba and E. V. Sundaram, Collect. Czech. Chem. Commun., 58, 1624 (1993).
13. Sabita Patel and B. K. Mishra, Tetrahedron, 63, 4367 (2007).
14. K.Anandaratchagan , B. MD. Nawaz and K. Subramani Acta Chim. Pharm. Indica: 1(1), 2011, 44-50
15. Hiran B. L, Jain R. and Nalwaya N.: Oxid. Commun.(2003), 26 (4), 561.
16. Dangarh B.K.,Hiran B. L., & Joshi S. N.; OxidationCommunications, (2012),35,2,352.
17 K. Balasubramanian and V. Pratibha, Indian J. Chem., 25(B), 326 (1986).
18 Hiran B. L, Jain R. and Nalwaya N.: Oxid. Commun.(2003), 26 (4), 561.
19 Amis: J. Chem. Educ. (1953), 30, 351.
20 Thangarajan A. and Gopalan R.: J. Indian Chem. Soc., (1990), 67,453.
21 Wieberg K. B. and EvansT. R: J. Am. Chem. Soc., (1958), 80, 3019.
22 Glasston S., Laidler K.J. and Eyring H. : The Theory of Rate Processes, Mc Graw Hill New York (1947).