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Kinetics of oxidation of ChloroamineT in Presence of CTAB

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ABSTRACT: Oxidation of amino acid follows pseudo first order kinetics. The rate of the reaction speeds up with increase in concentration of amino acid at constant acidic medium, the value of rate constant increases. Variation of hydrogen ion concentration on the reaction was observed by changing the concentration of HCl. It was observed that the reaction slows down with increase in the hydrogen ion concentration obeying second order rate of the reaction.

INTRODUCTION

Oxidation of α-amino acids is a long known reaction which leads to amines with a range of applications from the synthesis of biologically active compounds to the preparation of synthesis. The most commonly used method employs thermolysis of the amino acid in the presence of catalytic amount of an aldehyde. Other non enzymatic methods include irradiation with UV light heating in diphenylmethene solvent[7] or thermolysis in a high boiling solvent in the presence of a peroxide catalyst. However some unnatural α-amino acids do not undergo oxidation.

The kinetics of oxidation of some amino acid in perchloric acid with Cl- ion as a catalyst was studied by Hiremath[1] *et al.* the results were compared with those obtained with chlorine water and HOCl as oxidant. It is observed that the reaction in first order with respect to 1-chlorobenzotriazole [CBT] and [amino acid] each and fractional order in [Cl-] and [H+] ions. The kinetics of oxidation of α-amino acids by N-chlorosuccinimide (NClS) and N-bromosuccinimide (NBS) in aqueous medium has been investigated by Ramachandran[2] *et al.* Results show that the observed rate of oxidation is first order in (oxidant) and zero order in [substrate]. The kinetics and mechanism of the oxidation of amino acids by proxomonosulfate (PMS) has been studied by Ramachandran and Vivekanandam[3]. The observed rate is first order in [oxidant] and [amino acid] and inverse first order in hydrogen ion concentration. The kinetics and mechanism of oxidation of L-theonine in acid media by sodium N-chloro-p-tolene-sulphonamide (CAT) has been investigated by Gowda *et al.* Gowda and Mahadevappa4-6 have investigated the kinetics and mechanism of oxidations of amino acids by sodium N-chlorotoluene-p- sulphonamide (chloromine-T) in acid and alkaline media at 35 °C. chloromine-T and related aryl sulphonamide derivatives have got potential applications in the varying field ranging from disinfectant, antiseptic and its reactivity with other functional groups. Chloramine-T and its related compounds are extensively used as analytical reagents. The diverse mode of action of N-halogeno-N-metallo reagents (chloramines-T and related aryl sulphonamide derivatives) is attributed to their ability to act as source of (a) haloniumcations (x^+) (b) hypohalite species (HOX) (c) anions (e.g., sufonamidate or carbanidate anions) which act both as bases and nucleophiles, and (d) nitrenoids has been significant. These reagents are stable in aqueous solution and behave as strong electrolytes acting as strong oxidants in both acidic and alkaline media. As a result extensive studies related to the oxidation of a variety of functional groups are reported in the literature. The studies include the oxidation of sulphur compounds8-10 (Sulfides, Selenides, Sulfoxides, and Sulfimides), nitrogen compounds11-14 (Nitroso, Nitro, Azo groups, Diaryldiazomethanes, Diaryhydrazones, α-amino acids and Isonitriles).

Chloramine-T reacts with the functional groups containing oxygen (e.g. alcohols, aldehydes,

ketones, phenolexpoxides etc.). Extensive studies of the kinetics and mechanism of chloramine-T oxidation of alcohols to aldehydes in alkaline, neutral, and acidic conditions have appeared[15-21]. Certain alcohol oxidations were catalyzed by Osmium. In acid media, primary alcohols[22] are oxidized to the aldehydes by chloramines-T via initial protonation to give N-chlorotoluene-p-sulfonamide. The oxidation of aldehydes by alkaline chloramines-T whereas in alkaline medium both enolizable and nonenolizable aldehyde is effected by the presence an absence of Osmium (VIII) but in acidic medium [23-25]. Aldehydes which are capable of enolization can be oxidized. It was suggested[26] that an "activated complex" facilitated the ability of chloramines-T to abstract a hydride ion from the hydrate aldehyde. Alkaline chloramine-T oxidizes, carbohydrates[27] Phenols react with chloramines-T to yield chlorination product[28-32] Recently, it has been reported[33] that chloramine-T is a potentially more exhaustive oxidizing agent in degradation of rubber than Cl. The biological application of chloramine-T has been found[34] in the radiolabelling of bioactive molecules by halogenations. CAT may be used either as a solution or in an immobilized from (iodobeads) to release radioactive elemental iodine or other halogens by oxidation of their salts. The reaction of choloramine-T with amino acid and related compounds[35] (B-alanine, L-alanine, and L-alanine ethyl ester) under pseudo first order conditions (where amino acids in large excess over CAT) showed that the overall reaction was second order. The oxidation of oxalic acid[36] by trichloromelamine (TCM) and chloramines-T (CAT) follows second order kinetic in [TCM] while the rate is independent of [S] and [H+] concentrations. The ruthenium (III) catalyzed[37] oxidation of maleic and acrylic acid by chloramines-T in alkaline medium showed first order dependence of rate with respect to oxidant and the catalyst concentrations.

Jinxin[38] *et al.* reported the flow injection kinetic spectrophotometric method for the determination of trace iodine in geological samples using CAT. The oxidation of p-cresol[39] by chloramine-T in the presence of cetyltrimethylaammoium bromide (CTAB) showed first order dependence on the oxidant concentration, but it has zero order with respect p-cresol. The kinetics of oixidation of indoles[40] to corresponding oxindole by N- chloro-N-sodio-p-tolune sulphonamide in alkaline medium is catalyzed by osmium (VIII) at 30 °C showing first order dependence each in chloramines-T, and indole.)

EXPERIMENTAL

The following reagents like Lysine, chloroamine T, Sodium sulphate, Hydrochloric acid and Potassuim iodide were used during the kinetics and mechanistic studies of oxidation of Lysine by Sodium-N- chloro-p-tolunesulfonamide (chloramines_T). No further purification of reagents was done. For the preparation of the stock solutions doubly distilled water was used as a solvent. Chloramine-T (CAT) was measured idometrically against standardised thiosulfate. Kinetic experiment were performed under varying conditions of [substrate], [H^+], temperature. The concentration of oxidant kept constant at 0.002 moldm-3throughout the kinetic experiments as the variation of [oxidant] itself had no effect on the observed rate constant. All the kinetic runs were carried out under pseudo-first order reaction condition.

ANALYSIS OF PRODUCT

For identification of the products, the calculated amount of chloramine-T (CAT) and acidified solution of amino acid were mixed together under the reaction conditions identical to the kinetic experiment. The reaction mixture was kept overnight at 30 °C. The presence of aldehyde in the product was detected by their characteristic color reaction with Schiff's reagent. The evaluation of ammonia was confirmed by the reaction with Nesseler's reagent. The presence of amine was detected by carbylamines test. Carbon dioxide evolved during the oxidation of amino acids.

STOICHIOMETRY

Varying ratios of amino acids to CAT was mixed in HCl medium at 30 °C and kept for 24hours. Estimation of unreacted CAT (as determined iodometerically) showed that one mole of each amino acid, lysine consumed one mole of CAT as reported by Gowda and Lakshmi Rao[42]

$R'CH(NH_2)COOH + RNCl\text{-}Na^+ + H_2O \rightarrow R'CHO + CO_2 + RNH_2 + NH_3 + Na^+ + Cl^-$

Where R = CH3C6H4SO2

And R2 = (CH2)4NH2 (Lysine)

KINETIC RUNS

All the reaction were carried out in a glass stopper conical flask at the required temperature. The temperature was maintained in a thermostat water bath at (+/-) 0.1 °C of desired value.

Kinetic experiments were performed under pseudo-first order conditions employing 10-fold (or greater) excess of amino acid over CAT. Duplicate kinetic runs showed that the rates were reproducible to within (+/-) 5%. The pseudo-first order rate constant $K_{obs}(S^{-1})$ was computed from the linear ($r > 0.980$) least square plot of log R versus time (where R is the micro burette reading). Requisite amount of amino acid, hydrochloric acid and potassium iodide were taken in a conical flask and measured amount of CAT solution was taken in another flask. The two flask were thermally equilibrated for 15 mins in the thermo stated water bath. Then CAT solution was added to flask containing amino acid solution and was mixed thoroughly by shaking. The progress of the reaction was followed by measuring the unreacted CAT (by iodometrically method) in a measured aliquot (10 ml) of the reaction mixture at various time intervals. The reaction was studied up to 80% consumption of CAT

Table 1
Effect of concentration of Lysine on the observed rate constant (kobs)

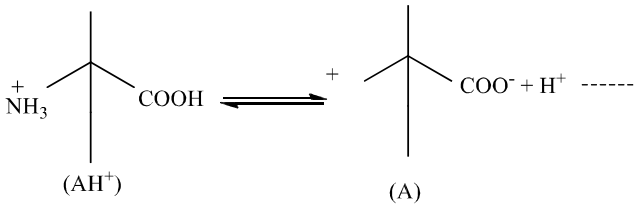
Conc. Temp.	*0.02M*	*0.04M*	*0.06M*	*0.08M*	*0.10M*
30°C	1.5×10^{-3}	2.57×10^{-3}	3.75×10^{-3}	5.30×10^{-3}	6.95×10^{-3}
35°C	2.10×10^{-3}	3.50×10^{-3}	4.10×10^{-3}	5.60×10^{-3}	7.2×10^{-3}
40 °C	3.15×10^{-3}	4.2×10^{-3}	5×10^{-3}	6.5×10^{-3}	10.8×10^{-3}

Table 2
Effect of concentration of [H⁺] on the observed rate constant (kobs)

Conc. Temp.	*0.05M*	*0.10M*	*0.15M*	*0.20M*
30°C	4.68×10^{-3}	3.90×10^{-3}	2.50×10^{-3}	1.5×10^{-3}
35°C	6.66×10^{-3}	4.50×10^{-3}	2.70×10^{-3}	1.75×10^{-3}
40 °C	10.15×10^{-3}	8.75×10^{-3}	6.2×10^{-3}	3.5×10^{-3}

REACTION MECHANISM

The oxidative decarboxylation of amino acids has raised several interesting questions. Some authors have suggested that amino group is the most likely reactive site but other have favoured attack at the carboxylic group. In certain cases protonated amino group has been proposed as the active site. It is reasonable to assume that the oxidant attack requiring withdrawal of electron from the protonated amino acid is completely protonated.



Under this condition the oxidant attack at the carboxylic group may be favored. The oxidant, sodium N-chloro-p-toluenesulphonamide may also produce a large number of oxidizing species such as, HOCl, Cl2 and H2OCl. However, it has been shown that at low pH, the principal species present in the acidic medium are RNHCl and RNCl involved in the equilibrium.

$$RNHCl \rightleftharpoons RN^{-}Cl + H^{+}$$

In view of the above following mechanism for oxidative decarboxylation of lysine may be proposed as:

$$AH^{+} \overset{K_A}{\rightleftharpoons} A + H^{+} \quad (1)$$

$$OXH \overset{K_O}{\rightleftharpoons} OX^{-} + H^{+} \quad (2)$$

$$A + OXH \xrightarrow{k_1} \quad (3)$$

$$A + OX^{-} \xrightarrow{k_2} \quad (4)$$

$$AH^{+} + OXH \xrightarrow{k_3} \quad (5)$$

$$AH^{+} + OX \xrightarrow{k_4} \quad (6)$$

K_A and K_O may be defined as

$$K_A = \frac{[A][H]^{+}}{[AH^{+}]} \text{ and } K_O = \frac{[OX^{-}]}{[OXH]}$$

Using the mass –balanced equation for the amino acid concentration, [A] and [AH^{+}] may be expressed in terms of $[A]_o$ as below:

$$[A]_o = [A] + [AH^{+}]$$

$$= [A] + \frac{[A][H^{+}]}{K_A}$$

$$[A]_o = \frac{[A]}{K_A}\left(K_A + [H^{+}]\right) \quad (7)$$

Also for $[AH^+]$, we get

$$[A]_o = [A] + [AH^+]$$

$$= \frac{K_A[AH^+]}{H^+} + [AH^+]$$

$$= \frac{[AH^+]}{H^+}(K_A + [H^+]) \quad (8)$$

Similarly using the mass balanced for the oxidant concentration [OX] and [OXH] may be obtained as

$$[OX]_T = [OX^-] + [OXH]$$

$$= \frac{[OX^-]}{K_o}(K_o + [H^+]) \quad (9)$$

Also $$= \frac{K_{O[OXH]}}{H^+} + [OXH]$$

$$= \frac{[OXH]}{H^+}(K_O + [H^+]) \quad (10)$$

Reaction rate = $(k_1\ [OXH] + k_2\ [OX])[A] + (k_3\ [OXH] + k_4\ [OX]\ [AH^+]$ (11)

Simplifying the product,

$$(K_A + [H^+])(K_o + [H^+]) = K_A K_o + (K_A + K_o)[H^+] + [H^+]^2$$
$$= (K_o + K_o)\ [H^+]$$

Assuming that $[H^+]^2$ term is negligible and $K_A K_o << 1$

Reaction rate = $(k_1[H^+] + k_2K_o)\frac{K_A[A]o[OX]T}{(K_A + K_o)[H^+]} +$

$$\left[(k_3[H^+] + k_4K_o)\frac{[A]o[A^+][OX]T}{(K_A + K_o)[H^+]}\right]$$

$$= \left(\frac{(k_1K_A + k_2K_AK_o)}{k_3[H^+] + k_4K_o}\right)\frac{[A]o[OX]T}{(K_A + K_o)}$$

Assuming $k_3 << 1$

Reaction rate =

$$\left\{\frac{k_1K_A + k_4K_o}{(K_A + K_o)} + \frac{k_2K_AK_o}{(K_A + K_o)}.\frac{1}{[H^+]}\right\}[A]o[OX]_T \quad (12)$$

$$= k_{obs}\,[OX]_T$$

$$= k[A]_o\,[OX]_T$$

Where

$$k_{obs} = \left\{\frac{k_1K_A + k_4K_o}{(K_A + K_o)} + \frac{k_2K_AK_o}{(K_A + K_o)}.\frac{1}{[H^+]}\right\}[A]_o \quad (13)$$

$$= \left\{1_{k_H} + 2_{k_H}\frac{1}{[H^+]}\right\} \quad (14)$$

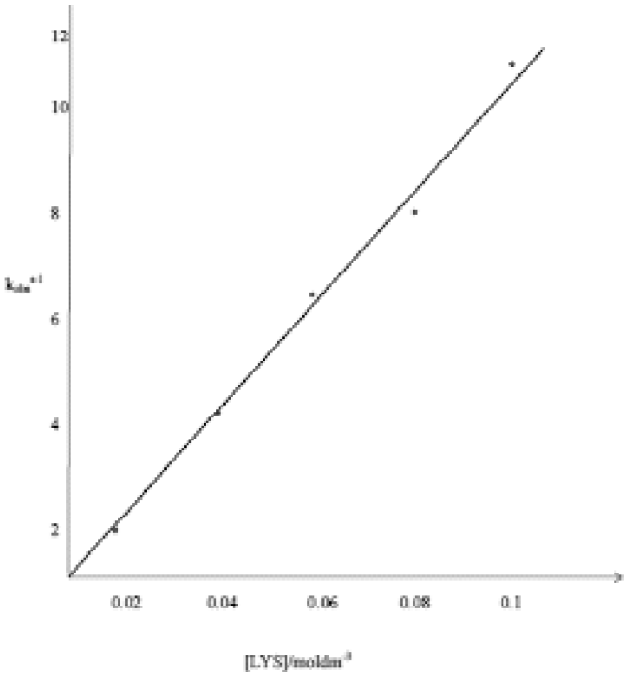
Where

$$^1k_H = \frac{k_1K_A + k_4K_o}{(K_A + K_o)}$$

$$^2k_H = \frac{k_1K_AK_o}{(K_A + K_o)}$$

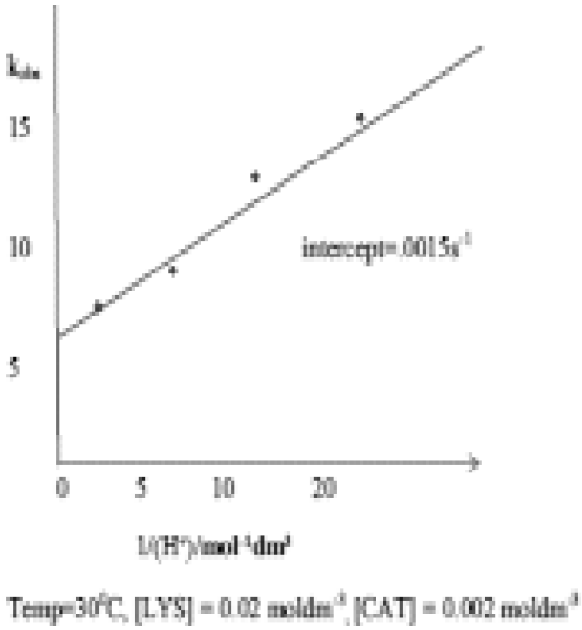
The first order observed rate k_{obs} have been obtained from the plots of log R vs time where R is the titration value at time under different conditions of hydrogen ion concentration and temperature.

The plot kobs versus [A]0 are found to be linear passing through origin under all conditions by equation (13). The plot of k_{obs} vs $1/[H^+]$ are found to be linear giving a positive intercept represented by equation (14).



Temp=30°C, $[H^+]$= 0.05 moldm^{-3}, [CAT]=0.002 moldm^{-3}

Fig : Plot of kobs vs [LYS]



References

[1] Rajashekhar, C. Hiramath, Sanabaghatta, M. Mayannaand Nagaswami Venkatasubramanian Bull. Chem.Soc. Perkin Tarns 11, 1569 (1987).

[2] a) M.S Ramachandaran, D. Easwaramoorthy, V.Rajasingh and T.S Vivekarandam, Bull. chem.soc. of Japan, 63, 2397.

[3] M.S Ramachandram T.S vivekanandam, J.chem. Soc. Perkin Trans, 1341.

[4] Ramachandram, M.S T.S Vivekanandam, and Raj R.P.M.M.

[5] Metzler, D.E; Ikawa M. and Snell, E.E J. Am. Chem. Soc, 637, 648, (1954).

[6] Mahadevappa, D. S, Rangappa, K. S; Gowda, N. M. M. and Gowda, B.T, J. Phys.chem, 85, 3651.

[7] Gowda, B.T and Sherigara, B.S; J. Chem. Soc.61, 158(1987).

b)Anupama Agarwal, Suman Mittal and Kalyan K. Banerji, Indian J. chem., 26A, 339 (1988).

[8] F. G Mann and W.J Pape, J. chemSoc., 1052(1992).

[9] S. Tamagaki, S.Oae, and K.Sakaki, Tetrahendron Lett., 649 (1969).

[10] D.C arr, T.P. Saden, S.Oae and R.W Turner, Tetrahedran Lett., 649 (649).

[11] N. Furukka, T. Ommata, and S.oae, chem. commun, 590 (1973).

[12] W.V Furrar and masson Gulland, J.chem.Soc., 368 (1944).

[13] A. Sochenberg, and E.Singer, and W. Knofel, Tetrahedran Lett., 1819.

[14] A. Schoenbarg, E.Singer, chem. Ber., 101, 3445(1968).

[15] H. D Dakin, Biochem. J. 10, 319(1916).

[16] G. Shiemannand p.Navok, Angew. chem. 40.1032(1968).

[17] K Weber and Valic, Z. phys.chem., 239, 24 (1968).

[18] S.P Mushram, M.C Agarwal and B.Prasad, J.chem. Soc. B., 1712(1971).

[19] S. D. Mahadevappa and H.M.K. Naidu, Talanta, 20, 349, (1973).

[20] S.P Mushram, R.M Mehorata, and R.Sanehi, Proc, Natl. Acad. Sci., India Sect. A., 43, 105, (1973).

[21] D.S. Mahadevappa and H.M.K Naidu, Aust.J. chem.., 27, 1203, (1907).

[22] S.P Mushran, K.C Gupta, and R. Sanehi, J.chem Soc. perkin Trans. 2, 1590 (1974).

[23] R. Sanehal, M.C.Agarwal and S.P Mushran, Indian J. chem., 311 (1972).

[24] M.CAgarwal and S.P. Mushran, Z. Naturforsch, Teil B., 27, 401 (1972).

[25] B. Singh, A.Singh, and M.Singh, Res.Bull. East Punjab Univ., No. 30, 55(1953).

[26] S. P. Mushran, R.M Maharotra, and R. Sanehi, J. Indian chem. Soc., 51, 594, (1974).

[27] S. P. Mushran and M.C Agarwal, J.chem. Soc.Perkin Trans. 2, 762 (1973).

[28] R. Sanehi, K.C Gupta, R.Meharotra, and S.P Mushran, Bull. chem. Soc. Jpn; 48, 330 (1975).

[29] T. Higuchi and A. Hussain, J.chem. Soc. B., 549 (1973).

[30] F. E Hardy and J.P. Johnson, J. chem. Soc. Perkin Trans. 2, 742 (1973).

[31] J.M. Antelo. J. M. Cahazo, J. Casado, M.A Harraez, An. Quim., 70, (1974); Chem. Abstr., 82, 72315 X (1975).

[32] V. Balasbramanianand V. Thiagarajan, Int. J.chem. Kinet., 7, 605 (1975).

[33] Steve Reiber, Rubber World, 210 (3), 38 (1994).

[34] Anwar A. Hussai, Janan A. Jona, Akihir Yamada and Lewis W. Ditter, Anal.Biochem., 224, 211, (1995).

[35] Hussain, Anwar A., Awad, Raid, Crookes, Peter A. and Ditter, Lewis W., Anal.Biochem., 214, 495(1993).

[36] Satyanarayana, M.V., Sundar, B. Syama and Murti, P.S. Radhakrishnan, J.Inst.chem. (India), 65, 58, (1993).

[37] Saxena, Rashmi, Asian j. chem.6, 81, (1994).

[38] Li, Jixin; Shao, Yili and Lilu, Guojun, Yankuang, Ceshi, 12, 11, (1993).

[39] Thapak, T.R.; Chaturved, A.M.; Sharma, Vibha and Solanki, S.K., Orient.J.chem., 9 (1993).

[40] Rangappa, KanchugarkoppalS.andEasterline, Daniel T., Pilyhedron 12, 1719 (1993).

[41] Chaturvedi, A.M.; Thapak, T.R, and Solanki, S.K, Orient. J. chem., 9, 377(1993).

[42] Gowda, B. T and VijayaLaxmiRao, R; Indian J. chem., 27A, 39 (1988).