Kinetic Studies in the Mechanism of Oxidation of Glycine by Chloramine-T in Micellar System

Y.R. KATRE*, S.K. SOLANKI, SANGEETA PATIL and GHANAT K. JOSHI
Department of Chemistry, Kalyan Mahavidyalaya, Bhilai Nagar-490 006, India
E-mail: kumjps_gha@yahoo.co.in

The kinetic investigation of the oxidation of glycine by chloramine-T has been made in the presence of anionic surfactant *i.e.*, sodium dodecyl sulphate (NaDS) at 313 K. The rate shows first order dependence on the oxidant but is fractional order with glycine. Increase in the concentration of NaDS inhibits the reaction rate. Various activation parameters have been calculated.

Key Words: Kinetic, Oxidation, Glycine, Chloramine-T, Micellar system, Anionic surfactant.

INTRODUCTION

The change in the rate of chemical reaction in presence of surfactant has provoked great interest during three decades, since the study of micellar catalyzed reactions might provide a basic model for the interpretation of some aspects of enzymatic catalysis[1-4].
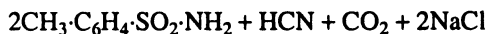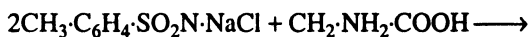
The literature survey shows that the kinetics of oxidation of amino acids have been reported by several workers[5-7]. But the study of the oxidation of glycine by Chloramine-T (CAT) in the micellar system has not been made so far. Presently, therefore, this problem has been undertaken to investigate the applicability of the Hill's model.

EXPERIMENTAL

All solutions were prepared in doubly distilled water and the chemicals used were of BDH and AR quality. Distilled acetic acid was used.

Stoichiometry of the Reaction

In the oxidation process one mole of glycine consumes two moles of chloramine-T (CAT) both in presence and in absence of the surfactant, for the required conditions.

$$2CH_3 \cdot C_6H_4 \cdot SO_2N \cdot NaCl + CH_2 \cdot NH_2 \cdot COOH \longrightarrow$$

$$2CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + HCN + CO_2 + 2NaCl$$

The product HCN is hydrolyzed to HCOOH which was identified and tested.

RESULTS AND DISCUSSION

(a) Dependence of rate on [CAT] and [glycine]: The plot of log (a − x) *vs.* time for variation of CAT concentration shows that parallel lines are obtained. This indicates that the order of reaction with respect to CAT is first order, while the reaction has fractional order with respect to glycine concentration.

TABLE-1

[NaDS] = 3.0×10^{-3} mol dm^{-3};   [AcOH] = 20% (v/v);   Temperature = 313 K

10^3 [CAT] mol dm^{-3}	10^2 [glycine] mol dm^{-3}	k × 10^2 min^{-1}
0.5	2.0	2.044
1.0	2.0	2.016
2.0	2.0	1.973
2.5	2.0	1.974
3.0	2.0	2.038
2.0	0.5	1.303
2.0	1.0	1.576
2.0	1.5	1.728
2.0	2.0	1.973
2.0	3.0	2.180

(b) Dependence of rate on surfactant concentration: The reaction was studied at different concentrations of the surfactant (0.5×10^{-3} to 3×10^{-3} mol dm^{-3}). It is observed that, with the increase of surfactant concentraction, rate constant value first decreases and then slight enhancement of the rate may be due to the increase in concentration of organic substrate and ionic reactant in the stern layer of micelles[8] (Fig. 1). The graphical plot of log $\left[\dfrac{k_\psi - k_w}{k_m - k_\psi}\right]$ *vs.* log [D] is a

Surfactant Variation
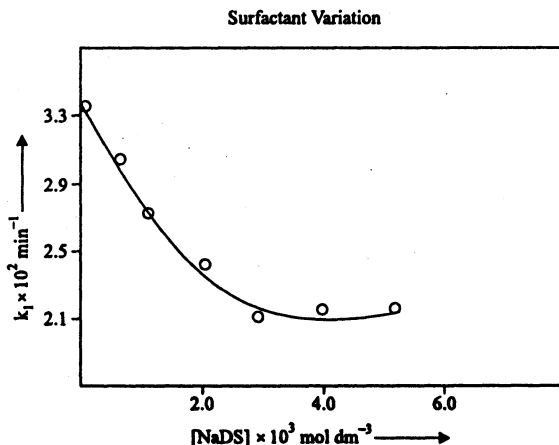
Fig. 1.   Plot of k_1 *vs.* [NaDS]

straight line (Fig. 2) and from it the index of cooperativity and k_D value is obtained. k_D value found is 6.9×10^{-2} M, which is consistent with the other case of similar type of behaviour.
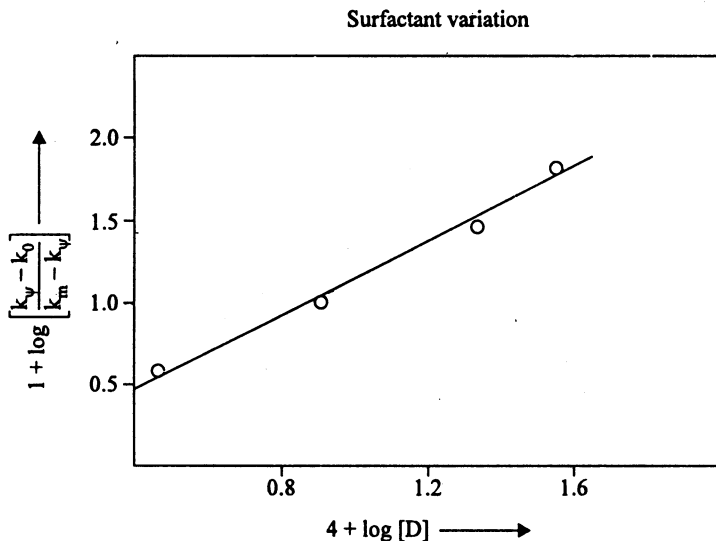
Surfactant variation

Fig. 2.   Plot of log $\left[\dfrac{k_\psi - k_0}{k_m - k_\psi}\right]$ vs. log [D]

(c) Effect of variation of acetic acid concentration: It has been observed that the rate constant decreases with the increase in concentration of acetic acid.

(d) Effect of scavenger salt: Scavenger salt concentration variation indicates that there is acceleration of the reaction velocity with the increase of scavenger concentration. This may be due to the complex formation tendency of Hg^{2+} ion.

(e) Solvent effect: On increasing the percentage of solvent (methanol) concentration, the value of rate constant is also increased.

(f) Effect of temperature: The reaction has been studied at different temperatures and the kinetic parameters have been calculated (Table-2).
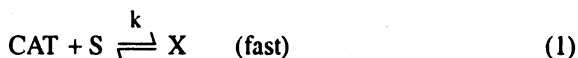
TABLE-2
ACTIVATION PARAMETERS

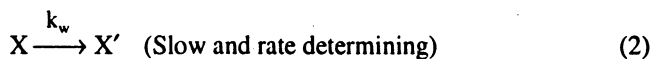| ΔE_a (kJ mol^{-1})	p_z (dm^3 mol^{-1} min^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
59.61	1.73×10^{10}	−49.34	57.00	72.45

The activation parameters clearly exhibit the behaviour of anionic surfactant in acidic medium. The negative value of entropy of activation shows that the decomposition of activation complex is a quite slow process.

(g) Reaction mechanism: On the basis of experimental results and findings the given probable reaction mechanism has been suggested as follows: As in this case, oxidation proceeds by both the paths, *i.e.*, in absence and presence of the surfactant, hence it can be expressed as:

Case I: In absence of the surfactant:

$$CAT + S \overset{k}{\rightleftharpoons} X \quad \text{(fast)} \tag{1}$$

where S is the substrate (amino acid)

$$X \overset{k_w}{\longrightarrow} X' \quad \text{(Slow and rate determining)} \tag{2}$$

$$\overset{OR}{X + X_1 \rightleftharpoons X_1'} \tag{2a}$$

where X_1' is the halide ion.

$$X' + n \, CAT \longrightarrow Products \quad \text{(fast)} \tag{3}$$

where n is the number of moles of CAT.
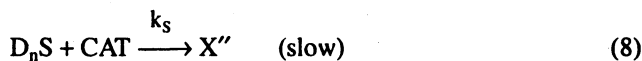
Therefore the rate of the reaction is:

$$-\frac{d[CAT]}{dt} = k_1[X] \tag{4}$$

On substitution, we have the equation

$$-\frac{d[CAT]}{dt} = \frac{k_w K[CAT][S]}{1 + K[S]} \tag{5}$$

Case II: In presence of the surfactant:

$$nD \rightleftharpoons D_n \tag{6}$$

$$D_n + S \overset{K_D}{\rightleftharpoons} D_n S \tag{7}$$

$$D_n S + CAT \overset{k_S}{\longrightarrow} X'' \quad \text{(slow)} \tag{8}$$

$$X'' + n \, CAT \longrightarrow Products \quad \text{(fast)} \tag{9}$$

The total rate of the reaction can be shown by

$$-\frac{d[CAT]}{dt} = \frac{k_w K[S][CAT]}{1 + K[S]} + \Sigma k_S[D_n S][CAT] \tag{10}$$

By taking the approximation, the rate can be shown as:

$$-\frac{d[CAT]}{dt} = k_w[S][CAT] + \Sigma k_S[D_n S][CAT] \tag{10a}$$

$$= k_w\{[S]_0 - \Sigma[D_n S]\}[CAT] + \Sigma k_S[D_n S][CAT] \tag{10b}$$

where $[D_nS]$ is the concentration of substrate associated with micelle and k_S is the rate constant in presence of micelle.

From equation (7),

$$K_D = \frac{[D_nS]}{\{[S]_0 - [D_nS]\}[D_n]_0} \qquad (11)$$

Therefore,

$$[D_nS] = \frac{K_D[D_n]_0[S]_0}{K_D[D_n]_0 + 1} \qquad (12)$$

or

$$\frac{[D_nS]}{[S]_0} = f_c = \frac{K_D[D_n]_0}{K_D[D_n]_0 + 1} \qquad (13)$$

From equation (10b), we have the form

$$-\frac{d[CAT]}{dt} \cdot \frac{1}{[CAT][S]} = k_{obs} = k_W(1 - f_C) + k_S f_C \qquad (14)$$

By combining the equations (13) and (14),

$$k_{obs} = k_W - k_W f_C + k_S f_C \qquad (15)$$

Hence

$$k_{obs} - k_W = (k_S - k_W)f_C \qquad (16)$$

$$= (k_S - k_W)\frac{K_D[D_n]}{K_D[D_n] + 1} \qquad (17)$$

or

$$k_{obs} = k_W + \frac{(k_S - k_W)K_D[D_n]}{1 + K_D[D_n]} \qquad (18)$$

$$k_{obs} = \frac{k_W + k_S K_D[D_n]}{1 + K_D[D_n]} \qquad (19)$$

The last expression is overall rate expression, which is applicable to both absence and presence of the surfactant.

The rate constant k_{obs} can be shown by

$$k_{obs} = -\frac{d[CAT]}{dt} \cdot \frac{1}{[CAT]} = \frac{2.303}{t} \cdot \log\frac{a}{(a - x)} \qquad (20)$$

or

$$k_{obs} = -\frac{d[CAT]\{1 + K[S]\}}{dt\, K[CAT][S]} \simeq \frac{-d[CAT]\, K[S]}{dt\, K[S][CAT]} \text{ when } 1 \ll K[S]$$

Hence substrate may have fractional order with respect to its concentration. The expressions (10) and (19) show that:

  (i) The order of reaction with respect to chloramine-T is one.

 (ii) The order of reaction with respect to substrate (amino acid) is fractional.

(iii) The expression (19) clearly indicates the rate dependency of reaction with respect to surfactant concentration.

(iv) The step (2a) in the reaction mechanism shows the dependency of reaction rate on halide (chloride) ion concentration.

REFERENCES

1. E.J. Fendler and J.H. Fendler, *Adv. Phy. Org. Chem.*, **8**, 271 (1970).
2. F.J. Fendler and J.H. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York (1975).
3. F.H. Cordes (Ed.), Reaction kinetics in Micelles, Plenum Press. New York (1973).
4. K.L. Mittal, Micellization, Solubilization and Microemulsions, Plenum Press, New York, Vol. 2 (1977).
5. N. Grover, N. Kambo, Upadhyay and K. Santosh, *Indian J. Chem*, **41A**, 2482 (2002).
6. V. Nagar, S.K. Solanki and V.R. Shastry, *Orient. J. Chem.*, **5**, 336 (1989).
7. M. James, Practical Physical Chemistry J.A. Churchill Ltd., London (1967).
8. F.J. Fendler, C.L. Day and J.H. Fendler, *Phys. Chem.*, **76**, 1460 (1972).

DESCRIPTION THE THIRD IASTED INTERNATIONAL CONFERENCE ON BIOMEDICAL ENGINEERING (BioMED 2005)

16–18 FEBRUARY 2005

Contact:
IASTED Secretariat BioMED 2005
#80, 4500-16th Avenue N.W.
Calgary, Alberta
Canada T3B 0M6
Tel: 403-288-1195; Fax: 403-247-6851
E-mail: calgary@iasted.org
Website: http://www.iasted.org