KINETICS STUDIES ON THE MECHANISM OF THE RELATIVE CATALYTIC ACTIVITIES OF SURFACTANTS IN THE OXIDATION OF AMINO ACIDS BY CHLORAMINE–T

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ABSTRACT

The kinetics of oxidation of amino acids by chloramine–T in the presence of two different surfactants (anionic and cationic surfactants) has been studied. The kinetic results show that the reaction is fractional and first order with respect to substrate and oxidant, respectively. The influence of halides, ionic strength and solvent on the rate has been studied. The effect of surfactants on the reaction show that the reaction velocity is highly sensitive to the variation of surfactant concentration. A probable reaction path has been suggested and discussed in the light of various experimental results and findings.

Key words : Oxidation, Chloramine–T, Surfactants.

INTRODUCTION

During last decade, the study of micelle undergone almost explosive growth particularly as an aid in synthesis and reaction control. The results clearly demonstrate that the micelles promote chemical reactivity by increasing the local reactant concentration. An appropriate kinetic analysis for surface reactions in micellar solution is developed and shown to offer a reasonable explanation. The present work on the influence of surfactants on the oxidation of amino acids by chloramine–T has been undertaken in an attempt to develop a kinetic model analogous to the Hill model describing enzymatic reactions[1–4].

MATERIALS AND METHOD

Cetyltrimethyl ammonium bromide (CTAB) (BDH) and sodium dodecyl sulphate (NaDS) (Loba chemle) were used after purification. Distilled acetic acid was used. Aqueous solution of alanine (Sarabhai chemical) and serine (BDH) were prepared and standardized. All solutions were prepared in double distilled water. The kinetic determination of the reactions rates was made using Ostwald's isolation method.

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RESULTS AND DISCUSSION

The relative catalytic activities of surfactant on the oxidation of amino acids by chloramine–T has been studied in the acidic medium.

$$2\ RNNaCl + R'CH\ NH_2COOH \longrightarrow 2\ RNH_2 + 2\ NaCl + CO_2 + R'CN$$

Where $R = CH_3C_6H_4SO_2$ $R' = CH_2OH$ (serine), CH_3 (alanine)

Dependence of rate on [CAT] and [amino acids]

When the amino acid is in large excess, plot of log (a – x) versus time are linear, indicating first order dependence on [CAT]. The reaction has fractional order with respect to substrate concentration.

Dependence of rate on the [Surfactant]

The reaction was studied at different concentrations of the surfactant (5.0 x 10^{-4} to 6.0 x 10^{-4} M) in the presence of NaDS and CTAB. The rate of reaction decreases with the increase in NaDS concentration. (Table–1), while the rate of reaction increases with increase in CTAB concentration and than it decreases up to certain limit. This behaviour is in accordance with the miceller catalysis of organic reaction of anion neutral molecular type. The inhibition by NaDS may be due to increasing concentration of unreactive counter ions and increasing affinity of unreactive counter ions for the Stern layer. Since there is a possibility of competition between reactive and nonreactive ions for sites in the Stern layer, the rate of reaction decreases (Fig. 1).
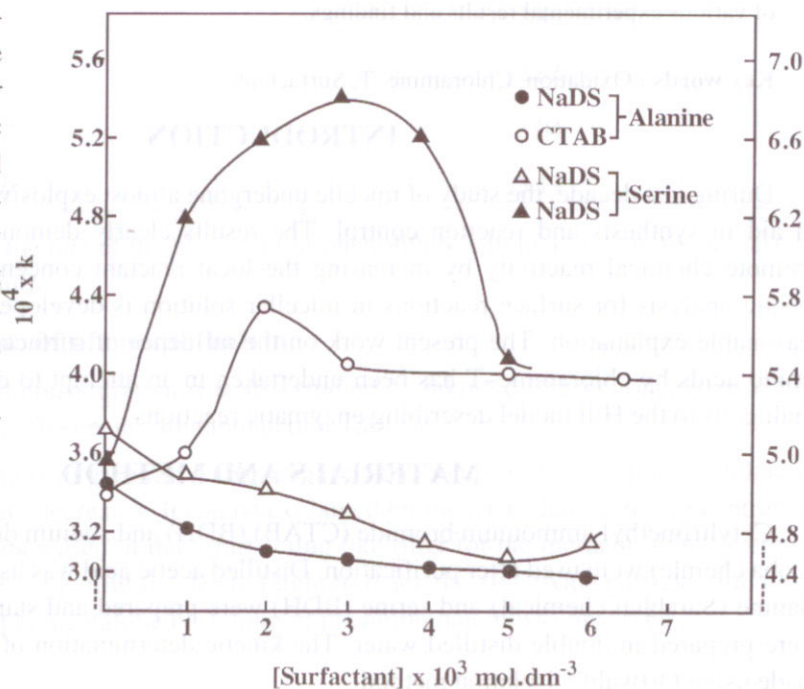

Fig. 1

Table 1. Effect of surfactant concentration on rate of oxidation of amino acids by CAT.

[Surfactant] x 10^3 M	10^4 x k (sec^{-1})		10^4 x k (sec^{-1})	
	NaDS^a	CTABa	NaDS^b	CTAB^b
0.0	3.42	3.40	5.12	5.0
1.0	3.24	3.60	4.90	6.20
2.0	3.13	4.37	4.82	6.60
3.0	3.09	4.05	4.70	6.80
4.0	3.04	4.04	4.59	6.60
5.0	3.02	4.02	4.44	5.45
6.0	2.90	3.95	4.59	–

(a) Alanine (b) Serine $[CAT] = 6.0 \times 10^{-3}$ M   [Amino acid] $= 3.0 \times 10^{-2}$ M

pH = 5.5   Temperature = 303 K

Effect of other parameters

(i) **Halides** – Addition of chloride ions to the reaction mixture has no significant effect on the rate.

(ii) **Ionic Strength** – The rate is unaffected by an increase in the ionic strength of the medium.

(iii) **Temperature** – The reaction has been studied at 303 K and 313 K and the activation parameters have been evaluated in both the cases (Table 2).

The value of energy of activation shows that the reaction is more favorable in the presence of CTAB as compared to NaDS. The fairly high values of negative $\Delta S^{\#}$ and positive $\Delta H^{\#}$ in the case of oxidation of alanine and serine indicate the formation of more ordered activated complexes and that the transition state is highly solvated[5].

Table 2. Activation parameters of amino acids

	In presence of NaDS				In presence of CTAB			
	Alanine		Serine		Alanine		Serine	
Temperature (K)	303	313	303	313	303	313	303	313
Rate constant k x 10^4 sec.$^{-1}$	3.24	6.94	4.91	8.98	4.05	8.45	6.60	11.32
E_a KJ	60.03		47.58		57.96		42.51	
P_z x 10^{10} Lit. mol^{-1} sec^{-1}	7.29		0.79		4.01		0.13	
$\Delta H^{\#}$ KJ mole^{-1}	23.84		18.89		23.02		16.88	
$\Delta S^{\#}$ J mole^{-1} K^{-1}	−9.78		−14.20		−10.97		−17.62	
$\Delta G^{\#}$ KJ mole^{-1}	20.88		15.59		19.696		11.53	

Reaction Mechanism

On the basis of experimental results, a tentative mechanism has been suggested as follows:

As we know in this case that the oxidation proceeds by both the paths, i.e. in absence and presence of the surfactant. Hence, we can express–

Case I : In absence of the surfactant

$$CAT + S \xrightleftharpoons[(fast)]{K} X \qquad \qquad ...(1)$$

Where S is the substrate (amino acid)

$$X \longrightarrow X' \qquad \qquad ...(2)$$

(Slow and rate determining)

$$X + X_1 \xrightleftharpoons{OR} X_1' \qquad \qquad ...(2a)$$

where X_1' is the halide ion.

$$X' + n\,CAT \xrightarrow[fast]{} Products \qquad \qquad ...(3)$$

where n is the number of moles of CAT.

Therefore, the rate of the reaction is –

$$-\frac{d\,[CAT]}{dt} = k_1\,[X] \qquad \qquad ...(4)$$

on substitution, we have the equation

$$-\frac{d\,[CAT]}{dt} = \frac{k_w\,K\,[CAT]\,[S]}{1 + K\,[S]} \qquad \qquad ...(5)$$

Case II : In presence of the surfactant

$$nD \rightleftharpoons D_n \qquad \qquad ...(6)$$

$$D_n + S \xrightleftharpoons{K_D} D_n.S \qquad \qquad ...(7)$$

$$D_n.S + CAT \xrightarrow[slow]{k_s} X^n \qquad \qquad ...(8)$$

$$X^n + n\,CAT \xrightarrow[fast]{} Products \qquad \qquad ...(9)$$

The total rate of the reaction can be shown by

$$-\frac{d\,[CAT]}{dt} = \frac{k_w\,K\,[S]\,[CAT]}{1+K\,[S]} + \Sigma\,k_s\,[D_n\,S]\,[CAT] \qquad ...(10)$$

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

$$-\frac{d\,[CAT]}{dt} = k_w\,[S]\,[CAT] + \Sigma\,k_s\,[D_n\,S]\,[CAT] \qquad ...(10a)$$

$$= k_w\,\{[S]_0 - \Sigma\,[D_n\,S]\}\,[CAT] + \Sigma\,k_s\,[D_n\,.\,S][CAT] \qquad ...(10b)$$

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) –

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

Therefore,

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

or $\qquad \dfrac{[D_n\,S]}{[S]_0} = f_c = \dfrac{K_D\,[D_n]_0}{K_D\,[D_n]_0 + 1} \qquad ...(13)$

From education (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 $\qquad k_{obs} = k_w + \dfrac{(k_s - k_w)\,K_D\,[D_n]}{1 + K_D\,[D_n]} \qquad ...(18)$

$$k_{obs} = \frac{k_w + k_s K_D [D_n]}{1 + K_D [D_n]} \qquad \qquad ...(19)$$

The last expression is overall rate expression, which is applicable to both; in 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 $\qquad k_{obs} = -\frac{d [CAT] \{1 + K[S]\}}{dt \quad K [CAT] [S]} \simeq \frac{-d [CAT] K [S]}{dt \, K[S] [CAT]} \quad \begin{array}{l} \text{when} \\ 1 \ll K[S] \end{array} \qquad ...(21)$

Hence, substrate may have fractional order w.r.t. its concentration.

The expressions number (10) and (19) show that –

(i)   The order of reaction with respect to CAT is one.

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

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

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

REFERENCES

1.   W. Tonellato, "Solution Chemistry of Surfactants", K. Mittal, Ed., New York, Science Series, **2**, (1979). p. 541

2.   R. Fornasier, and U. Tonellato, J. Chem. Soc., Faraday 1, **76**, 1301 (1980).

3.   S. N. Katgeri, D. S. Mahadevappa and H. M. K. Naidu, Indian J. Chem. A, **19**, 19 (1980).

4.   Neeti Grover, Neetu Kambo, Upadhyay and K. Santosh, Indian J. Chem. Sect. A, **41**, 2482 (2002).

5.   D. S. Mahadevappa, S. Anand, M. B. Nadegawads and K. B. Rangappa, J. Indian Chem. Soc., **61**, 323 (1984).