Asian Journal of Chemistry Vol. 2, No. 2 (1990), 122–126

Kinetic and Mechanistic Studies in the Oxidation of L-Leucine by Chloramine-T in the Micellar System

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The kinetic investigations of the oxidation of L-leucine by chloramine-T in the presence of cationic surfactant i.e. cetyl trimethylammonium bromide (CTAB) have been conducted at 30°C. The rate constants increase initially and then decreases with the increasing concentration of CTAB. The micellebinding constant (K) and co-operativity index (n) have been calculated. The effects of halide ions, scavenger salt, solvent and ionic strength on the reaction rate have been studied. The reactions were studied at different temperatures and the values of activation parameters have been calculated.

INTRODUCTION

It is well known that the rates of chemical reactions are modified by the presence of micellar catalysis has provoked a great interest during last two decades, since the study of micelle catalyzed reactions might provide a basic model for the interpretation of some aspects of enzymatic catalysis[1-4].

The survey of literature shows that the kinetics of oxidation of L-amino acids have been reported by several workers[5]. But the study of the oxidation of amino acid (L-leucine) by 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 model.

RESULTS AND DISCUSSIONS

The kinetics of oxidation of leucine by CAT have been studied in the presence of cationic surfactant (CTAB) in the acidic medium.

(A) Dependence of rate on [CAT] and [Leucine]

When the amino acid is in large excess, plots of log (a-x) vs time is found to be linear, indicating first order dependence on [CAT]. The pseudo first order rate constants in chloramine-T calculated at different initial concentrations of the reactants are found to be independent of the substrate concentrations. Hence the reaction has fractional order with respect to amino acid concentrations (Table 1).

(B) Dependence of rate on surfactant concentration

The reaction was studied at different concentration of the surfactant (1.0×10^{-4} to 4.0×10^{-4}M). It has been observed that the reaction rate increases initially with the increase of surfactant concentration and then

TABLE 1

[CTAB]-2.0 × 10^{-5}Mol dm^{-3}, [$HClO_4$]-.02M, ACOH-15%(V/V)
Temperature-30°C

10^3 CAT mol dm^{-3}	10^2 (leucine) mol dm^{-3}	k × 10^{-3} min^{-1}
0.5	1.0	10.41
1.0	1.0	9.82
1.5	1.0	9.80
2.0	1.0	9.52
2.5	1.0	9.65
3.0	1.0	9.70
2.0	1.5	9.36
2.0	2.0	9.41
2.0	2.5	9.52
2.0	3.0	9.43
2.0	3.5	9.80

decreases upto certain limit. (Fig. 1). This behaviour is in accordance with the micellar catalysis of organic reactions of anion-neutral molecular type. With increasing concentration of CTAB the relative concentrations of organic substrate and ionic reactant in the stern layer of the micelle increases quite rapidly[6]. The acceleration of rate beyond 2.0 × 10^{-5}M

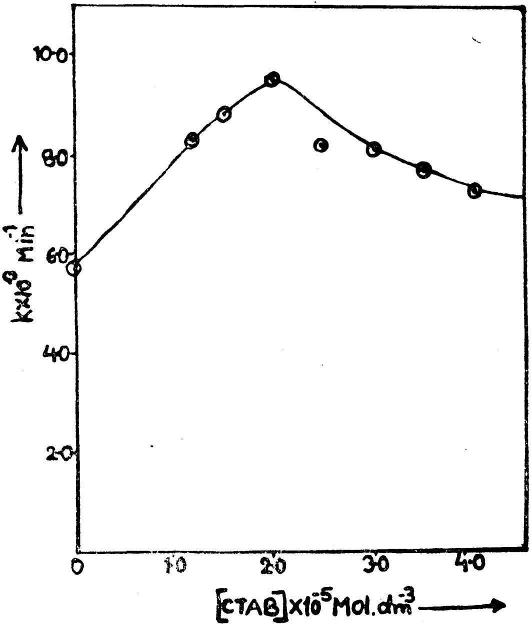

Fig. 1. Dependence of rate on detergent concentration

CTAB, may be due to the possibility of competition between reactive and unreactive ions for sites in the stern layer.

(C) Influence of the solvent

The rate of oxidation of leucine is affected by varying the concentration of solvent (methanol). It is observed that reaction rate decreases with the increase of the solvent concentration (Table 2). This may be due to the possible interaction of negative ion and a dipole interaction.[7]

TABLE 2

[CAT]-2.0 × 10^{-3} Mol dm^{-3}, [Leucine]-1.0 × 10^{-2} Mol dm^{-3}, ACOH-15% (V/V), [$HClO_b$]-.02 M, [CTAB]-2.0 × 10^{-5} Mol dm^{-3}

Methanol %	$k \times 10^{-3}$ min^{-1}
1%	10.00
5%	8.53
10%	7.54
20%	6.41

TABLE 3

ARRHENIUS DATA

	(a)	(b)
E_a K Cal mol^{-1}	26.23	47.68
$\Delta H^{\neq}$ K Cal mol^{-1}	23.21	16.93
$\Delta S^{\neq}$ K Cal mol^{-1}	−48.05	−32.17

(a) In the presence of CTAB, (b) In the absence of CTAB.

Theoretical treatment of micellar data

The effect of changing the reaction medium from an aqueous to a micellar phase does not significantly affect the activity of a cationic function: enhancement of its nucleophilic properties due to desolvation is apparently not relevant. This is surprising since the properties of the stern layer, in terms of dielectric constant and solvation capability, would have suggested higher rates in the micellar than in the aqueous medium.

The micellar catalysis or inhibition could be applied theoretically by making certain simplifications and assuming that only one substrate is incorporated into a micelle and that the aggregation number N of the micelle is independent of the substrate[8]. On the basis of these concepts, the following scheme is proposed.

$$\begin{tikzcd} \mathrm{Dn + S} \arrow[rr, shift left, "K"] \arrow[dr, "ko"'] & & \mathrm{DnS} \arrow[ll, shift left] \arrow[dl, "km"] \\ & \mathrm{Products} & \end{tikzcd}$$

Scheme 1

The concentration of micelles, Dn is given by

$$[\mathrm{Dn}] = \frac{\mathrm{C_D} - \mathrm{CMC}}{\mathrm{N}} \tag{1}$$

Where $\mathrm{C_D}$ is the stoichiometric concentration of the detergent. For a system where catalysis is observed at detergent concentration close to CMC, the scheme 1 provides an equation of the form

$$\frac{k_{\mathrm{obs}} - k_0}{k_m - k_{\mathrm{obs}}} = \mathrm{K}(\mathrm{C_D} - \mathrm{CMC})/\mathrm{N} \tag{2}$$

From the above equation the plot of $\frac{k_{\mathrm{obs}} - k_0}{k_m - k_{\mathrm{obs}}}$ versus ($\mathrm{C_D}$ — CMC) is linear in the present case, and the value of binding constant K/N calculated is 13×10^{-4}M. Equation (2) shows that no catalysis is expected below CMC, however the results show catalysis below the reported CMC (2.0×10^{-5}M in acidic medium) for CTAB; indicating that the substrate promotes micellisation of the cationic surfactant or there may be a possibility of existance of the small aggregation of micelles which catalyse the oxidation. At higher surfactant concentration two possible molecular mechanisms have been proposed. The first mechanism states that with increasing surfactant, the counterions also increases, thereby inhibiting the approach of ionic reagents. According to the second mechanism—once sufficient surfactant is available for all the substrates, further addition of surfactant deactivates ionic reactants as a result the velocity of reaction decreases. This is to say that ionic reactants are attracted by micellar surfaces which does not contain any substrate with a consequent dimunition of these at the surface which contain substrate.

The catalysis by CTAB can also be explained alternatively by applying Piszpiwicz scheme[10]. According to this scheme the decomposition of substrate micelle complex into the free components resulting into an equation

$$\log \left[\frac{k_{\mathrm{obs}} - k_0}{k_m - k_{\mathrm{obs}}}\right] = \mathrm{n} \log [\mathrm{D}] - \log k_{\mathrm{D}} \tag{3}$$

From the above equation a graph of $\left[\frac{k_{\mathrm{ob_2}} - k_0}{k_m - k_{\mathrm{obs}}}\right]$ v/s log [D] is linear with a slope '*n*' called index of co-operativity. The value of *n* obtained in the present case is $n = 2.75$ indicating positive co-operativity, i.e. induced interaction of the additional substrate molecules due to the interaction of micelle with the first substrate molecule.

The models discussed in this paper conforms to the behaviour of micellar catalyzed reaction, therefore, appears to be analoguus to a Hills model for enzyme catalyzed reaction.

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[*Received*; 7 February 1989; *Accepted*: 30 August 1989] AJC-86

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