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Kinetics and Mechanism of Oxidation of L-Alanine by *N*-Bromophthalimide in the Presence of Sodium Dodecyl Sulfate[1]

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Abstract—The kinetics of oxidation of L-Alanine (Ala) by *N*-bromophthalimide (NBP) was studied in the presence of an anionic surfactant, sodium dodecyl sulfate, in acidic medium at 308 K. The rate of reaction was found to have first-order dependence on [NBP], fractional order dependence on [Ala] and inverse fractional order dependence on [H^+]. The addition of reduced product of the oxidant [Phthalimide] has decreased the rate of reaction. The rate of reaction increased with increase in inorganic salts concentration i.e., [Cl^-] and [Br^-], whereas a change in ionic strength of the medium and [$Hg(OAc)_2$] had no effect on oxidation velocity. The rate of reaction decreased with a decrease in dielectric constant of the medium. CH_3CN was identified as the main oxidation product of the reaction. The various activation parameters have been computed and suitable mechanism consistent with the experimental findings has also been proposed. The micelle-binding constant has been calculated.

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1. INTRODUCTION

Surfactants, which have hydrophilic and hydrophobic groups in structure, have unique properties and can form micelle at a certain concentration. The effects of surfactant and its micelle on chemical reactions are always an interesting field of research for chemists and biologists [1, 2]. Micelle catalyzed reactions had become an area of rapidly increasing interest and a number of extremely important thermodynamic and kinetic studies of organic reactions have been performed in micellar solutions. There is an extensive evidence on the ability of aqueous micelles and other associated colloids to influence the reaction rates, equilibria, concentration or depletion of reactants in the interfacial region [3–14]. Micellar catalysis and inhibition have received [15–22] considerable attention in view of analogies drawn between micellar and enzyme catalysis. Micellar effects on the rates are sensitive to the nature of counter ions and to head group bulk [23]. Transition of spherical to larger micelles may be caused by salt or surfactant additions [24] or solute solubilization [25]. It is well known that the addition of a salt decreases the electrostatic interactions between monomers in the micelle and also affects the partitioning of organic compounds between micelle and bulk solvent [26]. Micellar catalysis can be enhanced by adding some salts indicating that the rate enhancement is sensitive to changes in micellar morphology and charge density [27]. Amino acids are resistant to hydrolyzing agents and they do not react readily with reducing agents, but are very reactive with oxidizing agents in general [28–42]. Amino acids act not only as the building blocks in protein synthesis but also they play a significant role in metabolism. Amino acids can undergo many types of reaction depending on whether a particular amino acid contains non-polar groups or polar substituents. Ala is present in prostate fluid and it may play a role in supporting prostate health. It is a source of energy for muscle tissue [43], the brain and the central nervous system. It strengthens the immuno system by producing antibodies, helps in the metabolism of sugar and organic acids. Oxidative decarboxylation of alanine is one of the well-documented biochemical processes. The exact mechanism of the chemical process of oxidative decarboxylation of alanine is not well understood. The kinetics of glycine oxidation by NBP in the presence of SDS was earlier reported [44].

Literature survey reveals that kinetics of oxidation of Ala by NBP in micellar system has not yet been reported. This prompted us to study the detail kinetics of oxidation of Ala by NBP in the presence of SDS. Objectives of the present study are to: (i) elucidate a plausible mechanism, (ii) identify the oxidation products, (iii) deduce an appropriate rate law, (iv) ascertain the reactive species of oxidant i.e., NBP, (v) calculate activation parameters, and (vi) effect of SDS micelle on the rate of oxidation.

2. EXPERIMENTAL

2.1. Materials

N-Bromophthalimide (NBP) was used as obtained (99% purity) whose melting point was found to be 481 K. Solutions of NBP were prepared in 80% distilled acetic acid and stored in a black-coated flask to

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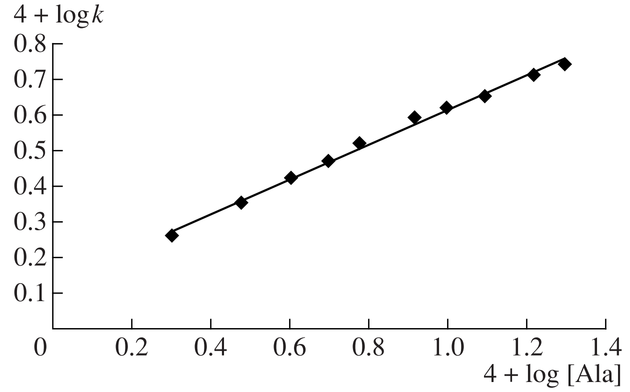


Fig. 1. The plot of $\log k$ vs. $\log[\mathrm{Ala}]$ on reaction conditions with [NBP] = 1×10^{-4} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [H$^+$] = 5×10^{-3} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [CH_3COOH] = 50%, T = 308 K.

prevent photochemical deterioration. The prepared solution was then standardized iodometrically [45] against standard sodium thiosulphate solution using starch as an indicator. A standard aqueous solution of SDS (AR) and Ala (sd-fine) were prepared in double distilled water. A standard aqueous solution of mercuric acetate (GR) was acidified with 20% distilled acetic acid. Perchloric acid (G.R.) diluted with double-distilled water was standardized by acid-base titration. All other standard solutions of KCl, KBr, $NaClO_4$ and phthalimide were prepared with double-distilled water.

Table 1. The effect of varying concentration of NBP, alanine and perchloric acid on the rate of oxidation at 308 K

[NBP] × 10^4, mol dm^{-3}	[Ala] × 10^4, mol dm^{-3}	[H$^+$] × 10^3, mol dm^{-3}	$k \times 10^4$, s^{-1}
0.6	5.0	5.0	3.0
0.8	5.0	5.0	3.0
1.0	5.0	5.0	2.9
2.0	5.0	5.0	3.0
4.0	5.0	5.0	2.9
1.0	2.0	5.0	1.8
1.0	3.0	5.0	2.2
1.0	4.0	5.0	2.6
1.0	5.0	5.0	2.9
1.0	6.0	5.0	3.3
1.0	8.3	5.0	3.8
1.0	10.0	5.0	4.1
1.0	12.5	5.0	4.4
1.0	16.6	5.0	5.1
1.0	20.0	5.0	5.4
1.0	5.0	1.0	5.5
1.0	5.0	2.0	4.0
1.0	5.0	4.0	3.4
1.0	5.0	5.0	2.9
1.0	5.0	6.0	2.6
1.0	5.0	8.0	2.2

Note: Solution conditions: [SDS] = 8.1×10^{-3} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [CH_3COOH] = 50%.

2.2. Determination of Rate Constant

The plots of $\log[\mathrm{NBP}]_t$ vs. time were always found to be linear up to nearly 80% of the reaction and the first order rate constant was evaluated from the slopes of these plots in presence of surfactant. The observed rate constants were reproducible within ±5% in replicate kinetic run.

2.3. Kinetic Measurements

The reaction was carried out in glass stoppered Pyrex vessel whose outer surface was black coated to eliminate photochemical effects. Requisite amounts of the solutions of [Ala], [Hg(OAc)$_2$], [SDS], [$HClO_4$], CH_3COOH, and water (to keep the total volume constant for all runs) were taken in the reaction vessel and thermostated at 308 K for thermal equilibrium. A measured amount of the oxidant solution which was also thermostated at the same temperature was rapidly added to the reaction mixture. The progress of the reaction was followed by estimating the amount of unconsumed NBP iodometrically in aliquots withdrawn from the reaction mixture at regular time intervals. The course of the reaction was studied for two half-lives. The first order rate constants calculated were reproducible.

2.4 Stoichiometry and Product Analysis

Various sets of experiments were performed with different [NBP] and [Ala] concentrations, under the condition of [NBP] $\gg$ [Ala]. The stoichiometry of the reaction was carried out by equilibrating the mixture consisting of NBP, Ala, SDS, Hg(OAc)$_2$, CH_3COOH, and $HClO_4$. Determination of unconsumed NBP revealed that for the oxidation of each mole of alanine two moles of NBP was required. Accordingly, the following stoichiometric equation could be formulated:

$$CH_3CH(NH_2)COOH + 2\,NBP$$
$$\longrightarrow CH_3CN + 2\,NHP + CO_2 + 2\,HBr$$

(where NHP is phthalimide).

The main oxidation product of the reaction, ethane nitrile was detected by spot test [46].

3. RESULTS AND DISCUSSION

3.1. Effect of Varying Concentration of NBP

The rate of oxidation reaction was found to be first order with respect to NBP in all the cases studied. The plots of $\log(a - x)$ vs. time were found to be straight lines, indicating that the order with respect to the oxidant was one. The results are presented in (Table 1).

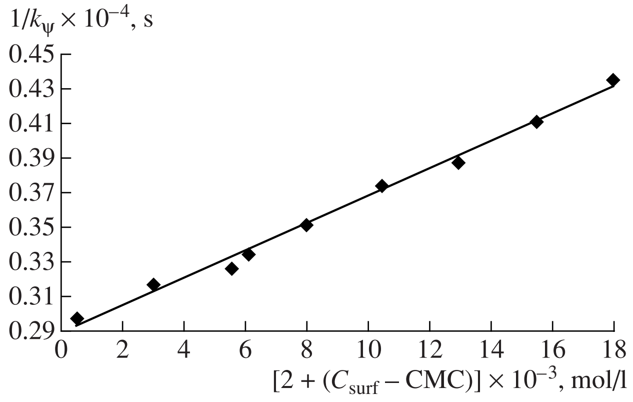


Fig. 2. The plot of k_Ψ^{-1} versus (C_{surf} – CMC) on reaction conditions with [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}, [CH_3COOH] = 50%, T = 308 K.

3.2. *Effect of Varying Concentration of Alanine*

The rate of reaction increased with increasing [Ala]. A plot of $\log k$ vs. $\log[\text{Ala}]$ was linear with a fractional slope (0.48), indicating that the order with respect to alanine was fractional order. The results are presented in (Table 1, Fig. 1).

3.3. *Effect of Varying Concentration of SDS*

The rate constant decreased with increasing concentration of SDS. The reported critical micelle concentration (CMC) of SDS is 8.1×10^{-3} mol dm^{-3} at 298 K. From the plot of k_Ψ^{-1} versus [2 + (C_{Surf} – CMC)], binding constant ($K_s + K_0$) was calculated. The inhibition effect by SDS may be due to increased concentration of unreactive counterions for the Stern layer as there is possibility of competition between reactive and nonreactive ions for sites in the Stern layer (Table 2, Fig. 2).

3.4. *Effect of Varying Concentration of $Hg(OAc)_2$*

Change in [$Hg(OAc)_2$] to the reaction mixture showed an insignificant effect on the oxidation rate. It has been reported earlier [47] that Hg(II) can act as a homogeneous catalyst, co-catalyst and oxidant. In order to ascertain the real role of $Hg(OAc)_2$, experiments were performed with different initial concentrations of $Hg(OAc)_2$ with and without the presence of NBP under similar experimental conditions. The kinetic observations in the presence of NBP showed that the reaction velocity was almost constant with the increase in concentration of $Hg(OAc)_2$, neglecting its role as catalyst and co-catalyst in the reaction. The reaction did not proceed under the similar conditions with $Hg(OAc)_2$ without using NBP, indicating noninvolvement of $Hg(OAc)_2$ as oxidant. Thus, in view of such kinetic observations, $Hg(OAc)_2$ acts only as a Br^- scavenger [48] due to formation of the complex $[HgBr_4]^{2-}$. Therefore, all the experiments were carried out in the presence of $Hg(OAc)_2$.

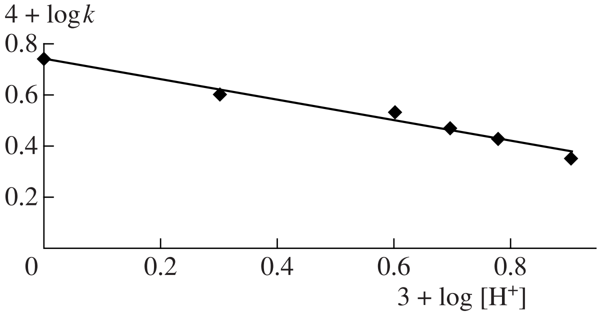


Fig. 3. The plot of $\log k$ vs. $\log[HClO_4]$ on reaction conditions with [NBP] = 1×10^{-4} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [CH_3COOH] = 50%, T = 308 K.

Table 2. The effect of varying concentration of sodium dodecyl sulfate, mercuric acetate and acetic acid (%) on the rate of oxidation at 308 K

[SDS] × 10^3, mol dm^{-3}	[Hg^{2+}] × 10^4, mol dm^{-3}	[CH_3COOH], %	$k \times 10^4$, s^{-1}
0.0	2.0	50.0	3.4
2.5	2.0	50.0	3.3
5.0	2.0	50.0	3.1
7.5	2.0	50.0	3.0
8.1	2.0	50.0	2.9
10.0	2.0	50.0	2.8
12.5	2.0	50.0	2.6
15.0	2.0	50.0	2.5
17.5	2.0	50.0	2.4
20.0	2.0	50.0	2.3
8.1	1.0	50.0	2.9
8.1	2.0	50.0	2.9
8.1	4.0	50.0	3.0
8.1	6.0	50.0	2.9
8.1	8.0	50.0	2.9
8.1	10.0	50.0	3.0
8.1	2.0	20.0	6.9
8.1	2.0	30.0	5.5
8.1	2.0	40.0	4.2
8.1	2.0	50.0	2.9
8.1	2.0	60.0	1.8

Note: Solution conditions: [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}.

3.5. *Effect of Varying Concentration of $HClO_4$*

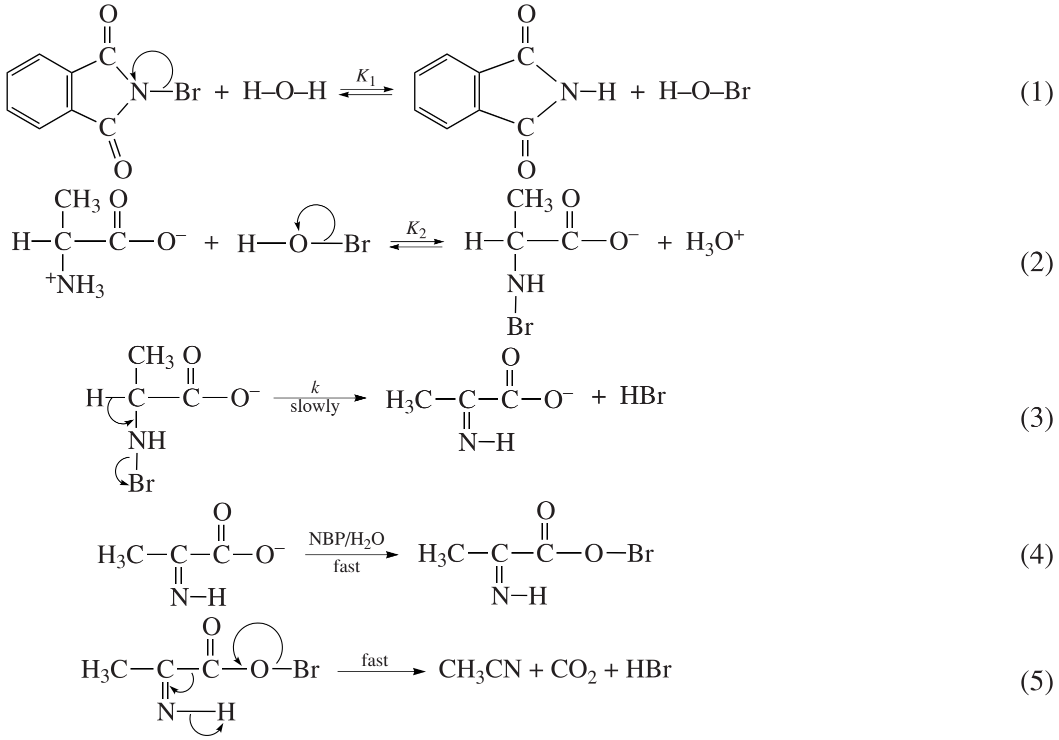
The rate constant decreased with an increase of [H^+] from 1×10^{-3} to 8×10^{-3} mol dm^{-3}. The retardation by [H^+] may be mainly attributed to the conversion of the more reactive neutral species of Ala to the less reactive protonated form. The observed straight line in the $\log k$ vs. $\log[H^+]$ indicates that the order with respect to [H^+] is inverse fractional order (–0.40) (Table 1, Fig. 3).

3.6. *Effect of Varying Concentration of Acetic Acid*

The rate constant of the reaction decreased with increasing acetic acid percentage from 20 to 60%. The rate of oxidation was found to depend on the polarity of the medium. When the polarity of the solvent was increased, the rate of reaction decreased. In order to determine the effect of dielectric constant (polarity) of the medium on the rate of reaction, the micellar catalyzed oxidation of Ala by NBP was studied for various concentrations of acetic acid. The data clearly revealed that the reaction rate decreased with increase in the concentration of acetic acid, i.e., with increasing dielectric constant or polarity of the medium.

3.7. *Effect of Varying Concentration of Phthalimide and Ionic Strength of the Medium*

Addition of phthalimide (a reduced product of the oxidant) decreased the rate of reaction. Change in [$NaClO_4$] of the reaction mixture showed an insignificant effect on the rate of oxidation. The negligibly small effect of ionic strength on the reaction is presumably due to the fact that the reaction takes place between a neutral and charged species (Scheme 1).



Scheme 1. The reaction mechanism for the reaction between Alanine and *N*-bromophthalimide in the acidic medium.

3.8. *Test for Free Radical*

Addition of acrylamide (under N_2 atmosphere) did not decrease the rate of oxidation. There was no polymer formation, confirming the absence of free radicals in the reaction mixture.

3.9. *Effect of Inorganic Electrolytes*

The surface potential of the ionic micelles decreases with the increase of concentration of the gegenions. This reduces the CMC and it can also change the shape and size of the micelles. The effect of added salts on the rate of reaction was also explored because salts as additives, in micellar systems, acquire a special ability to induce structural changes which may, in turn, modify the substrate-surfactant interaction. The salt effect on micellar catalyzed reactions has been rationalized by assuming a competition between the reactant and the counterion for a “binding site” on or in the micelle. The substrate molecule interacts with the micelle electro-

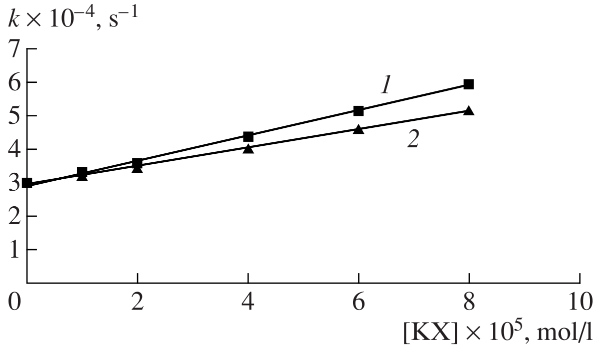


Fig. 4. Effect of variation of inorganic salts ((*1*) [KCl] and (*2*) [KBr]) on reaction conditions with [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [CH_3COOH] = 50%, *T* = 308 K.

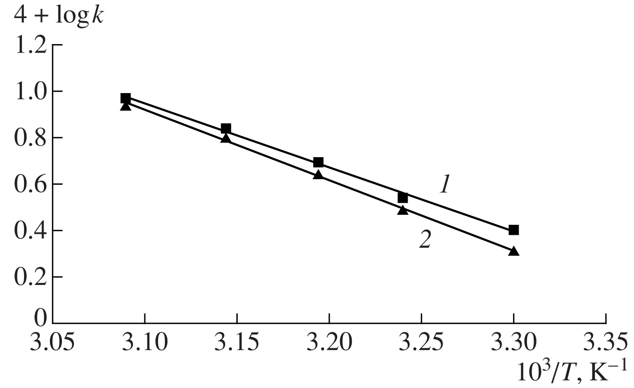


Fig. 5. Effect of variation of temperature on reaction conditions with (*1*) In absence of surfactant and (*2*) in presence of SDS [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [CH_3COOH] = 50%.

statically and hydrophobically, and structural changes occur on salt addition [49]. Positive effect of [Cl^-] and [Br^-] on the oxidation velocity was found. The results are presented in (Table 3, Fig. 4).

3.10. Activation Parameters

Activation parameters are believed to provide useful information regarding the environment in which chemical reactions takes place. The reactions were studied at different temperatures (308–323 K). From Arrhenius plots (Fig. 5), the value of activation energy (E_a) was calculated and the values of $\Delta S^{\#}$ and $\Delta G^{\#}$ were computed from Eyring equation (Table 4). A higher value of E_a in presence of SDS shows that the inhibition effect on the rate of reaction. The larger negative value of $\Delta S^{\#}$ in the absence of surfactant indicates that more ordered activated complex is formed. The fairly high positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ indicate that the transition state is highly solvated. The nearly same values of $\Delta G^{\#}$ in the absence and in presence of surfactant suggest operation of similar reaction mechanism in both the cases.

4. MECHANISM

It has been reported earlier by several workers [50–64] that NBP is good oxidizing and brominating agent

Table 3. The effect of varying concentration of inorganic salts on the rate of oxidation at 308 K

[KBr] × 10^5, mol dm^{-3}	[KCl] × 10^5, mol dm^{-3}	$k \times 10^4$, s^{-1}
1.0	–	3.2
2.0	–	3.4
4.0	–	4.0
6.0	–	4.5
8.0	–	5.1
–	1.0	3.3
–	2.0	3.5
–	4.0	4.3
–	6.0	5.1
–	8.0	5.9

Note: Solution conditions: [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [CH_3COOH] = 50%.

Table 4. Temperature effect and activation parameters observed for the oxidation of Alanine

T, K	$k \times 10^4$, s^{-1}	
	in absence of surfactant	in presence of SDS
303	2.4	2.0
308	3.4	2.9
313	4.8	4.4
318	6.8	6.4
323	9.3	8.8
ΔE_a, kJ mol^{-1}	53.4	58.6
$\Delta H^{\#}$, kJ mol^{-1}	50.8	55.9
$\Delta S^{\#}$, J K^{-1} mol^{-1}	–33.7	–25.4
$\Delta G^{\#}$, kJ mol^{-1}	61.5	64.0

Note: Solution conditions: [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [CH_3COOH] = 50%.

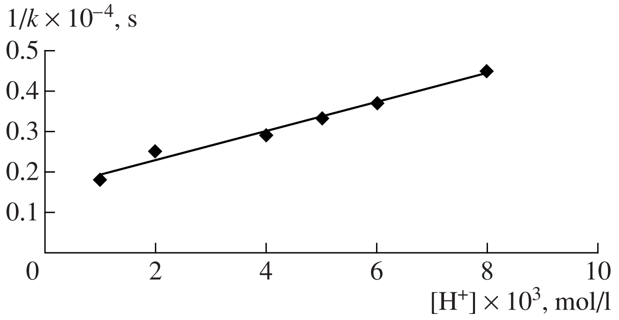


Fig. 6. The Plot of $1/k'$ versus [$HClO_4$] on reaction conditions with [NBP] = 1×10^{-4} mol dm^{-3}, [Ala] = 5×10^{-4} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [CH_3COOH] = 50%, T = 308 K.

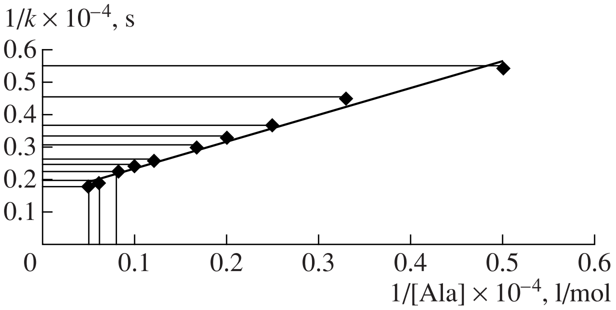


Fig. 7. The plot of $1/k'$ versus 1/[Ala] on reaction condition with [NBP] = 1×10^{-4} mol dm^{-3}, [SDS] = 8.1×10^{-3} mol dm^{-3}, [Hg^{2+}] = 2×10^{-4} mol dm^{-3}, [H^+] = 5×10^{-3} mol dm^{-3}, [CH_3COOH] = 50%, T = 308 K.

because of large polarity of >N–Br bond. NBP, like other similar *N*-halo imides, may exist in various forms in acidic medium, i.e., free NBP, protonated NBP, Br^+, HOBr, $(H_2OBr)^+$, as per the following equilibria:

$$\text{NBP} + H^+ \rightleftharpoons \text{NHP} + Br^+, \qquad (6)$$

$$\text{NBP} + H^+ \rightleftharpoons (\text{NBPH}^+), \qquad (7)$$

$$\text{NBP} + H_2O \rightleftharpoons \text{HOBr} + \text{NHP}, \qquad (8)$$

$$\text{HOBr} + H^+ \rightleftharpoons (H_2OBr)^+. \qquad (9)$$

Addition of phthalimide in the reaction mixture decreases the rate of oxidation in acidic media suggesting that the pre-equilibrium step involves a process in which phthalimide is one of the products. When NBP or $(NBPH)^+$ is assumed as the reactive species, the derived rate laws fail to explain the negative effect of phthalimide. Hence neither of these species can be considered as the reactive species. When $(H_2OBr)^+$ is taken as the reactive species, the rate law obtained shows first order kinetics with respect to hydrogen ion concentrations, contrary to our observed negative fractional order in [$HClO_4$], although it fully explains the negative effect of phthalimide. Therefore, the possibility of cationic bromine (Br^+) as reactive species is ruled out. Thus, the only choice left is HOBr, which, when considered as the reactive species of NBP, leads to a rate law capable of explaining all the kinetic observations and other effects. Hence, in the light of kinetic observations, HOBr can safely be assumed to be the main reactive species of NBP for the present reaction.

The α-amino acid is known to exist in the following equilibria in aqueous solution.

$$\underset{\text{Amino acid (S)}}{RCHNH_2COOH} \rightleftharpoons \underset{\text{Anion (S}^-)}{RCHNH_2COO^-} + H^+ \rightleftharpoons \underset{\text{Zwitter ion (S}^0)}{RCHN^+H_3COO^-}. \qquad (10)$$

The dissociation of amino acid depends upon the pH of the solution. In strongly acidic or strongly alkaline solution, amino acid dissociates as shown in below:

$$\underset{\text{Cation (S}^+\text{H)}}{RCHN^+H_3COOH} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Zwitter ion (S}^0)}{RCHN^+H_3COO^-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Anion (S}^-)}{RCHNH_2COO^-}. \qquad (11)$$

In fact, under the experimental conditions the concentration of anion-form will be very low and the possibility of its participation in the reaction will be least. The possible reactive reducing species may either be the cation-form or zwitter ion of amino acid. Further, considering (S^+H) as the main reactive species the rate law deduced would show a first order dependence in [H^+] contrary to our experimental results. Thus, the only possible active species controlling the rate of oxidation seems to be the zwitter ion (S^0). Hence, (S^0) is the main active species was proposed in the following reaction scheme. Under the present experimental conditions, [H^+] (5×10^{-3} mol dm^{-3}), Ala exists in the form of zwitter ionic species, (S^0), to an extent of 63%, the remaining 37% being present in the protonated form, (S^+H).

On the basis of the above experimental findings, taking HOBr as the most reactive species of NBP, Scheme 1 can be proposed for micellar effect on the kinetics of oxidation of Ala by NBP in acidic medium.

The rate of disappearance of NBP is given as

$$\frac{-d[\text{NBP}]}{dt} = \frac{kK_1K_2[\text{Ala}][\text{NBP}]_T}{[\text{NHP}][H^+] + K_1K_2[\text{Ala}] + K_1[H^+]}, \qquad (12)$$

where $[\text{NBP}]_T = [\text{NBP}] + [\text{HOBr}] + [X^-]$.

The above rate law is in good agreement with the experimental results in the absence and the presence of surfactant.

$$\text{Rate} = k'[\text{NBP}]_T$$

$$k' = \frac{\text{rate}}{[\text{NBP}]_T} = \frac{kK_1K_2[\text{Ala}]}{[\text{NHP}][\text{H}^+] + K_1K_2[\text{Ala}] + K_1[\text{H}^+]}, \tag{13}$$

$$\frac{1}{k'} = \frac{[\text{NHP}][\text{H}^+]}{kK_1K_2[\text{Ala}]} + \frac{1}{k} + \frac{[\text{H}^+]}{kK_2[\text{Ala}]}. \tag{14}$$

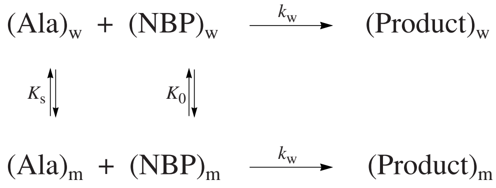
According to Eq. (14) if a plot is made between $1/k'$ and $[\text{H}^+]$ or $1/[\text{Ala}]$, then straight line having a positive intercept on the $1/k'$ axis should be obtained. When $1/k'$ values are plotted against $[\text{H}^+]$ and $1/[\text{Ala}]$, straight line with positive intercept on $1/k'$ axis were obtained (Figs. 6, 7) which clearly proves the validity of the rate law expressions Eq. (12) and hence the proposed mechanism. From the slopes and intercepts of the straight line the values of k, K_1, and K_2 have been calculated and found as $6.45 \times 10^{-4}\ \text{s}^{-1}$, 1×10^{-1} and 9.5×10^{-4} respectively.

5. IN THE PRESENCE OF SURFACTANT

5.1. Kinetic Model to Explain the Micellar Effects

One of the most important properties of micellar system is their ability to affect the rate of the chemical reaction. The effect of surfactants on reaction kinetics is called micellar catalysis and involves several contributing factors. Micellar catalysis of reactions in aqueous solutions is usually explained on the basis of distribution of reactants between water and the micellar pseudo phase which occurs at different rates. If the solubility of the reactant is greater in the micelle than in water, then the local concentration is increased in the micelle. Further, it was thought that only electrostatic interaction occurs between micelle and reactant, however, later it was explained that the reaction rates are also affected by hydrophilic interactions. The inhibition of rates constant of surfactant may be explained with the help of Berezin's model [65] for bimolecular reactions.

Berezin's model. Berezin and co-workers developed the first general treatment based on the pseudo phase model and successfully simulated spontaneous and bimolecular reactions between neutral and organic reactants. The inhibition of rates at higher concentration of SDS may be explained with the help of Berezin's model, which involves solubilization of both the reactants in the micellar phase. The zwitterionic alanine species are present in the interfacial layer of a micelle, since amino acids are practically insoluble in organic media. According to the Berezin's et al. a solution above the critical micelle concentration (CMC) may be considered as a two-phase system consisting of an aqueous phase and a micellar pseudo-phase. The reactants {substrate (S) and oxidant (O)} may be distributed as shown in Scheme 2.



Scheme 2. The Berezin's model present for a bimolecular reaction occurring in aqueous and micellar phase.

A quantitative rate expression for a bimolecular reaction occurring only in aqueous (k_w path) and micellar (k_m path) phase for the pseudo-first order rate constant is given below:

$$k_\Psi = \frac{k_\text{w} + k'_\text{m}K_\text{s}K_0(C_\text{Surf} - \text{CMC})}{[1 + K_\text{s}(C_\text{Surf} - \text{KKM})][1 + K_0(C_\text{Surf} - \text{CMC})]}, \tag{15}$$

where, K_s and K_0 are the association constants of Ala and NBP, respectively with SDS, C_Surf is the analytical concentration of SDS, $k'_\text{m} = k_\text{m}/V$, V being molar volume of the micelle and k_w and k_m are the pseudo-first order rate constant in absence and presence of micelles, respectively. Since the oxidant is a charged species and the substrate is large zwitter ionic, the hydrophilic and electrostatic repulsions will be large and hence it may be expected that K_s and K_0 will be low.

Since C_Surf is small it may be possible that $k_\text{w} \gg k'_\text{m}K_\text{s}K_0(C_\text{Surf} - \text{CMC})$ so that the Eq. (15) takes the form

$$k_\Psi = \frac{k_\text{w}}{1 + (K_\text{s} + K_0)(C_\text{Surf} - \text{CMC}) + K_\text{s}K_0(C_\text{Surf} - \text{CMC})^2}. \tag{16}$$

Again, since $(C_\text{Surf} - \text{CMC})$ is very small, the terms containing $(C_\text{Surf} - \text{CMC})^2$ may be neglected, and the Eq. (16) may be rearranged as:

$$\frac{1}{k_\Psi} = \frac{1}{k_\text{w}} + \frac{K_\text{s} + K_0}{k_\text{w}}(C_\text{Surf} - \text{CMC}). \tag{17}$$

Table 5. Critical micelle concentration (CMC values of SDS in different experimental conditions) at 308 K

Solutions	CMC × 10^3, mol dm^{-3}
1. H_2O	8.0, 8.1*
2. H_2O + [Ala] + [H^+] + [Hg^{++}] + 50% CH_3COOH + NBP	4.0

Note: ^{a} Literature value for SDS at 25°C = 8.1 × 10^{-3} mol dm^{-3}.
Solution conditions: [NBP] = 1 × 10^{-4} mol dm^{-3}, [Ala] = 5 × 10^{-4} mol dm^{-3}, [Hg^{2+}] = 2 × 10^{-4} mol dm^{-3}, [H^+] = 5 × 10^{-3} mol dm^{-3}, [SDS] = 8.1 × 10^{-3} mol dm^{-3}, [CH_3COOH] = 50%.

Plot of k_Ψ^{-1} versus $[2 + (C_{\text{Surf}} - \text{CMC})]$ for Ala is linear (Fig. 2) with positive slope and positive intercept which is in conformity with the rate law.

Other parameters for the oxidation of Ala by NBP in presence of SDS:

$$K_s + K_0 = 26.9 \text{ mol}^{-1} \text{ dm}^3, \quad k_w \times 10^4 = 3.4 \text{ s}.$$

5.2. CMC Determination

Surfactants spontaneously aggregate above a certain concentration called critical micelle concentration (CMC) to form micelle, whose determination has considerable practical importance, normally to understand the self-organizing behavior of surfactants in exact ways. Micelle aggregates affect chemical reactivity primarily by binding or excluding reactants and only secondarily by changing the free energy of activation. The critical micelle concentration values of the surfactant (SDS) were determined conductometrically (Digital conductivity meter, model 611 E, Electronic India Company) in the presence and absence of reactants at 308 K. The CMC values were determined from plots of the specific conductivity versus surfactant concentration. The breakpoint of nearly straight line portions in the plots is taken as an indication of micelle formation and this correspond to the CMC of surfactant. The CMC values of SDS in different experimental conditions at 308 K are summarized in (Table 5, Fig. 8). The CMC values are lower than those given in literature for aqueous solutions of SDS without added electrolyte, which were found to be approximately about ~4 × 10^{-3} mol dm^{-3} in reaction mixture for Ala. The difference among the CMC values arises from the well-known effect of added electrolyte, which lowers the CMC by causing a decrease in the repulsion between the polar head groups at the micelle surface. Our results of decrease in CMC value are in accord with the earlier observations of micelle formation at relatively low surfactant concentration [66–68].

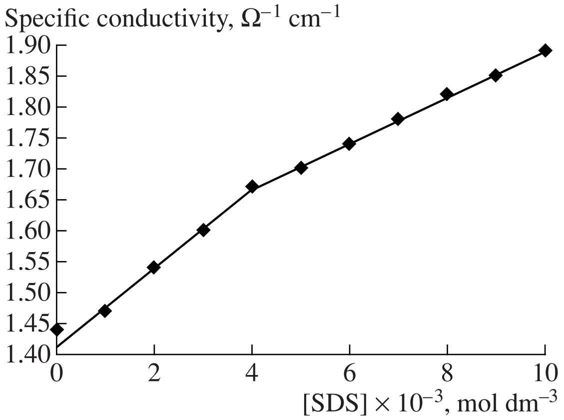


Fig. 8. Effect of variation of SDS on reaction conditions with [NBP] = 1 × 10^{-4} mol dm^{-3}, [Ala] = 5 × 10^{-4} mol dm^{-3}, [Hg^{2+}] = 2 × 10^{-4} mol dm^{-3}, [H^+] = 5 × 10^{-3} mol dm^{-3}, [CH_3COOH] = 50%, T = 308 K.

5.3. Influence of SDS on k_Ψ

A continuous decrease a k_Ψ was observed with the increase in [SDS] at constant substrate [Ala] and oxidant [NBP]. The inhibition of the reaction is due to the fact that the alanine zwitterions are repelled by SD^- head group of the micelles having negative charge at the surface. Thus, are previously stated, the reactive alanine species are present in the micellar interfacial layer. The lower value of (K_s + K_0) for association of NBP-Ala complex with SDS micelles explains satisfactorily the binding mode of the alanine species with the anionic SDS micelles. The increase in $\Delta H^\#$ in micellar phase as compared to water phase can be explained by considering the repulsion between the zwitterionic alanine and head group of SDS micelles. Activation parameters, when compared with those obtained in aqueous medium with amino acid, show that the presence of anionic micelles increases the $\Delta H^\#$ which indicates that the transition state is highly solvated in the micellar system. The magnitude of $\Delta G^\#$ is not significantly affected, showing that the same mechanism is being followed in aqueous as well as in the micellar media.

Comparative studies. Efforts were also made to compare the findings of this paper with the results reported for SDS catalyzed oxidation of Glycine (Gly) by NBP in acidic medium. First of all, focus was made on the points that how NBP affect the oxidation of Gly and Ala. In the reported SDS catalyzed oxidation of Gly [44] by NBP was observed first order kinetics with respect to NBP and fractional order with respect to Gly. The present study with respect to Ala on the rate of oxidation being very similar with the reported [44] SDS catalyzed oxidation by NBP. HOBr as a reactive species of NBP in the case of SDS catalyzed oxidation of Ala and $(NBPH)^+$ as a reactive species of NBP in the case of SDS catalyzed oxidation of Gly were proposed on the basis of negative effect of phthalimide and negligible effect of phthalimide on the rate of reaction, respectively. In Gly oxidation, the rate of reaction increased with increasing the concentration of perchloric acid but in the present study. The rate of reaction decreased with increasing the concentration of perchloric acid. In both the cases, ionic strength had no effect on the oxidation velocity. It was observed that binding constant of Gly oxidation is higher than Ala oxidation. It was also observed that the rate of oxidation of alanine was greater than that of glycine.

6. CONCLUSIONS

In the light of kinetic observations for the micellar effect on the kinetics of oxidation of Ala by *N*-bromophthalimide in the presence of perchloric acid, the following conclusions can be easily drawn:

(1) The reactive species of oxidant NBP is HOBr not NBP itself. Oxidation products were identified.

(2) Activation parameters were evaluated for catalyzed reactions.

(3) The critical micelle concentration values are lower than those given in the literature for aqueous solutions of SDS without added electrolyte.

(4) The rate of oxidation decreases with increasing concentration of SDS.

(5) The micellar effect can be correlated with the nature of the reducing substrates and the reactions conditions.

These micellar effects are quite important to understand and to substantiate the proposed mechanistic pathways. This may widen the applicability of NBP oxidimetry in organic synthesis. The Berezin's model conform the behavior of micellar-catalyzed oxidation reaction.

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