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# KINETICS OF L-ALANINE OXIDATION BY *N*-BROMOPHTHALIMIDE IN THE PRESENCE OF CETYLTRIMETHYLAMMONIUM BROMIDE

Ghanat K. JOSHI*

Late Lal Shyam Shah Govt. Naveen College, Mohla Dist.– Mohla-Manpur-A.Chowki (Chhattisgarh) India

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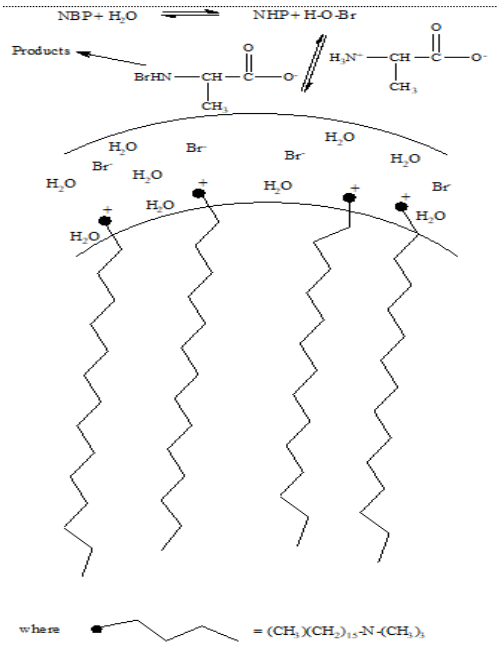
Kinetics of L-alanine (Ala) oxidation by N-bromophthalimide (NBP) is accelerated by cationic micelle of cetyltrimethylammonium bromide (CTAB). The values of $k_{obs}$ increase sharply with increasing [surfactant] and reach well-defined maxima at [surfactant] at or below the CMC, before decreasing to values corresponding to $k_{obs}=k'_M$. The rate maxima are due to the formation of premicellar complexes of substrate with one or a few surfactant monomers, but they "dissolve" in micelles at higher [surfactant]. A rationalization is provided for acceleration by a very dilute surfactant. The rate of reaction was found to have first-order dependence on [NBP], fractional order dependence on [Ala] and inverse fractional order depen dence 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.




## INTRODUCTION

Association colloids are assemblies of amphiphilic monomers with an ionic or polar group and apolar residues.[1] Self-association in water and some organic solvents, for example, diols and triols, generates micelles with head groups in contact with the solvent. Micelles can act as microreactors in influencing reaction rates and equilibria,[2] and similar behavior is observed with other association colloids, for example, vesicles[3] and microemulsions.[4] Very dilute amphiphiles, for example, surfactants, do not significantly affect reaction the rates of many reactions, but with

* Corresponding author: ghanatchem@gmail.com

increasing concentrations, micelles form and rate or equilibrium constants change.[2] In micellar-accelerated reactions, rate constants reach plateau values, but for bimolecular reactions with a constant concentration of reagent, they typically go through maxima. These changes of rate or equilibrium constants are described in terms of a two-state model with water and micelles behaving as discrete reaction regions or pseudophases.[2–5] Micellization occurs at the critical micelle concentration, CMC, which in some systems marks the onset of the reaction increase, but often reaction increase below the CMC, either because reactants induce micellization or because other species, so-called premicelles, are kinetically effective. As a result, a "kinetic" CMC is often used empirically in fitting rate-surfactant profiles, and Buckingham *et al*. note physical evidence for the possible existence of premicelles.[6] The term "premicelles" seems to be applied to any submicellar assemblies that form spontaneously or are generated by interactions with reactants. In the latter case, it is not easy to distinguish between reactant-induced micellization and the formation of premicelles.[7]

The change from monomeric surfactant to micelles occurs over a small range of concentration, which is sensitive to ionic and nonionic solutes, and there is a dispersion of micellar size, which is also sensitive to solutes. However, the simple pseudophase model, despite neglecting, except in dilute surfactant. The way to identify the kinetic behavior in spontaneous, unimolecular reactions where only one species is partitioned between water and micelles or other assemblies. For example, in bimolecular ionic reactions, one has to consider electrolyte effects on the CMC and competition between reactive and inert ions for the association of colloids.[2]

The pseudophase model predicts that overall first-order rate constants, $k_{obs}$, for a spontaneous micellar-accelerated reaction should increase monotonically until all the substrate is micellar-bound.[2] Conversely, for an inhibited reaction, $k_{obs}$ decrease monotonically to a constant value. This behavior is fitted by eq. 1:

$$k_{obs} = \frac{k'_W + k'_M K_S[Dn]}{1 + K_S[Dn]} \quad (1)$$

In eq. 1, $k$'W and $k'_M$ are first-order rate constants in the aqueous and micellar pseudophases, respectively, and $K_S$ is the association constant of substrate S with micellized surfactant (detergent) Dn, whose concentration is the total less that of monomer, given by the CMC.[8] This kinetic form is observed for many reactions, although often $k_{obs}$ increases at surfactant concentrations below the CMC, and occasionally values of $k_{obs}$ increase sharply with [D] < CMC but then decrease and follow eq. 1 at higher concentrations.[9] Typically their behavior in the presence of association colloids is described by eq. 1. The oxidation of Ala is accelerated by cationic surfactant at concentrations well below the CMC, but values of $k_{obs}$ increase monotonically, and we cannot distinguish between substrate-induced micellization and premicellar-assisted reaction. The rate constants increased monotonically at [surfactant] below the CMC in water, which was not unexpected because the substrate could induce micellization, and the increase does not necessarily show that the substrate is associated with premicelles. This paper describes the premicellar effect on the oxidation of Ala by NBP as viewed from the kinetic and mechanistic points. Hence, we felt it would be worthwhile to investigate the oxidative behavior of NBP with Ala to explore the kinetics and mechanistic aspects of the CTAB-catalyzed reactions. This study will help to predict why the rate accelerated by cationic surfactant is well below the CMC in acidic medium. In present communication, we report for the first time the results of the detailed investigation on the kinetic and mechanistic aspects of CTAB-catalyzed oxidation of Ala by NBP in acidic medium at 308 K. Objectives of the present study are to: (i) study the rate effect well below the CMC; (ii) elucidate a plausible mechanism; (iii) deduce an appropriate rate law; (iv) identify the oxidation products; (v) ascertain the reactive species of NBP, and (vi) find out the catalytic efficiency of CTAB.

## EXPERIMENTAL

### Materials

NBP was used as obtained (Aldrich, 95% purity), and the melting point of the sample was found to be 481 K. Solutions of NBP were prepared in 80% distilled acetic acid and stored in a black-coated flask to prevent photochemical deterioration. The prepared NBP solution was then standardized iodometrically[10] against the standard solution of sodium thiosulfate (Qualigens, AR) using starch as an indicator. A standard aqueous solution of CTAB (Sd-Fine, AR) and Ala (Sd-Fine, AR) was prepared

in double distilled water. A standard aqueous solution of mercuric acetate (Loba Chemie, GR) was acidified with 10% distilled acetic acid (Sd-Fine, AR). Perchloric acid (Loba Chemie, G.R.) diluted with double-distilled water was standardized by a standard solution of NaOH.

### Kinetic measurements

The reaction was carried out in a glass-stoppered Pyrex vessel whose outer surface was black-coated to eliminate photochemical effects. Requisite amounts of the solutions of [Ala], [$Hg(OAc)_2$], [CTAB], [$HClO_4$], $CH_3COOH$ and water (to keep the total volume constant for all runs) were taken in the 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 at regular time intervals. The course of the reaction was studied for two half-lives. The plots of log [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 the presence of surfactant. The observed rate constants were reproducible within ± 5% in the replicated kinetic run.

### Stoichiometry and product analysis.

Various sets of experiments were performed with different [NBP]:[Ala] ratios, under the condition of [NBP]>>[Ala]. The stoichiometry of the reaction was carried out by equilibrating the mixture consisting of NBP, Ala, CTAB, $Hg(OAc)_2$, $CH_3COOH$, and $HClO_4$.. After completion of the reaction, the unconsumed NBP was estimated iodometrically. This showed 1 mol of Ala is oxidized by 2 mol of NBP.

$$CH_3CH(NH_2)COOH + 2\ NBP \rightarrow CH_3CN + 2\ NHP + CO_2 + 2\ HBr \quad (A)$$

where NHP is phthalimide

The main product of oxidation, nitrile was detected by standard test.[11]

Procedure of standard test: one drop of liquid sample was placed in a test tube, and 2 ml of 1M hydroxylammonium chloride in propylene glycol and 1 ml of potassium hydroxide in propylene were added. The mixture was heated at its boiling point for 2 minutes and cooled, and 0.5 to 1.0 ml of ferric chloride solution was added. A red to violet color constituted a positive test.

## RESULTS AND DISCUSSION

### Significance of Rate Enhancements in Dilute Surfactant.

Although the pseudophase model, eq. 1, in its simplest form predicts that rate constants will increase only at the onset of micellization, as given by the CMC,[2,8] they often increase monotonically well below the CMC, which could be ascribed to reactant-induced micellization or to interactions with premicelles. For example, values of $k_{obs}$ for reactions of hydrophobic substrates with small inorganic ions typically increase at [surfactant] < CMC and increase to maxima, as predicted by pseudophase treatments.[2b] Similar behavior is often seen with micellar-mediated reactions of multivalent inorganic complexes and may be ascribed to interactions with premicelles.[12] Drennan *et al*. give a critical analysis of the formation of complexes of Ni(II) in dilute sodium dodecyl sulfate, where rate constants increase at surfactant concentrations below the CMC in water, and show that it is not necessary to invoke intervention of premicelles.[7] Micellization induced by interactions with multivalent inorganic ions is a common phenomenon in inorganic reactions. Although monotonic increases in rate constants in very dilute surfactant do not necessarily demonstrate involvement of premicelles, the situation is different for rate maxima in spontaneous reactions. Rate constants increase as substrate is transferred from water into surfactant-derived assemblies and then decrease to approximately constant values as substrate becomes micellar-bound; that is, the rate maxima demonstrate the existence of three distinct reaction environments, depending on [surfactant].[9] The situation is similar to that for detection of premicelles by fluorescence spectra, where the spectra are characteristic of aqueous, premicellar, and micellar environments.[13] The rate maxima in Fig. 1 cannot be ascribed to reactant-induced micellization. Once micelles form, they dissolve premicellar species, the substrate becomes micellar-bound, and $k_{obs}$ decrease toward the value of *k*'M.

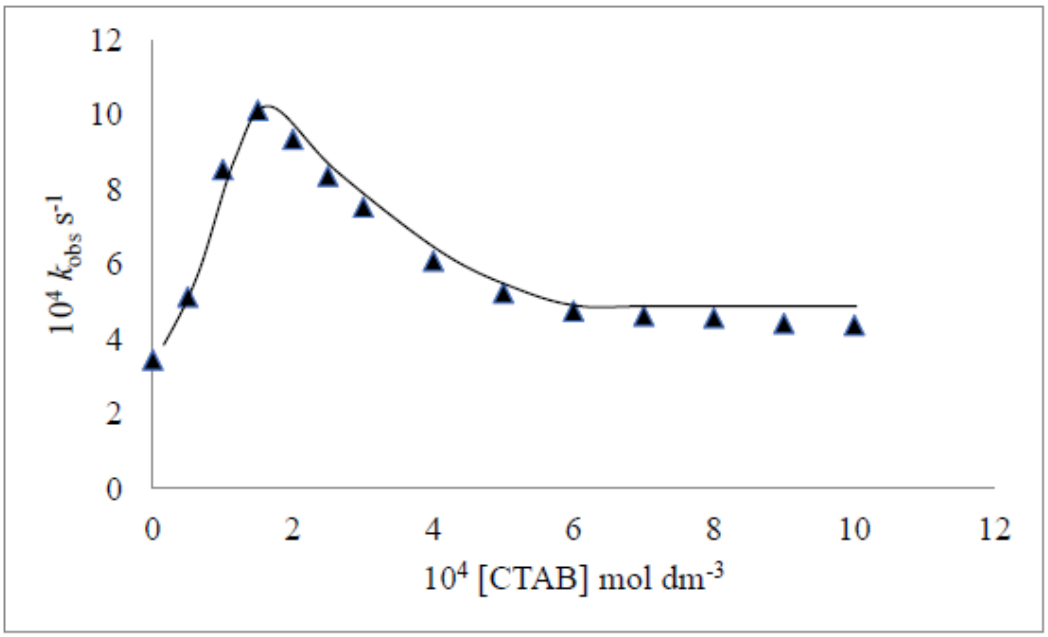



Fig. 1 – The plots of $k_{obs}$ versus [CTAB] for the reaction condition. [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [Ala] = $5\times10^{-4}$ mol dm$^{-3}$, [$H^+$] = $5\times10^{-3}$ mol dm$^{-3}$, [$Hg^{++}$] = $2\times10^{-4}$ mol dm$^{-3}$, $CH_3COOH$ = 50%, Temperature = 308 K.

**Rate Constants in Micelles.**

Head Group Effects. Our results on reactions in fully formed micelles show that micellar rate enhancements increase with increasing head group bulk.[14] The result is understandable because the rate is strongly accelerated by a decrease in the water content and polarity of the medium.[15a]. The head group of CTA+ should decrease the local polarity of the interfacial region, which we assume is the reaction site.[2] The increase in cationic head group bulk decreases the water concentration in the interfacial region.[16] The value of $k'_M$ for reactions in fully formed micelles is given by the value of $k_{obs}$ at high [surfactant].

**Role of Premicelles.**

Higher reaction rates in premicellar assemblies are unambiguously established for some spontaneous reactions by observation of rate maxima in very dilute surfactant, for example, decarboxylation,[9a] cyclization,[9b] and dianionic phosphate ester hydrolysis.[17] They probably play a role in the many reactions where rate constants increase (or decrease) at [surfactant] < CMC, although where the rate change is monotonic, reactant-induced micellization is possible and evidence for the existence of premicelles is ambiguous. Zwitterionic Ala are strongly inhibited by increases in the polarity and the water content of the medium,[15a,18] and micellar rate enhancements are understandable on this basis,[15b–e,19] but it does not explain the higher reactivity in premicelles as compared with micelles. Observation of rate increases in very dilute surfactant is dependent on the presence of the hydrophobic $–CH_3$ group, which promotes hydrophobic binding with $CTA^+$ ions and appears to be much more important than charge-charge interactions. An increase in the bulk of the cationic head groups would disfavor ion pairing in a very dilute surfactant. However, charge-charge interactions should become more important in the reactions. Small assemblies of substrate and hydrophobic quaternary ammonium ions can have a variety of conformations. For example, the effects of submicellar cationic surfactants on the fluorescence spectrum of 2-p-toluidinonaphthalene-6-sulfonate were interpreted by assuming that long n-alkyl groups of the surfactant wrap around the organic moiety of the probe.[13] However, this conformation does not explain our premicellar rate increases, which require the hydrophobic quaternary ammonium ion to shield the zwitterion from water. Zwitterions: Ala ions probably bind to micelles with the $–CH_3$ moiety inserting toward the apolar region, which leaves the $–CH_3$ moiety adjacent to the head groups in the interfacial region. This hypothesis is consistent with the known affinity of quaternary ammonium ions for arenes.[20] The rate of increases in premicelles requires association of the substrate with, at most, a few

surfactant ions. This association can be ascribed to the hydrophobic interactions of the long alkyl groups, but the rate increases require interactions to stabilize the transition state relative to the initial state. If interactions in premicelles are similar to those in micelles, reactions should not be faster in the former, and we have to assume that in premicelles the zwitterion is shielded from water and in the transition state charge dispersion is favored by interaction with the quaternary ammonium ion. Arrangements that fit these conditions are shown in Scheme 1

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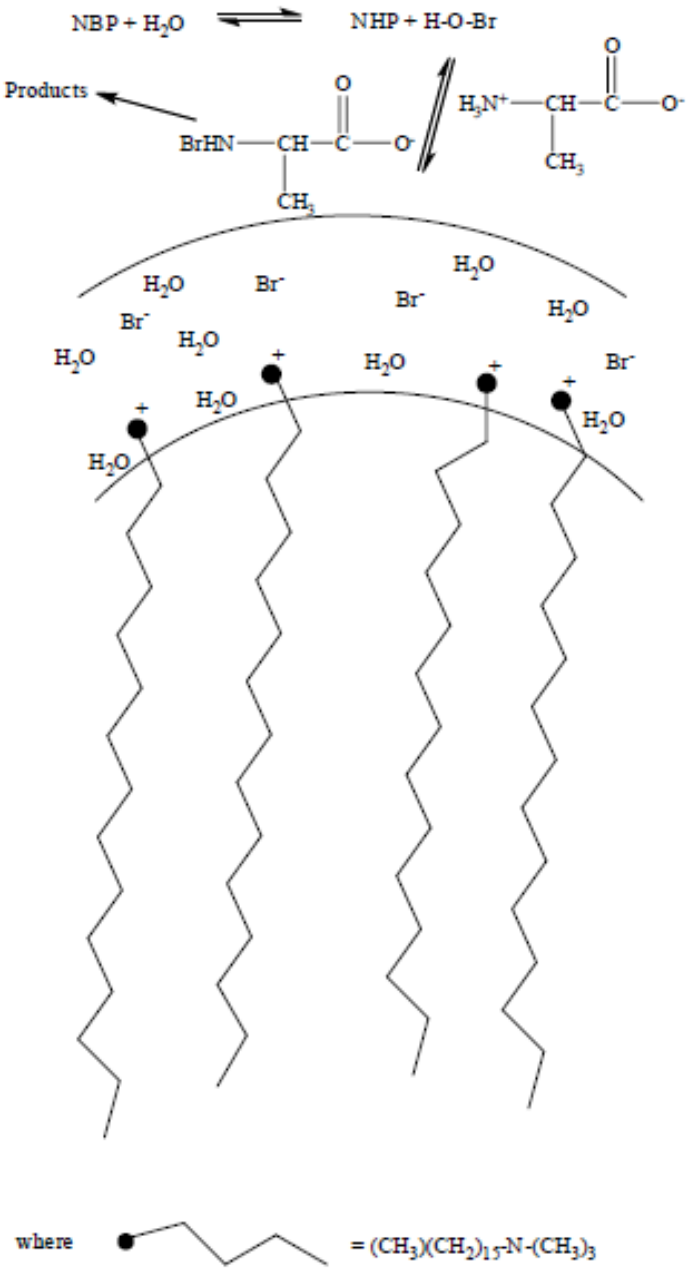



Scheme 1 – Reaction path of oxidation of Ala by NBP in the presence of CTAB.

***Effects of varying*** **[NBP] and [Ala]:** The rate of oxidation reaction with respect to NBP has been found to be first order in all the cases (from $0.6 \times 10^{-4}$ mol $dm^{-3}$ to $4 \times 10^{-4}$ mol $dm^{-3}$). The plots of log[NBP] versus time were found to be straight lines, indicating that the order with respect to oxidant was one. The results are presented in Table 1. The procedure for determining the rates of reaction directly by measuring tangents to the experimental concentration-time curves and introducing them as differentials in the kinetic equations. This theory is based on the proportionality of the instantaneous rate of a reaction

of the nth order involving only one reacting species to the $n^{th}$ power of its concentration.

$$v = -\frac{da}{dt} = k\,a^n$$

Therefore,

$$\ln v = \ln k + n \ln a$$

Plotting this function will yield a straight line, if the reaction is of simple order, with a slope n, and intercept ln k.

*Table 1*

Effect of [NBP], [Ala], $[H^+]$, $[Hg^{++}]$, [CTAB] and acetic acid % on the rate of oxidation reactions at 308 K

| **[NBP]×10⁴** | **[Ala] ×10⁴** | **[H⁺]×10³** | **[Hg⁺⁺]×10⁴** | **[CTAB] ×10⁴** | **$CH_3COOH$** | **$k_{obs}$ x10⁴** |
|---|---|---|---|---|---|---|
| **mol dm⁻³** | **mol dm⁻³** | **mol dm⁻³** | **mol dm⁻³** | **mol dm⁻³** | **%** | **s⁻¹** |
| 0.6 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.32 |
| 0.8 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.34 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.37 |
| 2.0 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.39 |
| 4.0 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.40 |
| 1.0 | 2.0 | 5.0 | 2.0 | 10 | 50 | 3.10 |
| 1.0 | 3.0 | 5.0 | 2.0 | 10 | 50 | 3.50 |
| 1.0 | 4.0 | 5.0 | 2.0 | 10 | 50 | 3.94 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.37 |
| 1.0 | 6.0 | 5.0 | 2.0 | 10 | 50 | 4.60 |
| 1.0 | 8.0 | 5.0 | 2.0 | 10 | 50 | 5.15 |
| 1.0 | 10.0 | 5.0 | 2.0 | 10 | 50 | 5.42 |
| 1.0 | 12.5 | 5.0 | 2.0 | 10 | 50 | 5.70 |
| 1.0 | 16.5 | 5.0 | 2.0 | 10 | 50 | 6.37 |
| 1.0 | 20.0 | 5.0 | 2.0 | 10 | 50 | 6.75 |
| 1.0 | 5.0 | 1.0 | 2.0 | 10 | 50 | 6.45 |
| 1.0 | 5.0 | 2.0 | 2.0 | 10 | 50 | 5.40 |
| 1.0 | 5.0 | 4.0 | 2.0 | 10 | 50 | 4.82 |
| 1.0 | 10 | 5.0 | 2.0 | 10 | 50 | 4.37 |
| 1.0 | 5.0 | 6.0 | 2.0 | 10 | 50 | 4.05 |
| 1.0 | 5.0 | 8.0 | 2.0 | 10 | 50 | 3.62 |
| 1.0 | 5.0 | 5.0 | 10 | 10 | 50 | 4.37 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10 | 50 | 4.32 |
| 1.0 | 5.0 | 5.0 | 4.0 | 10 | 50 | 4.35 |
| 1.0 | 5.0 | 5.0 | 6.0 | 10 | 50 | 4.38 |
| 1.0 | 5.0 | 5.0 | 8.0 | 10 | 50 | 4.33 |
| 1.0 | 5.0 | 5.0 | 10.0 | 10 | 50 | 4.35 |
| 1.0 | 5.0 | 5.0 | 2.0 | 0.0 | 50 | 3.44 |
| 1.0 | 5.0 | 5.0 | 2.0 | 0.5 | 50 | 5.12 |
| 1.0 | 5.0 | 5.0 | 2.0 | 1.0 | 50 | 8.54 |
| 1.0 | 5.0 | 5.0 | 2.0 | 1.5 | 50 | 10.13 |
| 1.0 | 5.0 | 5.0 | 2.0 | 2.0 | 50 | 9.35 |
| 1.0 | 5.0 | 5.0 | 2.0 | 2.5 | 50 | 8.36 |
| 1.0 | 5.0 | 5.0 | 2.0 | 3.0 | 50 | 7.53 |
| 1.0 | 5.0 | 5.0 | 2.0 | 4.0 | 50 | 6.09 |
| 1.0 | 5.0 | 5.0 | 2.0 | 5.0 | 50 | 5.24 |
| 1.0 | 5.0 | 5.0 | 2.0 | 6.0 | 50 | 4.75 |
| 1.0 | 5.0 | 5.0 | 2.0 | 7.0 | 50 | 4.62 |
| 1.0 | 5.0 | 5.0 | 2.0 | 8.0 | 50 | 4.57 |
| 1.0 | 5.0 | 5.0 | 2.0 | 9.0 | 50 | 4.42 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10.0 | 50 | 4.37 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10.0 | 20 | 8.34 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10.0 | 30 | 6.88 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10.0 | 40 | 5.67 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10.0 | 50 | 4.37 |
| 1.0 | 5.0 | 5.0 | 2.0 | 10.0 | 60 | 3.70 |

The rate constant value increased from 3.10 × $10^{-4}$ $s^{-1}$ to 6.75 × $10^{-4}$ $s^{-1}$ with increasing concentration of [Ala] from 2 × $10^{-4}$ mol $dm^{-3}$ to 20 × $10^{-4}$ mol $dm^{-3}$. A plot of log $k_{obs}$ *vs* log [Ala] was linear with a fractional slope (0.34) (Fig. 2), indicating fractional order with respect to [Ala]. The results are presented in Table 1.

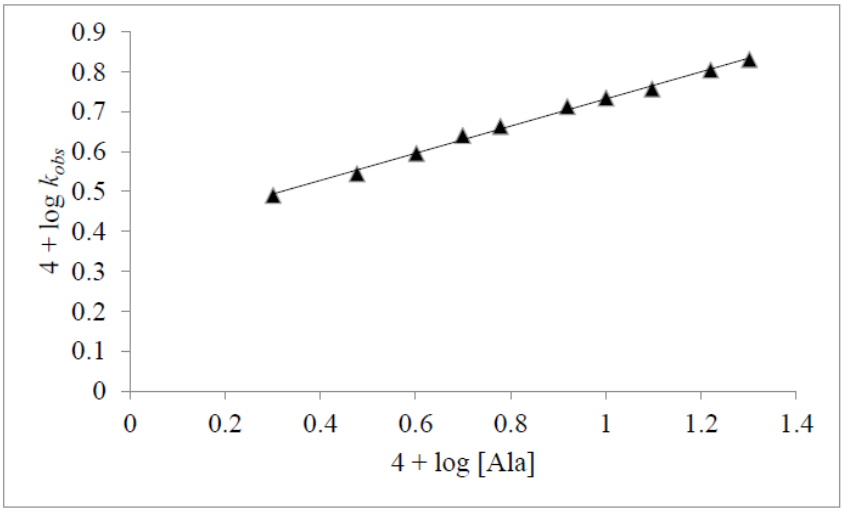



Fig. 2 – The plots of log $k_{obs}$ versus log [Ala] for the reaction condition. [NBP] = 1×$10^{-4}$ mol $dm^{-3}$, [$H^+$] = 5×$10^{-3}$ mol $dm^{-3}$, [CTAB] = 10×$10^{-4}$ mol $dm^{-3}$, [$Hg^{++}$] = 2×$10^{-4}$ mol $dm^{-3}$, $CH_3COOH$ = 50%, Temperature = 308 K.

***Effect of varying* [$Hg(OAc)_2$]**: The change in [$Hg(OAc)_2$] to the reaction mixture showed an insignificant effect on the rate of oxidation. It has been reported earlier[21] that Hg(II) can act as a homogeneous catalyst, co-catalyst, and oxidant. In order to ascertain the real role of $Hg(OAc)_2$ as a Br– scavenger, several 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 showed that the reaction velocity was almost constant, with the increase in concentration of $Hg(OAc)_2$ negating its role as a 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 an oxidant. Thus, in view of such kinetic observations, $Hg(OAc)_2$ acts only as a Br scavenger[22] due to the formation of the complex $[HgBr_4]^{2-}$. Therefore, all the experiments were carried out in the presence of $Hg(OAc)_2$. The results are presented in Table 1.

***Effect of varying* [$HClO_4$], [NHP] *and ionic strength***: The rate constant values decreased from 6.45 × $10^{-4}$ $s^{-1}$ to 3.62 × $10^{-4}$ $s^{-1}$ with an increase in [$H^+$] from 1 × $10^{-3}$ mol $dm^{-3}$ to 8.0 × $10^{-3}$ 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 plots of log $k_{obs}$ *vs* log [$H^+$] produced a straight line with a negative slope (–0.26), indicating that the order with respect to the [$H^+$] ion is a negative fractional value. The results are presented in Table 1 and Fig. 3. Addition of NHP (a reduced product of the oxidant) slightly decreased the rate of reaction. The change in [$NaClO_4$] to the reaction mixture showed an insignificant effect on the rate of oxidation. The negligible effect of ionic strength on the reaction is presumably due to the fact that the reaction takes place between a neutral and the charged species in a rate-limiting step.

***Effect of varying dielectric constant***: The constant rate of the reaction decreased with increasing acetic acid % from 20 to 60% (Table 1). 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 the 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 rate constant values decreased with an increase in the acetic acid %, *i.e.*, with a decreasing dielectric constant or polarity of the medium. The effect of the dielectric constant of the medium on the rate constant of a reaction between two ions has been described by the well-known equation given below.[23]

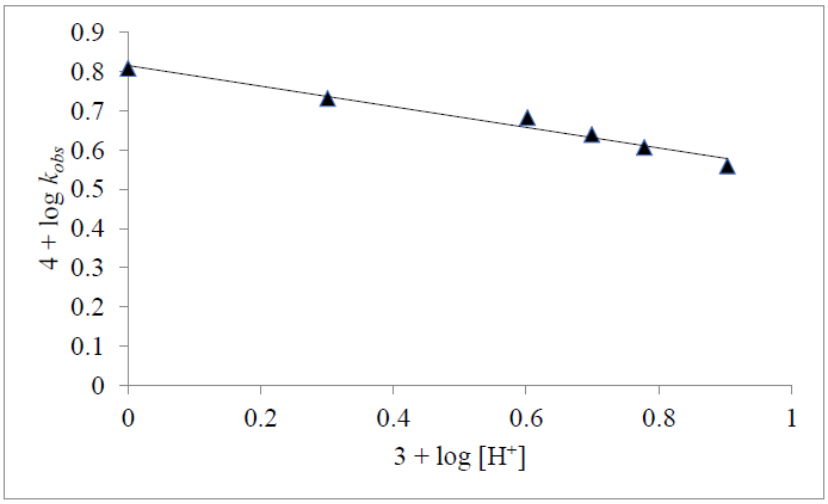



Fig. 3 – The plots of log $k_{obs}$ versus log [H⁺] for the reaction condition. [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [Ala] = $5\times10^{-4}$ mol dm$^{-3}$, [CTAB] = $10\times10^{-4}$ mol dm$^{-3}$, [Hg$^{++}$] = $2\times10^{-4}$ mol dm$^{-3}$, $CH_3COOH$ = 50%, Temperature = 308 K.

$$\log k_{obs} = \log k_0 - \frac{Z_A Z_B e^2 N}{2.303 (4\pi\varepsilon_0) d_{AB} DRT} \quad (B)$$

where $k_0$ is the rate constant in a medium of an infinite dielectric constant, $Z_A$ and $Z_B$ are the charges of reacting ions, $d_{AB}$ refers to the size of an activated complex, T is absolute temperature, and D is the dielectric constant of the medium. A plot is made between log $k_{obs}$ and 1/D; a straight line having a negative slope was obtained, indicating an interaction between a charged ion and a dipolar molecule. From the slope of the straight line, the $d_{AB}$ value has been calculated and found to be 8.14 Å (Fig. 4).

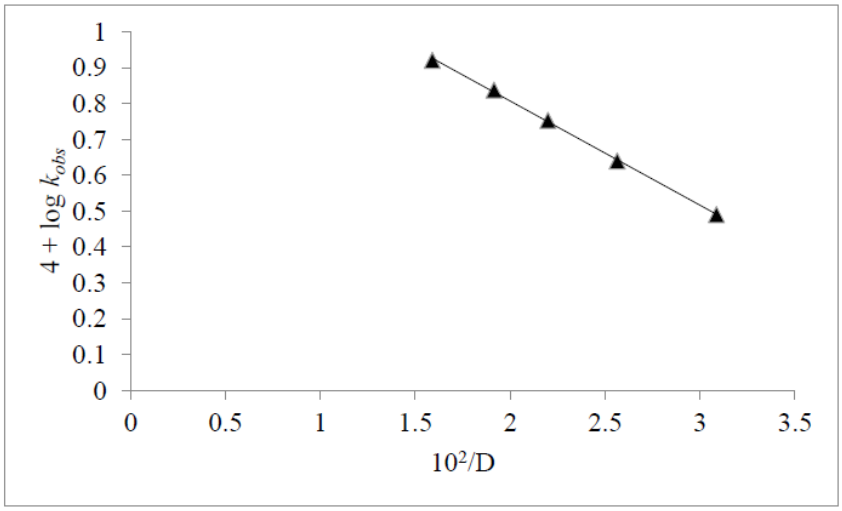



Fig. 4 – The plots of log $k_{obs}$ versus 1/D for the reaction condition. [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [Ala] = $5\times10^{-4}$ mol dm$^{-3}$, [H⁺] = $5\times10^{-3}$ mol dm$^{-3}$, [CTAB] = $10\times10^{-4}$ mol dm$^{-3}$, [Hg$^{++}$] = $2\times10^{-4}$ mol dm$^{-3}$, Temperature = 308 K.

***Test for free radicals*:** The generation of free radicals during the course of the oxidation was confirmed by using acrylonitrile monomer. A known amount of acrylonitrile was added to a reaction mixture containing NBP, Ala, $HClO_4$, and acetic acid. No precipitate was found in the reaction mixture. This indicates that free radicals are not formed in the reaction mixture.

***Effect of inorganic electrolytes***: The simplest possible aggregate of surfactant molecules is the micelle.[24] At the molecular level, a balance of interfacial forces controls the curvature of the surfactant film, which, in turn, determines the shape of the surfactant aggregates. It is now accepted that micelles are spherical near critical micellar concentration (CMC).[25] The transition from

spherical to larger micelles for ionic surfactants occurs upon a reduction of interhead-group repulsion.[26,27] It may be caused by salt[28] or surfactant additions[29-30] or solute solubilization.[31,32] It is not clear if, at a fixed surfactant concentration, micellar growth by increasing salt concentration is because of enhanced screening of the electrostatic interactions or due to a change in "electrical charge per head group". The salt effect on the Ala-NBP reaction was studied in the presence of CTAB micelles ($10 \times 10^{-4}$ mol dm$^{-3}$) at 308 K, keeping other variables constant. The addition of electrolytes, such as KBr or KCl, in the presence of an ionic surfactant, to the surrounding solution at first acts primarily to modify interactions between micelles. Micelles with charged surfaces bind counterions selectively, and their solution properties, such as size and morphology, phase stability, etc., are sensitive to counterion concentration and type. These changes are likely a result of differing interactions of the counterions with the charged head groups in the Stern layer. However, at sufficiently elevated salt concentrations, micelles grow above their size in pure water. The salt effect on micellar catalysis should be considered in light of its competition with the substrate molecule, which interacts with the micelle electrostatically and hydrophobically, and structural changes, which occur on salt addition.[33] 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. Micellar catalysis can be enhanced by adding some salts, indicating that the rate enhancement is sensitive to changes in micellar morphology and charge density,[34] *i.e.*, positive effects of [Br$^-$] and [Cl$^-$] on the oxidation velocity were found. The results are presented in Table 2.

*Table 2*

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

| [KX] × 10$^8$ | $k_{[Cl^-]} \times 10^4$ | $k_{[Br^-]} \times 10^4$ |
|---|---|---|
| mol dm$^{-3}$ | s$^{-1}$ | s$^{-1}$ |
| 1.0 | 4.62 | 4.65 |
| 2.0 | 4.99 | 5.10 |
| 4.0 | 5.72 | 5.82 |
| 6.0 | 6.39 | 6.55 |
| 8.0 | 7.140 | 7.32 |

Solution conditions: [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [Ala] = $5\times10^{-4}$ mol dm$^{-3}$, [H$^+$] = $5\times10^{-3}$ mol dm$^{-3}$, [CTAB] = $10\times10^{-4}$ mol dm$^{-3}$, [Hg$^{++}$] = $2\times10^{-4}$ mol dm$^{-3}$, $CH_3COOH$ = 50%.

## Activation Parameters

Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. The reactions were studied at different temperatures (303–323 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 the Eyring equation (Table 3). The value of Ea in the presence of CTAB shows the catalytic effect on the rate of reaction. The negative value of $\Delta S^{\#}$ in the presence of a cationic surfactant indicates that a more ordered activated complex is formed. The fairly positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ indicate that the transition state is highly solvated. The value of energy of activation shows that the reaction is slow and enthalpy is controlled. The values of activation parameters show that the activated complex so formed is more bulky in the presence of surfactant.

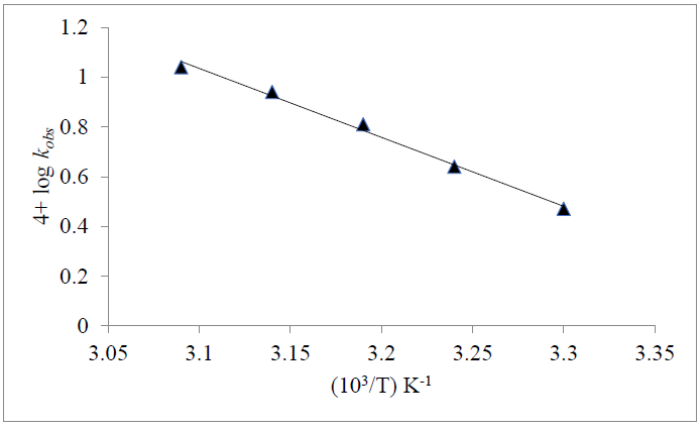



Fig. 5 – Arrhenius plots log $k_{obs}$ versus (1/T) for the reaction condition. [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [Ala] = $5\times10^{-4}$ mol dm$^{-3}$, [H$^+$] = $5\times10^{-3}$ mol dm$^{-3}$, [CTAB] = $10\times10^{-4}$ mol dm$^{-3}$, [Hg$^{++}$] = $2\times10^{-4}$ mol dm$^{-3}$, $CH_3COOH$ = 50%.

*Table 3*

Activation parameters for CTAB catalyzed reactions of oxidation of L-ala by NBP

| Parameters | $k \times 10^4$ $s^{-1}$ |
|---|---|
| 303 | 2.95 |
| 308 | 4.37 |
| 313 | 6.46 |
| 318 | 8.71 |
| 323 | 10.96 |
| $\Delta E_a$ (kJ $mol^{-1}$) | 50.93 |
| $\Delta H^{\#}$ (kJ $mol^{-1}$) | 48.28 |
| $\Delta S^{\#}$ ($JK^{-1}$ $mol^{-1}$) | –35.21 |
| $\Delta G^{\#}$ (kJ $mol^{-1}$) | 59.48 |
| log $P_Z$ | 5.30 |

Solution conditions:
[NBP] = $1\times10^{-4}$ mol $dm^{-3}$, [Ala] = $5\times10^{-4}$ mol $dm^{-3}$, $[H^+]$ = $5\times10^{-3}$ mol $dm^{-3}$, [CTAB] = $10\times10^{-4}$ mol $dm^{-3}$, $[Hg^{++}] = 2\times10^{-4}$ mol $dm^{-3}$, $CH_3COOH$ = 50%.

***Binding Constant***. The binding constant $K_S$ depends on the extent of hydrophobic bonding between the surfactant and substrate. It can be expected that $K_S$ will increase with an increase in the chain length of both the surfactant and the substrate. However, if the hydrophobic group of the substrate is too long, it may be solubilized so deeply in the micelle that access to its reactive site by a reagent in the aqueous solution phase is hindered, and, therefore, solubilization will inhibit the reaction.[35] In this paper we calculate the binding constant ($K_S$) to be $1.06 \times 10^4$ $M^{-1}$ and the taken kinetic CMC to be 1.5 mol $dm^{-3}$.

## MECHANISM

*N*-halophthalimides have been used in organic synthetic methodology, especially in the oxidation and bromination reactions. In most cases, these reagents are converted to phthalimide at the end of reactions as a nontoxic chemical. It had been reported earlier by several workers[36–42] that NBP is an oxidizing and brominating agent because of the large polarity of the >N–Br bond. NBP capable of producing $Br^+$ reasonably shows that NBP, like other similar N-halo imides, may exist in various forms in acidic medium, that is, free NBP, protonated NBP, $Br^+$, HOBr, and $(H_2OBr)^+$, as per the following equilibria:

$$NBP + H^+ \rightleftharpoons NHP + Br^+ \quad (C)$$

$$NBP + H^+ \rightleftharpoons (NBPH)^+ \quad (D)$$

$$NBP + H_2O \rightleftharpoons HOBr + NHP \quad (E)$$

$$HOBr + H^+ \rightleftharpoons (H_2OBr)^+ \quad (F)$$

Since on assumption of NBP or $(NBPH)^+$ as the reactive species, the rate law fails to explain the negative effect of phthalimide. Hence, neither of these species, NBP and $(NBPH)^+$ can be taken 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. When HOBr is taken as the reactive species, the rate lawfully explains negative effect of $[H^+]$ and [NHP]. Thus, HOBr is taken as the most reactive species, which gives the rate law capable of explaining all the kinetic observation and other effects. In light of kinetic observations, HOBr can safely be assumed to be the main reactive species of NBP for the present reaction. On the basis of the above experimental findings (Scheme 2), it can be proposed for a micellar effect on the kinetics of oxidation of Ala by NBP in an acidic medium.

The rate of disappearance of NBP is given as

$$\frac{-d[NBP]}{dt} = \frac{kK_1K_2[Ala][NBP]_T}{[NHP][H^+] + K_1K_2[Ala] + K_1[H^+]} \quad (8)$$

where $[NBP]_T = [NBP] + [HOBr] + [X^-]$.

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

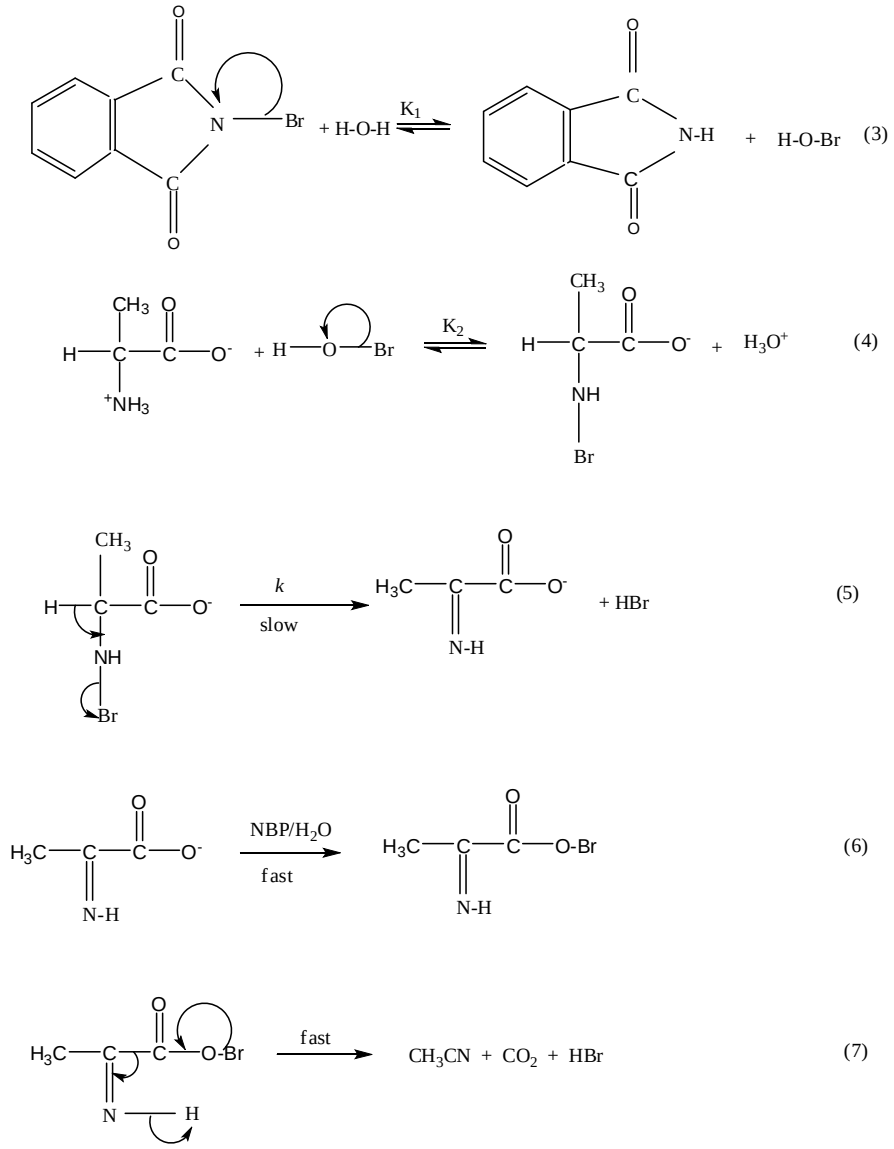
$$\text{rate} = k'[NBP]_T$$

$$k' = \frac{\text{rate}}{[NBP]_T} = \frac{kK_1K_2[Ala]}{[NHP][H^+] + K_1K_2[Ala] + K_1[H^+]} \quad (9)$$

$$\frac{1}{k'} = \frac{[NHP][H^+]}{kK_1K_2[Ala]} + \frac{1}{k} + \frac{[H^+]}{kK_2[Ala]} \quad (10)$$

According to equation (10), if a plot is made between $1/k'$ and $[H^+]$ or 1/[Ala], then a straight line having a positive intercept on the$1/k'$ axis should be obtained. When $1/k'$ values are plotted against $[H^+]$ and 1/[Ala], straight lines with positive intercepts on the $1/k'$ axis are obtained (Figs. 6 and 7), which clearly proves the validity of the rate law expression equation (8) and hence the proposed mechanism. In the equation (8); denominator represents the partitioning of the NBP reagent among its various forms in the solution. From the slopes and intercepts of the straight line, the values of $k$, $K_1$ and $K_2$ have been calculated and found to be $6.99 \times 10^{-4}$ $s^{-1}$, $9.9 \times 10^4$ mol $dm^{-3}$, and $8.94 \times 10^2$ mol $dm^{-3}$, respectively. The $K_1$ and $K_2$ represents the equilibrium constant for active species

and intermediate complex respectively; they show how much intermediate is formed before the main reaction. The above rate law is in good agreement with the experimental results in absence of surfactant.




Scheme 2 – The reaction mechanism for the reaction between Ala and NBP in the acidic medium.

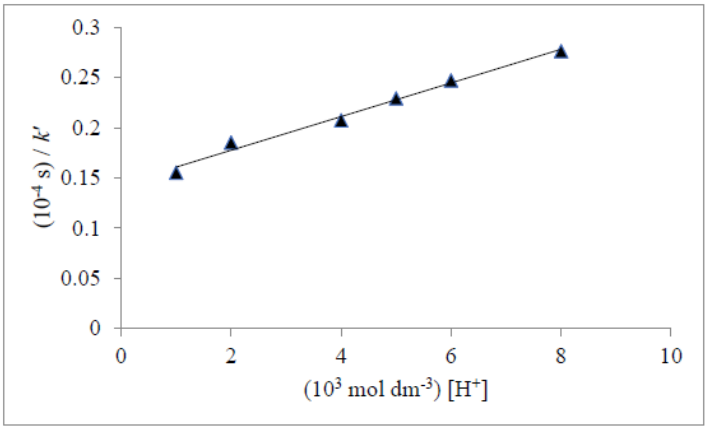



Fig. 6 – The plot of $1/k'$ *versus* $[H^+]$ for the reaction condition. [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [Ala] = $5\times10^{-4}$ mol dm$^{-3}$, [CTAB] = $10\times10^{-4}$ mol dm$^{-3}$, $[Hg^{++}] = 2\times10^{-4}$ mol dm$^{-3}$, $CH_3COOH$ = 50%, Temperature = 308 K.

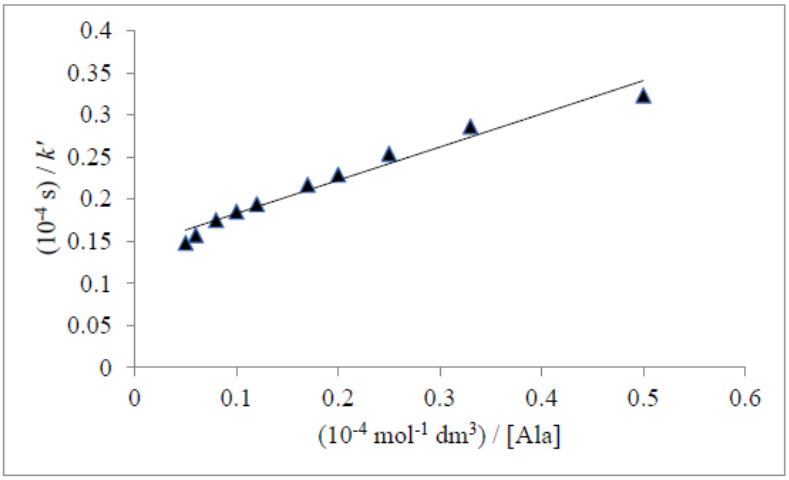



Fig. 7 – The plot of $1/k'$ *versus* 1/ [Ala] for the reaction condition. [NBP] = $1\times10^{-4}$ mol dm$^{-3}$, [$H^+$] = $5\times10^{-3}$ mol dm$^{-3}$, [CTAB] = $10\times10^{-4}$ mol dm$^{-3}$, [$Hg^{++}$] = $2\times10^{-4}$ mol dm$^{-3}$, $CH_3COOH$ = 50%, Temperature = 308 K.

## CONCLUSION

In the light of kinetic observations of the micellar effect of the kinetics of oxidation of Ala by N-bromophthalimide in the presence of perchloric acid, the following conclusions can easily be drawn: the reactive species of oxidant NBP is HOBr, not NBP itself. Oxidation products were identified, and activation parameters were evaluated for the catalyzed reaction. The critical micelle concentration values are much lower than those given in the literature for aqueous solutions of CTAB without added electrolyte. The rate of oxidation increases with increasing concentration of CTAB. In conclusion, it can be said that the cationic micelle of CTAB is an efficient catalyst for the oxidation of alanine by NBP in an acidic medium.

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