In the Presence of Sodium Dodecyl Sulfate : A Kinetic and Mechanistic Study

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Abstract

Kinetics of oxidative degradation of ethylenediaminetetraaceticacid (EDTA) by *N*-bromophthalimide (NBP) has been investigated in the presence of Sodium Dodecyl Sulfate in acidic medium at 298 K. The reaction shows first-order with respect to [NBP] and fractional order dependence on [EDTA] and inverse fractional order on [H^+]. The rate of reaction decreases with decrease in dielectric constant of the medium. Ethylene was identified as the main oxidation product of the reaction. Various oxidation products have been calculated with pseudo first order rate constants. The micelle binding constant has been calculated. The proposed mechanism and the derived rate law are steady with the observed kinetic data. The proposed reaction mechanism is well supported by kinetic data, spectrophotometric evidence and positive entropy of activation.

Keywords: NBP, EDTA, SDS, Oxidation, Kinetics, acid medium

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INTRODUCTION

The chemistry of aromatic sulphonyl halo amides or imides has considerable interest as they are the sources of hypohalite species, N anions and halonium cations which act both as bases and nucleophiles. The main groups are chloramine - T (CAT) and chloramine B (CAB). The mechanistic study of many of these reactions have been reported [1,2,3]. Bromamine- B is a mild oxidising agent and is found to be better oxidising agent than the chloro compounds.

The investigation of the redox reactions of organic sequestering agents such as EDTA with various oxidizing agents have been mentioned by Hanna et al [3] and Rao and Jagannadham [3] have been shown that HCHO and CO_2 are formed in the oxidation of EDTA by Ce(IV).The disodium salt of ethylenediaminetetraacetic acid Na_2H_2Y or EDTA is known as oxidising as well as chelating agent in complexometry reactions and is used for the identification of numeral of metal ions. Sanehi et al [4] have carried out a systematic investigation of the oxidation of EDTA with Chloramine – T (CAT) in acetate buffer medium, but products have not been identified. The Fe (III) catalysed oxidation of EDTA in aqueous solution at elevated temperatures (100–170^{0}C) has shown formation of EDTA [5]. During the oxidation of EDTA with a suspension of PbO_2 in H_2SO_4, formation of HCHO, CO_2 and N- hydroxyl-methylethyldiamine was observed [6]. The kinetic study of oxidation of glycine and L- alanine by NBP in the presence of SDS was reported in the earlier work [7].

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. The effects of surfactant and its micelle on chemical reactions are an interesting field of research

for chemists and biologists [8, 9]. There is an widespread evidence on the ability of micelles and other associated colloids to influence the reaction rates, equilibrium, concentration or depletion of the reactants in the interfacial region [10 - 21]. Micellar effects on the rates are sensitive to the nature of counter ions and to head group bulk [22]. The Transition of spherical to larger micelles may be caused by salt additions or solute solubilization [23, 24]. The addition of a salt decreases the electrostatic interactions between monomers in the micelle and also affects the partition of organic compounds between micelle and bulk solvent [25].

The aim of the present study is to propose the most probable reaction path for the kinetics of oxidation of EDTA by NBP in micellar system in the presence of SDS. It also aims to derive the promising mechanism and to study the effect of SDS micelle on the rate of oxidation

EXPERIMENTAL

A standard solution of SDS was prepared by dissolving required amount of SDS in a double distilled water. A standard solution of EDTA(SD fine) was prepared by using double distilled water and standardised by recognized method. An aqueous solution of NBP was prepared in 80% distilled acetic acid and stored in brown bottles to prevent photochemical decompositions. The prepared solution was then standardised iodometrically against $Na_2S_2O_3$ using starch as an indicator. Perchloric acid (G.R.) diluted with double distilled water and was standardized by acid-base titration. All other solutions such as KCl, KBr and $NaClO_4$ were prepared in double distilled water by dissolving necessary amounts of samples

Kinetic runs were performed under pseudo-first order conditions where concentration of EDTA was at least 10 fold excess over [NBP] at a constant temperature 25^0C. The appropriate amount of the reactants solutions such as [EDTA], [SDS], [$NaClO_4$] and water to keep the total volume constant for all runs were taken in the black coated conical flasks and thermostated at 298 K for thermal equilibrium. A measured amount of NBP solution was also thermostated at the same temperature was rapidly added to the reaction mixture. The progress of the reaction was followed by measuring the amount of unconsumed NBP iodometrically in aliquots withdrawn from the reaction mixture at regular time intervals. The remaining NBP was carried out upto 70% completion of the reaction. The pseudo-first order rate constants were determined from the plots of log [NBP] vs time. The first order rate constant was premeditated from the slopes of these plots in presence of surfactant. The observed rate constants were reproducible within ± 5% in duplicate kinetic run. Such plots were linear upto 65% completion of the reaction, after that deviate from the linearity due to retarding effect of the product phthalimide.

RESULTS AND DISCUSSION

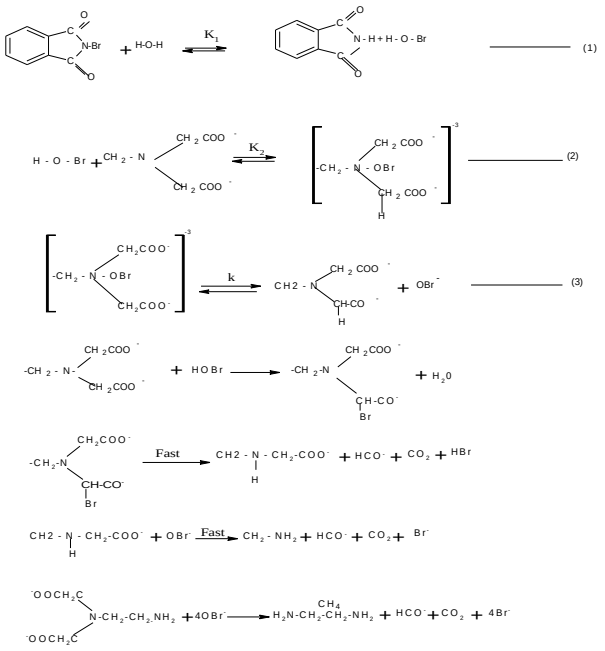
Different sets of experiments were performed with varying [NBP]: [EDTA] ratios under the condition [EDTA] >> [NBP]. Estimation of unconsumed NBP indicated that 1 mole of NBP was consumed to oxidise two mole of EDTA (1:2). The main oxidation product of the reaction were phthalimide, ethylene diamine and formic acid by spot test [26]. The addition of phthalimide in the range of 2.0×10^{-3}- 10.0×10^{-3} mol dm^3 at constant concentration of reactants and other conditions being constant, decreases the rate of the reaction. But the other products such as bromide, ethylene diamine and formic acid have no significant effect on the rate of the reaction. The liberated CO_2 was detected by lime water test. The reaction mixture was unsuccessful to begin polymerization of aqueous acrylamide solution, indicating the absence of free radicals.

The rate of oxidation reaction was found to be first order with respect to NBP in all the cases studied and was found to be increased with increase in concentration of NBP. The plots of $\log(a - x)$ vs time were found to be straight lines, indicating that the order with respect to the oxidant was unity and the order of all the reactive species were determined from the plots of $\log k$ vs log (concentration). The rate of reaction increased with increasing [EDTA] (Table 1).

The rate constant decreased with increasing concentration of SDS. The reported critical micelle concentration of SDS is 8.1×10^{-3} mol/dm^3 at 298K. The addition of phthalimide a reduced product of the oxidant decreases the rate of reaction. The effect

of ionic strength is found to be zero since the reaction takes place between the neutral and charged species reduces the CMC on the rate of reaction. The salt effect on micellar catalysed reactions has been rationalised by assuming a competition between the reactant and the counter ions for a binding site on or in the micelle. The substrate molecule interacts with the micelle electrostatically and hydrophobically. The structural changes occur on salt addition [27] due the positive effect of chloride and bromide on the oxidation of the reaction (Table 1).

On the basis of above experimental conditions HOBr is taken as the most reactive species of NBP. The **scheme 1** can be proposed for micellar effect of kinetics and oxidation of EDTA by NBP in acid medium.



MECHANISM

The NBP is good oxidising and brominating agent as reported earlier by several workers [28 – 43] because of large polarity of N – Br bond. NBP may exist in various forms in acid medium as shown below

$$NBP + H^+ \rightleftharpoons NHP + BR^- \quad \text{——— 4}$$

$$NBP + H^+ \rightleftharpoons (NBPH^+) \quad \text{——— 5}$$

$$NBP + H_2O \rightleftharpoons HOBr + NHP \quad \text{——— 6}$$

$$HOBR + H^+(H_2OBR)^+ \quad \text{——————} \quad 7$$

Addition of phthalimide decreases the rate of oxidation in acidic media suggesting that the free equilibrium step involves a process, in which phthalimide is one of the product. When NBP or $NBPH^+$ is assumed as the reactive species the derived rate laws failed to explain the negative effect of phthalimide. Kinetics with respect to hydrogen ion concentration controversy to our observed negative fractional order in $HClO_4$, although it fully explains the negative effect of the phthalimide. Therefore the possibility of cationic bromine as a reactive species is studied. Thus the choice of HOBr which when considered as the reactive species of NBP gives a rate law capable of explaining all the kinetic observations and other effects. The dissociation of NBP depends upon the pH of the solution in strongly acidic or alkaline medium. Under the experimental condition the concentration of anion formed is very low and possibility of its participation in the reaction will be learnt and the possible reactive reducing species may be a cation form. Further, the main reactive species and the rate law deduce would show a dependence on experimental results. Thus the only possible active species controlling the rate of oxidation to be zwitter ion.

Thus, according to **scheme 1,** the kinetics of this reaction seems to be consistent with the above mechanism. The addition of phthalimide a reduced product of the oxidant decreased the rate of reaction (Table 2). The negligible effect of ionic strength on the reaction is mainly due to the fact that the reaction takes place between a neutral and charged species.

The title reaction obeys the following rate law:

The rate of disappearance of NBP is given as

$$-\frac{d[NBP]}{dt} = \frac{kK_1K_2[EDTA]\,[NBP]_T}{[NHP]\,[H^+] + K_1K_2[EDTA] + K_1[H^+]} \quad .....8$$

Where $[NBP]t = [NBP]+[HOBr]+[X^-]$ 9

The above rate law is in good agreement with the

experimental results in the absence and the presence of surfactant.

$$\text{Rate} = k_1 [NBP]t \quad \text{.....10}$$

$$k^1 = \frac{\text{rate}}{[NBP]_t} \quad \text{.....11}$$

$$= \frac{k K_1 K_2 [EDTA]}{[NHP][H^+] + K_1 K_2 [EDTA] + K1[H^+]} \quad \text{.....12}$$

$$\frac{1}{K^1} = \frac{[NHP][H^+]}{k K_1 K_2 [EDTA]} + \frac{1}{k} + \frac{[H^+]}{k K_2 [EDTA]} \quad \text{....13}$$

According to Eq. (13) the plots of 1/*k*' Vs 1 / [EDTA] and 1/*k*' Vs [H^+] is a straight line having a positive intercept on the 1/*k*' axis should be obtained (Fig.1 & 2), which clearly proves the validity of the rate law expressions Eq.(12). From the slopes and intercepts of the straight line the values of *k*, K_1 and K_2 have been calculated and found as 5.25 x 10^{-4} s^{-1}, 1.3 x 10^{-1} and 8.63 x 10^{-4} respectively. Using these values, the rate constants over different conditions have been calculated and agree with the experimental rate constants. The value of K_1 is in agreement with earlier report [47].

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 the value of activation energy (E_a) was calculated and the values of $\Delta S^{\#}$ and $\Delta G^{\#}$ were computed from Eyring equation (Table 3). A advanced value of E_a in presence of SDS shows that the inhibition effect on the rate of the 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 (Table 3).

Table 1: The effect of [NBP], [EDTA] and [SDS] on the oxidation of EDTA by N bromophthalimide in acidic medium at 25°C. I = 0.05 mol / dm³

EDTA X10⁻³ moldm⁻³	NBP 10⁻⁴ moldm⁻³	SDS X10-3 mol /dm⁻³	k x10⁻⁴ s⁻¹	
			Experimental	Calculated
0.5	2.0	5.0	0.50	0.45
2.0	2.0	5.0	1.50	1.8
3.0	2.0	5.0	2.70	2.7
4.0	2.0	5.0	3.30	3.62
5.0	2.0	5.0	3.60	4.3
10.0	0.5	5.0	1.90	1.90
10.0	2.0	5.0	2.00	1.83
10.0	3.0	5.0	2.10	2.7
10.0	4.0	5.0	2.00	3.6
10.0	5.0	5.0	2.20	4.5
10.0	2.0	1.0	1.50	0.52
10.0	2.0	3.0	2.00	1.56
10.0	2.0.	5.0	2.60	2.6
10.0	2.0\	7.0	3.40	3.64
10..0	2.0	9.0	4.10	4.68

Table 2 : Effect of product phthalimide on the oxidation of EDTA by NBP in aqueous

Alkaline medium at 25°C.

[EDTA] = 5 X10^{-4}, [NBP] = 3X10^{-3}, [H+] = 3X10^{-3}, I = 0.05 mol /dm^3

[hthalimide] x 10^3 mol / dm^3	10^3 x k_{obs} s^{-1}	
	Expt*	Calc*
2	3.25	3.28
4	2.86	2.80
6	1.62	1.66
8	1.45	1.51
10	0.76	0.73

* Experimental and calculated values, error ± 5%

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

Conditions: [NBP] = 1 x 10^{-4}moldm^{-3}, [EDTA] = 5 x10^{-4}moldm^{-3}, [H^+] = 5 x 10^{-3}moldm^{-3}, [SDS] = 8.1 x 10^{-3}moldm^{-3}, [Hg^{2+}] = 2 x 10^{-4}moldm^{-3}, [CH_3COOH] = 50%.

T (K)	*k* x10^4 s^{-1}	
	In absenceof surfactant	In presenceof surfactant
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
"E_a, kJ mol^{-1}	47.09	51.6
"$H^{\#}$, kJ mol^{-1}	44.42	55.9
"$S^{\#}$, J $K^{-1}mol^{-1}$	-31.92	–35.4
"$G^{\#}$, kJ mol^{-1}	50.76	51.45

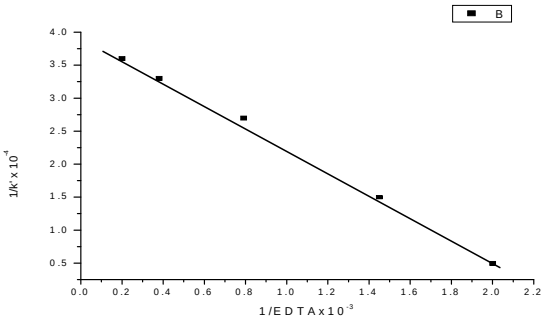


Fig. 1 The plot of 1/*k*' Vs 1 / [EDTA]

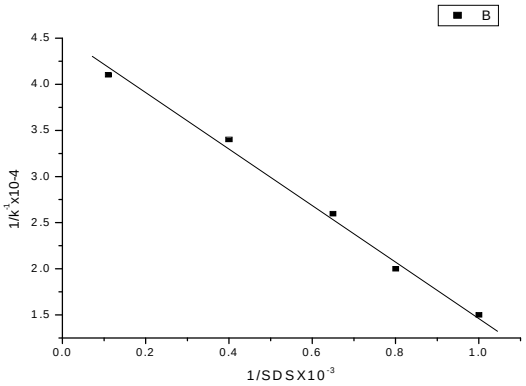


Fig. 2 The plot 1/ *k*' Vs [H^+]

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. The critical micelle concentration values of the surfactant (SDS) were determined conductometrically (Digital conductivity meter) 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 x 10^{-3}moldm^{-3} in reaction mixture for EDTA. 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 previous observations of micelle formation at relatively low surfactant concentration [44-46].

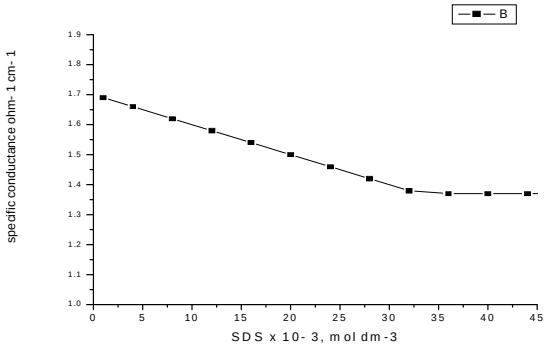


Fig 3 : Effect of variation of SDS on reaction conditions with[NBP] = 3 x 10^{-3}moldm^{-3}, [EDTA] = 3 x 10^{-4}mol dm^{-3}, [H^+] = 5 x 10^{-3}moldm^{-3}, [CH_3COOH] = 50%, *T* = 308 K.

COMPARATIVE STUDIES

The present study with respect to EDTA on the rate of oxidation by NBP was similar with the reported SDS catalyzed oxidation of glycine by NBP [47], but the rate of the reaction decreases with increase in the concentration of EDTA. HOBr act as a reactive species of NBP. In this case ionic strength had no effect on the oxidation velocity. It was also observed that binding constant of EDTA oxidation is higher than Alanine oxidation and the rate of oxidation of EDTA was lesser than that of alanine.

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