

A kinetic and mechanistic study on the Oxidation of EDTA by N–Bromosuccinimide in the Presence of Acid and Alkaline Medium– A comparative study

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Abstract: The oxidation of ethylene diamine tetra acetic acid (EDTA) by N– bromosuccinimide (NBS) in acidic and in alkaline medium at constant ionic strength using sodium dodecyl sulfate has been studied tritrimetrically. In both medium the order of the substrate is remains same. The SDS has increasing effect on the rate of reaction in the acid medium compared to alkaline medium. The reaction exhibit 8:1 stoichiometry and follow first order kinetics in [NBS]. The dependence of the rate on substrate concentration and media has been found from Arrhenius plots. To calculate thermodynamic parameters the reaction has been studied at four different temperatures. The reactive species hypobromite ion of the oxidant has been proposed in the mechanism. The derived rate law is consistent with the observed kinetic data.

Keyword: Kinetics, Reaction Mechanism, Oxidation, EDTA, NBS, SDS

INTRODUCTION

The substrate disodium salt of ethylenediaminetetra acetic acid or Na₂H₂Y is well known as a chelating agent in complexometry reactions and is engaged for detection of number of metal ions. The exploration of the redox reactions of EDTA with various oxidizing agents have been studied by Hanna et al [1] and Rao. In the oxidation of the substrate by Ce(IV), the main products HCHO and CO₂ found by Jagannadham [2]. In acetate buffer medium Sanehi et al [3] have carried out a efficient investigation of the oxidation of EDTA with Chloramines – T(CAT), but products have not been recognized. The Fe(III) catalyzed oxidation of EDTA in aqueous has been exposed for the formation of ethylene demine tetra acetic acid [4]. During the oxidation of EDTA with a suspension of PbO₂ in H₂SO₄, formation of HCHO, CO₂

and N- hydroxyl were observed [5]. Hence, different workers have identified various oxidants to study the oxidation of EDTA in acid and alkaline medium.

In chemical reactions the special effects of surfactant and its micelle are an interesting field of research for chemists and biologists [6,7]. The reaction rates, equilibrium, concentration or depletion of reactants in the interfacial region has widespread data on the capability of micelles and other related colloids [8-14]. The Transition of spherical to larger micelles may be caused by salt or surfactant additions [15]. It is also known that the addition of a salt decreases the electrostatic interactions between monomers in the micelle and also affects the separation of organic compounds between micelle. Micellar catalysis can be enhanced by adding some salts indicating that the rate

improvement is responsive to changes in micellar morphology and charge density [16].

For allylic chlorination and oxidation of organic compounds a large number of N-haloimides or amides including some N-fluoro compounds have been prepared and tested as reagents. N-bromosuccinimide (NBS) has been used as a potent oxidizing agent and analytical reagent especially in acid medium [17] as well as in alkaline medium [18]. However, there are only few reports on the oxidation of L-Alanine in the presence of SDS (19). In view of these facts, there is a scope for the study of reactions with NBS to get better insight of NBS reaction by using sodium dodecyl sulfate and to understand its redox chemistry. Herein, we report a comparative study of the kinetics of oxidation of EDTA with NBS in alkaline and acid medium to derive the mechanism of the reaction to elucidate appropriate rate law to identify the oxidant product of the reaction and to establish the reactive species of the oxidant.

EXPERIMENTAL

An aqueous solution of NBS was prepared afresh each day and standardized against sodium thiosulphate by the iodometric method. All the reagents were of analytical grade and their solutions were prepared by dissolving requisite amounts of samples in doubly distilled water. NaOH and NaClO₄ were used to provide the essential alkalinity and ionic strength respectively. Succinimide was prepared by a known method. Solution of EDTA was prepared by dissolving appropriate amount by using double distilled water and standardized by known process. From aqueous stock solution of substrate the required concentration of EDTA was prepared. A standard solution of SDS was

prepared by dissolving necessary quantity in double distilled water.

Kinetic Measurements

All kinetic measurements were performed in stoppered glass pyrex boiling tubes coated black to eliminate photo chemical effects. The reaction was initiated by mixing formerly thermostated solutions of NBS, SDS and EDTA which also contained the necessary quantities of NaOH and NaClO₄ to maintain requisite alkalinity and ionic strength respectively. The reactions were carried out by taking a known excess of [EDTA] over [NBS] at constant ionic strength of 0.05 mol dm⁻³ at 25^oC under pseudo first order conditions. The progress of the reaction was followed by iodometric determination of unreacted oxidant in aliquots (5ml each) of the mixture at regular time intervals. The plots of log [NBS] versus time give the pseudo first order rate constants and were reproducible within ± 5%. The retarding effect of one of the product i.e., succinimide deviate from linearity after 75% completion of the reaction. The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture in an atmosphere of nitrogen and in the presence of air. In spite of little contamination of carbonate in basic solutions, the effect of carbonate on the reaction was also studied and added carbonate had no effect on the reaction rate. However, fresh solutions were used while conducting the experiments.

RESULTS AND DISCUSSION

Varying the ratios of NBS and EDTA in the presence of NaOH, HClO₄ and SDS were kept to react for 48 hrs at 25^oC. The stoichiometry of the reaction had been studied under the kinetic condition of

[EDTA] >> [NBS]. After completion of the reaction, estimation of the unreacted NBS and EDTA were assayed as mentioned earlier. The results showed that eight mole of NBS consumes one moles of EDTA (8:1).

The products in the reaction mixture were extracted several times with ether. The combined ether extract was evaporated and subjected to column chromatography in silica gel (60-200 mesh) using gradient elution (chloroform). After initial separation, the solid product was further purified by recrystallization. The reduction product of NBS was succinimide (CH₂CO₂NH) and oxidation product of EDTA were identified by spot test [20] as formic acid and ethylene diamine and confirmed by TLC [21].

The effect of initially added product succinimide was studied in the range of 0.2 x 10⁴ to 2.0 x 10⁴ mol / dm³, keeping all other concentrations constant. It was found that the added product had retarding effect on the rate of reaction. The order of all the

reactive species were determined from the plots of log k_c vs log (concentration) other than oxidant. The observed rate constants k in alkaline medium and k₁ in acidic medium and various initial concentrations are given in Table 1. The identical value of k or k₁ at various initial [NBS] further confirmed a first order dependence of rate with respect to NBS in alkaline or acidic media.

The effect of ionic strength and solvent polarity in the reaction media did not show any remarkable effect on the rate of the reaction. The [OH⁻] results in an increased effect on the observed rate constant at fixed ionic strength (k or k₁) and Sodium dodecyl effect is negligible (Table 1).

The title reaction obeys the following experimental law:

$$-\frac{d[\text{NBS}]}{dt} = \frac{k_3[\text{NBS}]_r[\text{EDTA}][\text{H}_2\text{O}]}{[\text{NH}] + K_1[\text{H}_2\text{O}]\{[1+K_2[\text{EDTA}]]\}}$$

According to scheme 1, the experimentally obtained orders can be well accommodated.

Table .1 Effect of [NBS], [EDTA], [SDS], [HClO₄] and [OH⁻] on the oxidation of EDTA by N-bromosuccinimide in acid and alkaline media at 25 °C. I = 0.05 mole dm⁻³.

NBS x 10 ⁻³ mol/dm ⁻³	EDTA X 10 ⁻⁴ mol/dm ⁻³	SDS X 10 ⁻³ mol /dm ⁻³	k ₁ X 10 ⁻⁴ mol/dm ⁻³ (acid medium)		k X 10 ⁻⁴ mol/dm ⁻³ (alkaline medium)	
			[HClO ₄]10 ² mol/dm ⁻³	Experimental	[OH ⁻] 10 ³ mol/dm ⁻³	Calculated
0.5	10	5.0	2.0	1.88	2.0	5.20
1.0	10	5.0	2.0	1.9	2.0	5.20
2.0	10	5.0	2.0	2.0	2.0	5.20
3.0	10	5.0	2.0	2.3	2.0	5.20
4.0	10	5.0	2.0	1.9	2.0	5.20
5.0	10	5.0	2.0	2.0	2.0	5.20
15	0.7	5.0	2.0	4.9	2.0	2.69
15	2.0	5.0	2.0	5.2	2.0	3.83
15	3.0	5.0	2.0	5.5	2.0	5.20
15	6.0	5.0	2.0	6.3	2.0	5.80
15	7.0	5.0	2.0	7.8	2.0	6.39

15	10	1.0	2.0	1.9	2.0	4.22
15	10	4.0	2.0	2.4	2.0	4.20
15	10	6.0	2.0	3.4	2.0	4.30
15	10	8.0	2.0	4.4	2.0	4.40
15	10	10.0	2.0	5.0	2.0	4.30
15	10	12.0	2.0	5.6	2.0	4.20
15	10	5.0	0.5	1.97	2.0	3.84
15	10	5.0	1.0	1.98	0.5	4.80
15	10	5.0	2.0	1.98	1.0	5.20
15	10	5.0	3.0	1.95	1.5	6.22
15	10	5.0	4.0	1.92	2.0	7.68
15	10	5.0	5.0	1.96	3.0	8.66

Mechanism in alkaline medium

The oxidant NBS is known to exist in the following equilibria. NBS itself or OBr^- is supposed to be the reactive species of NBS in alkaline medium in the absence of mercuric acetate.

Mechanism of alkaline medium

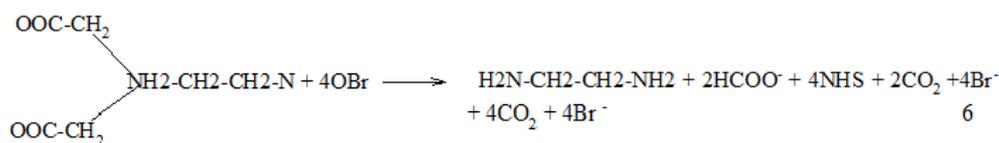
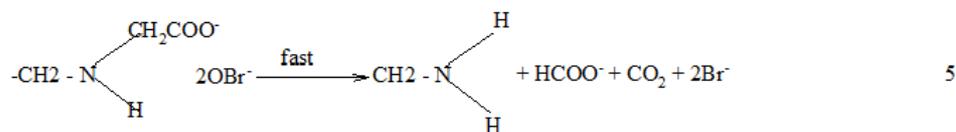
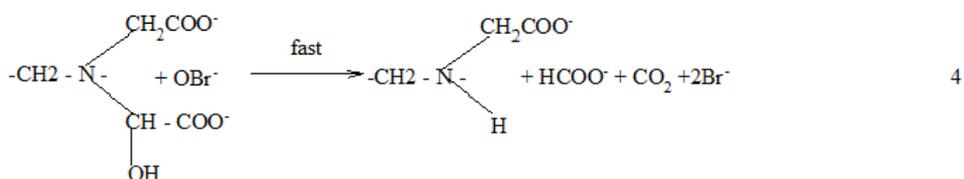
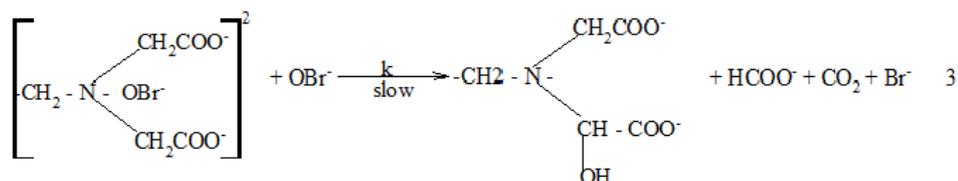
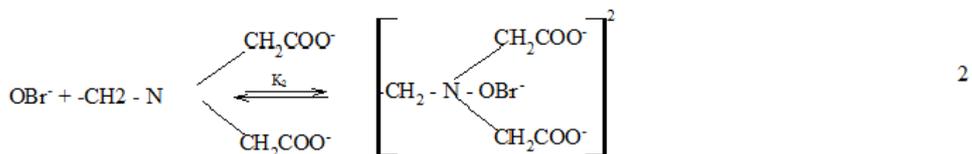
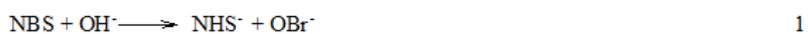
The oxidant itself or OBr^- was the main reactive species in alkaline medium. The oxidant was exist in the following equilibrium.



Scheme 1

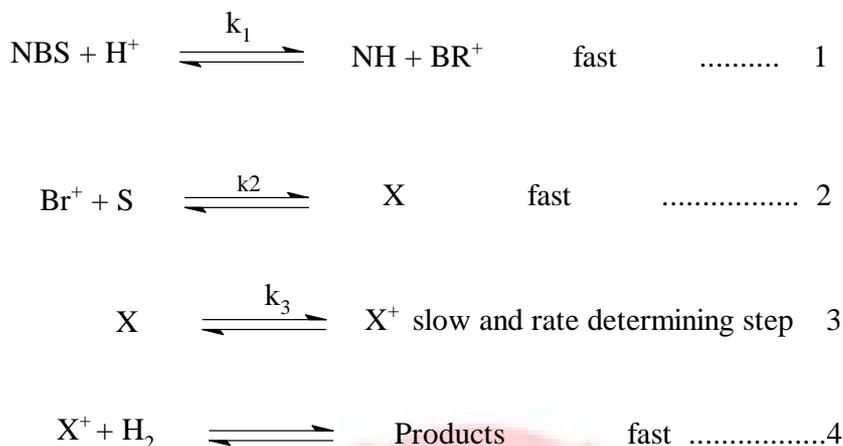


Although EDTA is a hexadentate ligand and can form six coordinate complexes with the central metal. On the basis of the above experimental results the mechanism for the reaction in alkaline medium may be proposed as follows:



Mechanism of Acidic Medium

Scheme 2



The rate law according to **Scheme 2**,

$$\frac{-d[\text{NBS}]}{dt} = \frac{k_3[\text{NBS}]_t[\text{EDTA}][\text{H}_2\text{O}]}{[\text{NH}] + K_1[\text{H}_2\text{O}]} \{ [1 + K_2[\text{EDTA}]] \}$$

According to Scheme 1 and 2, the kinetics of this reaction seems to be reliable with mechanism both in acid and alkaline media. Here, the reactive species OBr^- react with anionic form of EDTA to form a complex. This complex in slow step decomposes as intermediate and Br^- . The intermediate undergoes decomposition in further fast steps to form suitable products. The evidence for complex formation between oxidant and mixture of oxidant and substrate was obtained by UV-Visible spectra. Such complex formation has been obtained in other studies [22].

The thermodynamic parameters for the equilibrium and activation parameters for the rate determining step of scheme 1 and 2

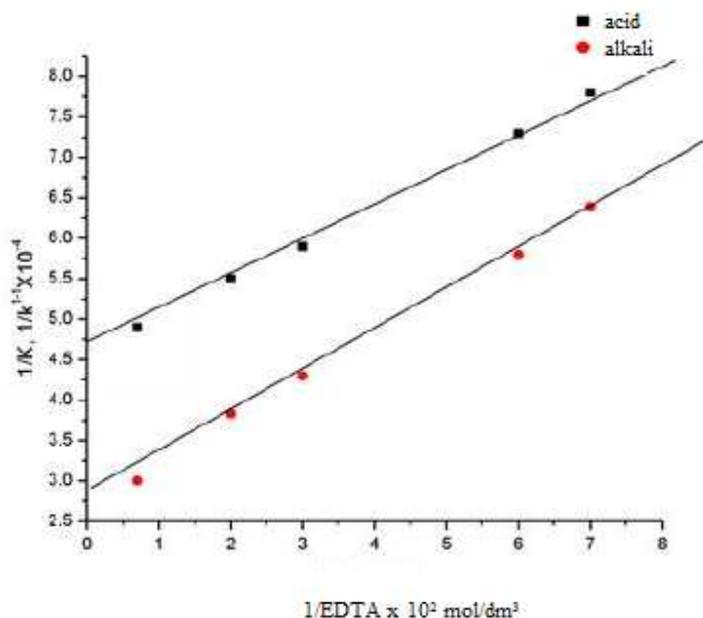
can be evaluated. The concentrations of EDTA and succinimide were varied at four different temperatures. The values of K_1 were obtained at such temperatures by the Van't Hoff's plot of K_1 with temperature ($\log K_1$ Vs $1/T$). As Arrhenius plot of $\log k$ Vs $1/T$ yield the activation parameters for the rate determining step in scheme 1 and 2. The activation parameters evaluated in both the experimental conditions are summarized in (Table.2). Nearly same values of ΔG^\ddagger suggest the involvement of similar type of complex in the mechanism. The information that reaction before the rate determining step is quite rapid involving low activation energy was obtained by the comparison of values.

Table. 2 Effect of variation of temperature on the rate constant and activation parameters in acid and alkaline media.

Parameter	Alkaline Medium	Acid Medium
$10_4(K_1)$ 35°C	4.6	8.4
$10_4(K_1)$ 40°C	9.2	15.3
$10_4(K_1)$ 45°C	13.0	19.9
$10_4(K_1)$ 50°C	20.7	29.1
E_a , KJ mol ⁻¹	76.55 ± 0.50	65.06 ± 0.05
Log A	9.88 ± 0.02	8.16 ± 0.02
$\Delta H^\#$ KJ mol ⁻¹	73.97 ± 0.50	62.48 ± 0.50
$\Delta S^\#$ KJ mol ⁻¹	-55.85 ± 0.50	-88.85 ± 0.50
$\Delta G^\#$ KJ mol ⁻¹	91.31 ± 10	90.07 ± 10

A plot of k or k₁ Vs concentration of EDTA was found to be deviate from linearity at higher concentration of EDTA. However the plot of 1/k or 1/k₁ Vs 1/ [EDTA] (Fig.1) was linear with a positive slope. This clearly shows that the order of reaction in substrate is less than unity at higher substrate concentrations in both the conditions i.e., in

acid and alkaline medium. The value of K₁ is in agreement with earlier report (22). The values of k of the slow step of Scheme 1 and 2 were obtained from the intercept of the 1/k or 1/k₁ Vs [NHS] plot at four different temperatures. The difference in the activation parameters for the alkaline and acid media reactions explains the acidic effect on the rate of the reaction.



Comparison of relative reactivity in acid and alkaline media

In the present research the detailed kinetic study was carried out on the oxidation of EDTA with NBS at pH 3 and 12, the other experimental conditions being held constant (Table.1). The kinetic patterns with respect to oxidant and substrate were identical in both the media. In the acid medium the rate of the reaction was increased by varying the concentration of SDS and the order was found to be fractional. But in the case of alkali the rate of reaction was accelerated in the same

concentration range as of acid and the order was found to be 0.6. The reaction rate was retarded by the addition of the reduction product of NBS was Succinimide in alkaline medium and NHBr in acid medium and OBr⁻ was considered to be the reactive species. Schemes 1 and 2 explain the detailed mechanistic interpretation in acid and alkaline medium respectively.

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