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Oxidation of ethylenediaminetetraacetic acid by N-bromosuccinimide in aqueous alkaline medium – A kinetic study

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The kinetics of oxidation of ethylenediaminetetraacetic acid (EDTA) by N-bromosuccinimide (NBS) in aqueous alkaline media was investigated at 25°C. Analysis of the results showed the reaction is first – order with respect to [NBS] and apparently less than unit order each with respect to [EDTA] and [alkali]. The influence of the reaction products, ionic strength, temperature effect and dielectric constant of the medium on the rate of reaction was studied. The proposed mechanism is consistent with the observed kinetics. The reaction constants involved in the mechanism were derived. There is a good agreement between the observed and calculated rate constants under different experimental conditions.

Key Words: NBS, EDTA, kinetics, oxidation

Introduction

The disodium salt of ethylenediaminetetraacetic acid ($\text{Na}_2\text{H}_2\text{Y}$ or EDTA) is well known as a chelating agent in complexometry and is employed for identification and differential estimation of a number of metal ions. The investigation of the redox reactions of organic sequestering agents such as EDTA with various oxidizing agents has become increasingly important in analytical and environmental chemistry¹⁻². Although this aspect of EDTA chemistry is described in detail in the literature, very little is known about the behavior of oxidants towards this compound. The oxidants so far used for the kinetic investigation have been mentioned previously. Hanna³ et al., and Rao³ have shown that HCHO and CO_2 are formed in the oxidation of EDTA by Ce (IV). Sanahi⁴ et al., have carried out a systematic investigation of the oxidation of EDTA with Chloramine-T (CAT) in acetate buffer medium, but the products have not been identified. The iron (III) catalyzed oxidation of EDTA in aqueous solution at elevated temperatures (100-170°C) has shown the formation of ethylenetriacetic acid⁵. Formation of HCHO, CO_2 N-hydroxymethylethylenediamine was observed⁶ during the oxidation of EDTA with a suspension of PbO_2 in H_2SO_4 . Formation of HCOOH, CO_2 and ethylenediamine was observed during oxidation of EDTA by chloramine-B in buffer medium⁷. Hence, different researchers have identified different products with different oxidants for EDTA oxidations.

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N-bromosuccinimide (NBS) has been used as an oxidizing agent and analytical reagent especially in acid medium⁸. However, the work on oxidation by NBS in alkaline media is scanty⁹. A literature survey reveals that no work was done on oxidation of EDTA by NBS in alkaline medium. Hence, the title reaction has been studied in order to interpret the mechanism and to understand the redox chemistry of NBS in such media.

Experimental

Stock solutions of EDTA (BDH) and NBS (Sisco) were prepared by dissolving appropriate amounts of samples in doubly distilled water. The solution of NBS was standardized against sodium tetrathionate¹⁰ and EDTA solution was standardized by a known procedure¹¹. Succinimide was prepared by a known method and recrystallised from alcohol and the stock solution was prepared by dissolving the required quantity in distilled water. All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of samples in doubly distilled water. NaOH and NaClO₄ were used to provide the required alkalinity and to maintain the ionic strength respectively.

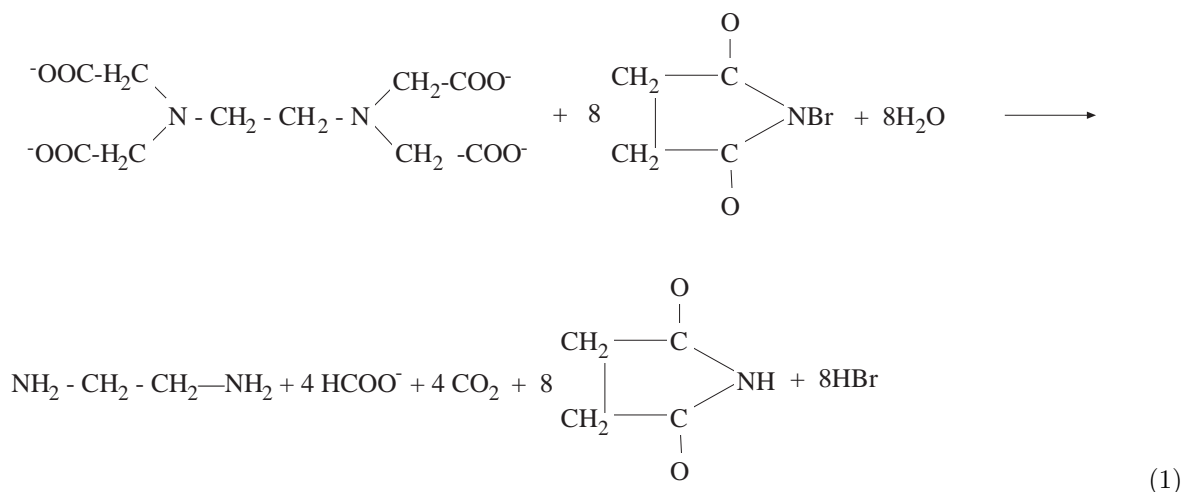
Kinetic measurements

All kinetic measurements were performed under pseudo-first order conditions with [EDTA] at least 10-fold in excess over [NBS] at a constant ionic strength of 0.05 mole dm⁻³. The reaction was initiated by mixing previously thermostated solutions of NBS and EDTA, which also contained the necessary quantities of NaOH and NaClO₄. The temperature was uniformly maintained at 25 ± 0.1°C. The progress of the reaction was followed by iodometric determination of the unreacted oxidant in aliquots (5ml each) of the reaction mixture withdrawn at regular time intervals. The pseudo-first order rate constants were evaluated by plots of log [NBS] versus time. The first order plot in almost all cases was linear up to 70% completion of the reaction. The *k_{obs}* values were reproducible within ±5% .

The effect of dissolved oxygen on the rate of the reaction was studied by preparing the reaction mixture and following the reaction under nitrogen atmosphere. No significant difference between the results obtained under nitrogen and those obtained in the presence of air was observed. In view of the ubiquitous contamination of carbonate in basic solutions, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used during the experiments.

Stoichiometry and Product analysis

Different sets of reaction mixtures containing different reactant concentrations at constant alkalinity and ionic strength were left to react for 24 hours at 25 ± 1.0°C. After the completion of the reaction, when [NBS] > [EDTA], the remaining NBS was assayed¹⁰ iodometrically as mentioned earlier. Under the condition [EDTA] > [NBS], the unreacted EDTA was estimated¹¹ as given in experimental section. The results indicated that 8 moles of NBS consumed 1 mole of EDTA according to equation (1).



The succinimide was found to be the main product. The other main reaction products were identified as formic acid and ethylenediamine by spot tests^{12a,b} and TLC using benzene ethylacetate mixture as solvent analysis¹³.

Results and Discussion

The reaction orders with respect to each reactant concentration of the reaction were determined from the slopes $\log k_{obs}$ versus \log (concentration) plots by varying the concentration of the reductant and alkali in turn, while keeping the others constant. The oxidant, N – bromosuccinimide was varied in the range 3.0×10^{-4} – 3.0×10^{-3} mol dm⁻³ and the linearity of the plot of \log [NBS] versus time indicated the reaction order in [NBS] as unity. This was also confirmed by varying [NBS], which did not show any change in pseudo-first order rate constants k_{obs} (Table 1). The substrate (ethylenediaminetetraacetic acid) concentration was varied in the range 5×10^{-3} – 5.0×10^{-2} mol dm⁻³ at 25°C, keeping all other reactant concentrations and conditions constant (Table 1). The reaction order in [EDTA] was found to be less than unity.

The initially added products, formic acid, ethylenediamine and Br⁻ had no significant effect on the rate of the reaction. However, the addition of succinimide in the range of 1.0×10^{-3} – 10×10^{-3} mol dm⁻³ at constant concentrations of reactants, the other conditions being constant, decreased the rate of reaction (Table 2).

The effect of [alkali] on the reaction rate was studied at constant concentrations of NBS and EDTA and keeping a constant ionic strength of 0.05 mol dm⁻³ at 25°C. The rate constants increased with the increase in [OH⁻] (Table 1) (order = 0.4).

The effect of ionic strength was studied by varying the sodium perchlorate (NaClO₄) concentration in the reaction medium. The ionic strength of the reaction medium was varied from 1.0×10^{-2} – 10×10^{-2} mol dm⁻³ at constant concentrations of NBS, EDTA and OH⁻. It was found that the rate constant increased slightly with increasing concentration of NaClO₄.

Table 1. Effect of [NBS], [EDTA] and [OH⁻] on the oxidation of EDTA by N – bromosuccinimide in aqueous alkaline medium at 25°C.

I = 0.05 mol dm⁻³

10 ² × [EDTA] (mol dm ⁻³)	10 ³ × [NBS] (mol dm ⁻³)	10 ³ × [OH ⁻] (mol dm ⁻³)	10 ⁴ × k _{obs} (s ⁻¹)	
			Expt*.	Calc*.
0.5	1.0	1.0	2.69	2.70
1.0	1.0	1.0	3.83	4.03
2.0	1.0	1.0	5.20	5.20
3.0	1.0	1.0	5.80	5.87
4.0	1.0	1.0	6.39	6.42
5.0	1.0	1.0	7.03	6.90
2.0	0.3	1.0	5.20	5.20
2.0	0.4	1.0	5.20	5.20
2.0	0.6	1.0	5.20	5.20
2.0	1.0	1.0	5.20	5.20
2.0	2.0	1.0	5.20	5.20
2.0	3.0	1.0	5.20	5.20
2.0	1.0	0.3	3.84	3.86
2.0	1.0	0.5	4.80	4.90
2.0	1.0	1.0	5.20	5.20
2.0	1.0	1.5	6.22	6.20
2.0	1.0	2.0	7.68	7.72
2.0	1.0	3.0	8.66	8.70

*Experimental and calculated

Table 2. Effect of product succinimide on the oxidation of EDTA by NBS in aqueous alkaline medium at 25° C.

[EDTA] = 2 × 10⁻², [NBS] = 1 × 10⁻³, [OH⁻] = 1 × 10⁻³, I = 0.05 mol dm⁻³.

10 ³ × [NH] (mol dm ⁻³)	10 ³ × k _{obs} (s ⁻¹)	
	Expt.*	Calc.*
1.0	2.92	2.94
2.0	2.44	2.54
4.0	1.32	1.38
5.0	1.25	1.22
7.0	0.85	0.89
10.0	0.65	0.69

*Experimental and calculated.

Error ± 5%

The relative permittivity (ϵ_T) effect was studied by varying the t - butanol – water content in the reaction mixture while all other conditions were constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids as in earlier work¹⁴. There was no reaction of solvent with oxidant under the experimental conditions used. The rate constants, k_{obs}, increased with decreases in the dielectric constant of the medium. The plot of log k_{obs} versus 1/ ϵ_T was linear (Fig 1).

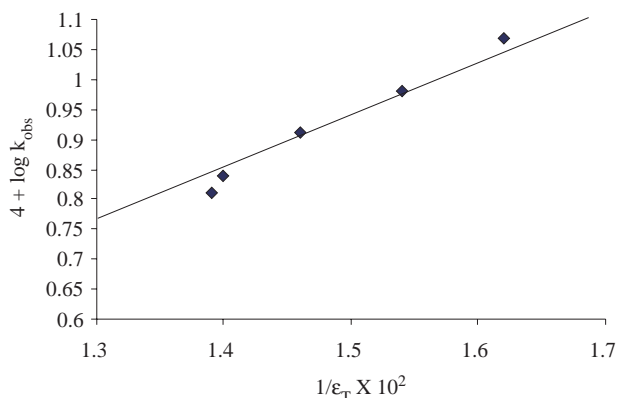
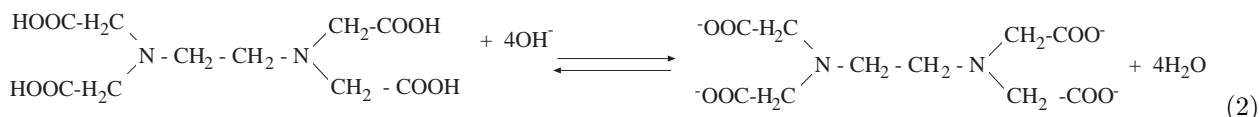


Figure 1. plot of $\log k_{obs}$ versus $1/\epsilon_T$

The reaction mixture was kept for 1 hour, with an acrylonitrile scavenger in an inert atmosphere. On diluting the reaction mixture with methanol, there was no formation of precipitate, indicating the absence of free radical intervention in the reaction.

EDTA is known to exist as zwitter ion in aqueous acidic medium¹⁵. However, in alkaline medium it exists as an anionic form as given below¹⁶:



The oxidant, NBS, is a two equivalent oxidant which oxidizes many substrates through NBS itself or hypobromite anion. The reaction exhibits 1:8 stoichiometry of EDTA and NBS with unit order dependence on $[\text{OH}^-]$ and unit order in $[\text{NBS}]$. It is interesting to note that the rate of the reaction is dependent on $[\text{substrate}]$ with less than unit order. The initial addition of one of the products, succinimide, retards the rate of reaction, which may be attributed to a decrease in the concentration of free OH^- as shown below:

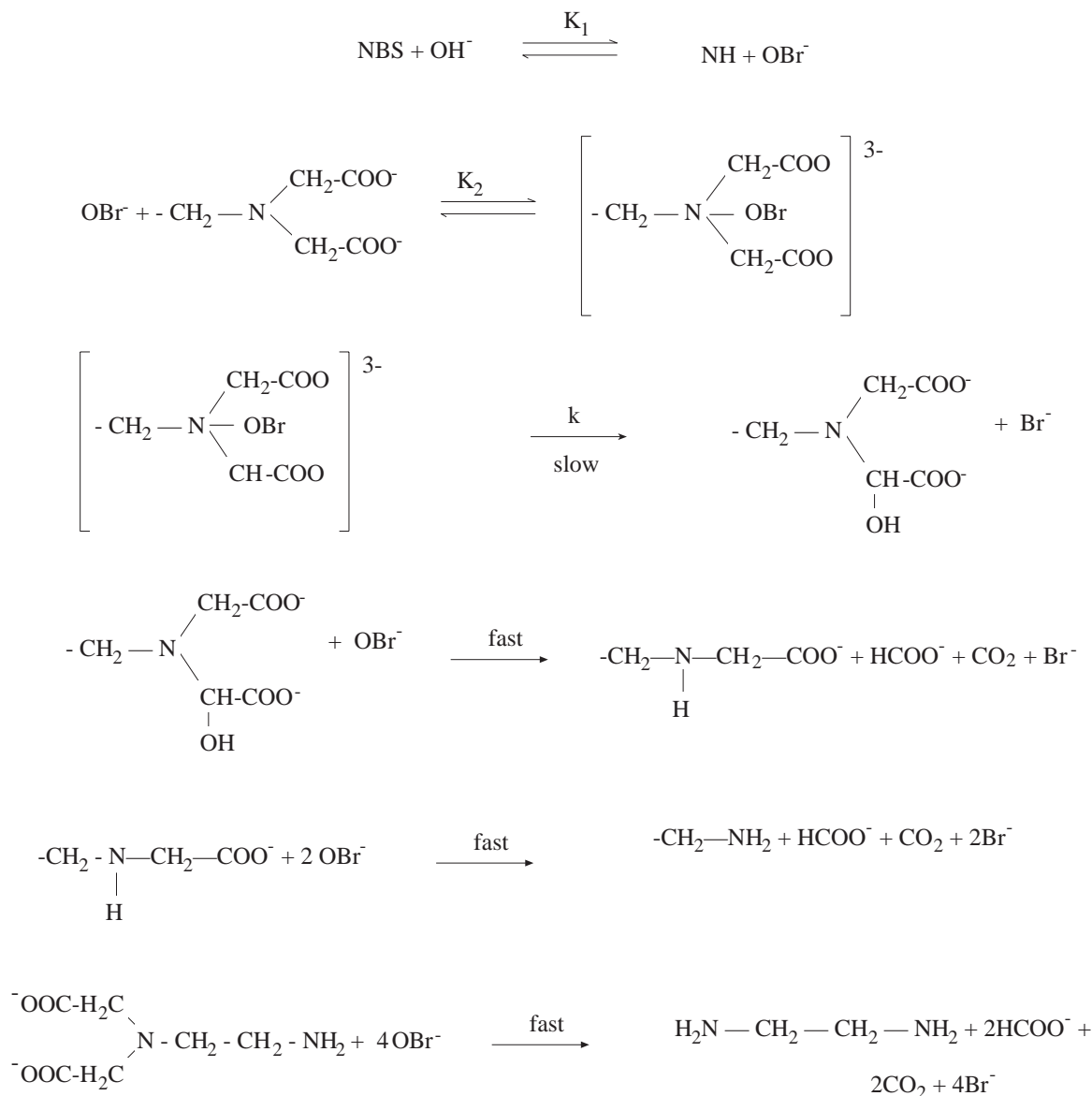


This reaction is possible because succinimide is a weak acid¹⁷ with pKa 9.6. Increase in rate with increase in $[\text{OH}^-]$ may be explained by the following equilibrium



where NH denotes succinimide. In the present study, the reactive species of NBS is OBr^- in view of the retarding effect of the initially added product, i.e., succinimide, which is also the case in earlier studies¹⁸. Hence, the active species of NBS, i.e., OBr^- , reacts with the anionic form of EDTA to form a complex which decomposes in a rate determining step to give an intermediate and product Br^- . This intermediate reacts with seven more molecules of active species of oxidant in further fast steps to give the products shown in Scheme. The evidence for complex formation between NBS and EDTA was obtained by the UV- vis spectra of NBS and a mixture of NBS and EDTA. A hypsochromic shift of about 5 nm of NBS from 250 nm to

235nm and hyperchromicity at 235 nm was obtained. This was also evidenced from the Michaelis – Menten plot of $1/k_{obs}$ Vs $1/[EDTA]$, which shows a non – zero intercept on the y – axis. Such complex formation between a substrate and an oxidant has also been evidenced in some other studies¹⁹, as EDTA is a strong multidentate complexing agent^{16–20}. The experimental results are in agreement with the Scheme.



Scheme

The thermodynamic parameters for the equilibrium (step 1 of the Scheme) and activation parameters for the rate determining step of the Scheme can be evaluated. The concentrations of EDTA and succinimide (as shown in Tables 1 and 2) were varied at several temperatures and the values of K_1 were determined at each temperature. The values of $K_1 \times 10^2$ were obtained as 15, 22, 35 and 38 at 298, 303, 308 and 313K respectively. The van't Hoff plot was prepared for variation of K_1 with temperature ($\log K_1$ Vs $1/T$) and

values of enthalpy of reaction ΔH entropy of reaction ΔS and free energy of reaction ΔG were calculated as $38 \pm 2 \text{ kJ mol}^{-1}$, $-29 \pm 2 \text{ JK}^{-1} \text{ mol}^{-1}$ and $22 \pm 2 \text{ kJ mol}^{-1}$ respectively. An Arrhenius plot of $\log k$ vs $1/T$ yielded the activation parameters for the rate determining step in the Scheme which are given in the temperature effect study. A comparison of values supports the fact that the reaction before the rate determining step is fairly rapid, involving low activation energy.

The Scheme leads to the following rate law (5):

$$\text{Rate} = \frac{kK_1K_2[\text{NBS}]_T[\text{EDTA}]_T[\text{OH}_T^- \text{NH}][\text{NH}]}{([\text{NH}] + K_1[\text{OH}_T^- - \text{NH}] + K_1K_2[\text{EDTA}][\text{OH}_T^- - \text{NH}])([\text{NH}] + K_1K_2[\text{NBS}][\text{OH}_T^- - \text{NH}])} \quad (5)$$

which explains all the observed orders. The subscript T refers to total concentration. Strictly, the factor $([\text{NH}] + K_1K_2[\text{NBS}][\text{OH}_T^- - \text{NH}])$ in the denominator on the right hand side of equation (5), in view of the low concentrations of NBS and OH^- used, approximates to $[\text{NH}]$, which cancels with the numerator term of $[\text{NH}]$. The rate law (5) takes the form given below:

$$\frac{\text{Rate}}{[\text{NBS}]_T} = k_{obs} = \frac{kK_1K_2[\text{EDTA}]_T[\text{OH}_T^- - \text{NH}]}{[\text{NH}] + K_1[\text{OH}_T^- - \text{NH}] + K_1K_2[\text{EDTA}][\text{OH}_T^- - \text{NH}]} \quad (6)$$

Equation (6) can be rearranged to the following form, which is suitable for verification:

$$\frac{1}{k_{obs}} = \frac{[\text{NH}]}{kK_1K_2[\text{EDTA}][\text{OH}_T^- - \text{NH}]} + \frac{1}{kK_2[\text{EDTA}]_T} + \frac{1}{k} \quad (7)$$

According to equation (7), the plots of $1/k_{obs}$ Vs. $1/[\text{EDTA}]$ and $1/k_{obs}$ Vs. $[\text{NH}]$ should be linear, as verified in Fig. 2. From the intercept of $1/k_{obs}$ Versus $1/[\text{EDTA}]$ the value of k was obtained as $0.80 \text{ s}^{-1} \pm 0.04 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. When this value was substituted in the value of the intercept of $1/k_{obs}$ versus $[\text{NH}]$, K_2 was obtained. The values of k and K_2 were substituted in the slope of plot of $1/k_{obs}$ versus $[\text{NH}]$ to obtain $K_1[\text{OH}_T^- - \text{NH}]$. The value of $[\text{NH}]$ was obtained by substituting k , K_2 and $K_1[\text{OH}_T^- - \text{NH}]$ values in the slope of the plot of $1/k_{obs}$ vs. $1/[\text{EDTA}]$. The value of K_1 was obtained as $15.0 \pm 0.70 \times 10^{-2}$ by substituting the value of $[\text{NH}]$ in $K_1[\text{OH}_T^- - \text{NH}]$. The value of K_1 obtained is in good agreement with earlier reports²¹. These values of k , K_1 and K_2 are further utilized to calculate the rate constants under different experimental conditions. There is a good agreement between calculated and experimental rate constants (Table 1).

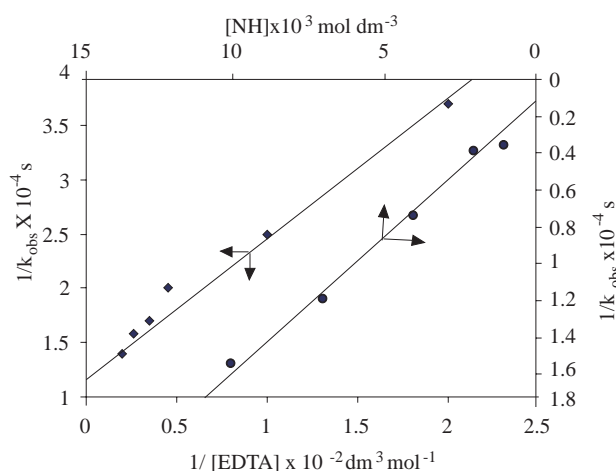


Figure 2. plot of $1 / k_{obs}$ versus $1/[EDTA]$ and $1/k_{obs}$ versus $[NH]$ (conditions as in Tables 1 & 2)

Effect of temperature

Kinetics were studied at 25, 30, 35, 40, and 45°C under varying EDTA concentrations with constant $[NBS] = 1.0 \times 10^{-3}$, $[OH^-] = 1.0 \times 10^{-3}$ and $I = 0.05 \text{ mol dm}^{-3}$. The rate constants, k , of the slow step of the Scheme were obtained from the intercepts of $1/k_{obs}$ versus $1/[EDTA]$. The rate constants $k \times 10^{-4}$ were obtained as 0.80 ± 0.04 , 1.70 ± 0.08 , 1.92 ± 0.09 , 2.80 ± 0.14 and 3.20 ± 0.16 at 25, 30, 35, 40 and 45°C respectively. Activation parameters for the slow step of the Scheme $E_a = 48 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -151 \pm 8.0 \text{ JK}^{-1} \text{ mol}^{-1}$, $\Delta H^\ddagger = 46.0 \pm 1.5 \text{ kJ mol}^{-1}$ and $\Delta G^\ddagger = 91 \pm 5 \text{ kJ mol}^{-1}$ were calculated from these data.

The slight increase in the rate of the reaction with an increase in ionic strength of medium qualitatively explains the reaction between two negative ions as seen in Scheme. The effect of solvent on the reaction kinetics has been described in detail in the earlier literature²²⁻²⁶. Increasing the content of t-butanol in the reaction medium leads to an increase in the rate of reaction, which seems to be contrary to the expected interaction between the species of opposite signs in a media of lower relative permittivity. However, an increase in the rate of reaction with a decreasing dielectric constant may be due to the stabilization of the complex (vide steps 4 and 5 of the Scheme) at low relative permittivity, which is less solvated than the anionic form of EDTA in an uncomplexed form at higher dielectric constant because of its larger size. The moderate values of ΔH^\ddagger and the negative ΔS^\ddagger support a rigid transition state of the complex from the reactants as seen in the Scheme.

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