



Kinetics and mechanistic study of micellar catalyzed oxidation of erythrose series sugar by sodium N-chloro-p-toluene sulfonamide in acidic medium

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Abstract

The present study investigates the micellar catalytic effect of cationic surfactant i.e. Cetyl Trimethyl Ammonium Bromide (CTAB) on the oxidation of erythrose series sugar D- Allose by Sodium N-chloro-p-toluene sulfonamide in the presence of acetic acid at 303K. The reaction followed first order kinetics with respect to oxidant and fractional order to substrate in a particular concentration range. The reaction dependence on H^+ ion concentration, addition of the reaction product, variation in ionic strength and dielectric constant of the medium was studied. The rate of reaction was influenced by a change in ionic strength of the medium and the dielectric effect. The micelle binding constant and positive co-operativity index for substrate have also been calculated. Different thermodynamic parameters have been computed and a plausible reaction mechanism consistent to the experimental findings, product analysis and reaction stoichiometry have been proposed.

Keywords: micelle, oxidation, surfactants, erythrose

1. Introduction

Sodium N-chloro p-toluenesulphonamide, which is commonly known as Chloramine-T has widely been used as an oxidizing agent in various chemical reactions [1-4]. The oxidation of erythrose series sugars by Chloramine -T (CAT) and Bromanine -T (BAT) has received much attention in previous years [5-8]. Kinetics and mechanism of oxidation of aldoses by bromine was also studied [9] but there are scanty work from the kinetic and mechanistic point of view on the oxidation of D-Allose by CAT in micellar system and acidic medium [10-13]. The catalytic activities of aqueous micelles play a significant role on the rate of reactions occurring in micellar system. Therefore, present work on oxidation of D-Allose in the presence and absence of cetyl trimethyl ammonium bromide (CTAB) i.e. a cationic surfactant has been taken for investigation.

2. Materials and Method

All the chemicals were used of analytical grade of purity. The chloramines-T solution was standardized by iodometric method and preserved in black painted bottle to avoid any photochemical deterioration. The stock solution of chloramine -T and all other solutions were prepared in deionized, doubly distilled water. Acetic acid was distilled over chromic acid before use. Cetyl trimethyl ammonium bromide's purity was confirmed by measuring its critical micelle concentration (CMC) by plotting surface tension versus log [surfactant] and also confirmed with the plot of specific conductance versus [surfactant] using conductometric determination method at 313K. The obtained values are well supported by literature values. The reaction vessels were also painted black just to avoid any photochemical decomposition during the course of reaction.

3. Result and Discussion

The purpose of the study is to determine the rate law of the overall reaction, its mechanism and analyze the dependency of rate on various aspects like substrate, surfactant, oxidant, dielectric constant, temperature etc. in acidic medium. Therefore, the oxidation of D-Allose by Chloramine-T in the presence and absence of cationic surfactant has been studied in acetic acid medium at 313K. The micellar catalyzed oxidation reaction rate depends on both substrate and surfactant concentrations. The following variation and effects have been examined.

4. The Rate Dependency on [D-Allose]

The dependence of rate constant on [D-Allose] was determined at different concentrations of D-Allose from 1×10^{-3} to $15 \times 10^{-3} \text{ mol dm}^{-3}$ at constant concentrations of other reactants at 313K. The linear plot of $\log k$ versus $\log [D\text{-Allose}]$ indicates the fractional order dependence in micellar media.

Table 1: AcOH = 20 % v/v, [CTAB] = $1.2 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. = 313 K

S. No.	[CAT] $\times 10^3 \text{ mol dm}^{-3}$	[D-Allose] $\times 10^3 \text{ mol dm}^{-3}$	In presence of [CTAB] $k_1 \times 10^3 \text{ min}^{-1}$
1.	0.4	10.0	34.3
2.	0.7	10.0	35.7
3.	1.0	10.0	36.6
4.	1.3	10.0	36.4
5.	1.5	10.0	38.4
6.	1.0	02.0	22.4
7.	1.0	05.0	26.2
8.	1.0	10.0	36.6
9.	1.0	12.0	39.2
10.	1.0	14.0	41.3

5. The Rate Dependency on [CAT]

To find out the order with respect to [CAT] the rate constants were determined at different concentrations ranging from 0.2×10^{-3} to 1.6×10^{-3} at constant concentration of other reactants at 313K. It was found that the values of rate constant were independent of the initial concentrations of CAT that indicating the order of reaction with respect to [CAT] is first order, which is well evident by obtaining a linear graph when plotted $\log[\text{CAT}]$ versus time.

Table 2: [D-Allose] = $10 \times 10^{-3} \text{ mol dm}^{-3}$, AcOH = 20 % v/v, [CAT] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. = 313 K

S. No.	[CTAB] x 10^3 mol dm^{-3}	In presence of [CTAB] $k_1 \times 10^3 \text{ min}^{-1}$
1.	0.0	13.1
2.	0.4	27.3
3.	0.6	29.5
4.	0.8	32.4
5.	1.0	34.4
6.	1.2	36.6
7.	1.4	39.3

6. The Rate Dependency on [CTAB]

To check the catalytic effect of cationic surfactant i.e. CTAB, the reaction was carried out at different concentrations of the surfactant. The reaction has been found to be catalyzed with the addition of CTAB. It is also observed that the reaction rate increases with the increase in the surfactant concentration up to a certain limit. The pre-micellar catalysis is due to the fact that small aggregates of surfactant molecules exist below the CMC and that start the catalyzing the reaction [14-16]. The behaviour is in accordance with the micellar catalysis of organic reactions of anion neutral molecule type. With the increasing concentration of CTAB the relative concentration of organic substrate and ionic reactants in the stern layer of the micelle increase rapidly. This behaviour is also analogous to the Hill model accommodates the plot of $\log [k_{\text{obs}} - k_0/k_m - k_{\text{obs}}]$ versus $\log[\text{CTAB}]$ which is linear with slope value indicating positive cooperativity i.e. induced interaction of additional substrate molecule due to the interaction of the

micelle with the first substrate molecule [17-21].

7. The Rate Dependency on Solvent

To observe the effect of changing solvent composition on the reaction rate, the reaction was studied by varying the concentration of solvent like methanol. With the increase of the solvent concentration the rate constant decreases. The possible interaction of negative ion and dipole interaction leads the reaction in that way may it be.

8. The Rate Dependency on [Hg (OAc) 2]

The scavenger effect of [Hg (OAc) 2] was observed in the sufficient range of it and was found to be negligible effect on the reaction rate.

9. Effect of initially added product [p-TS] on reaction rate:

The effect of addition of probable reaction product was studied and found that the rate of reaction decreases on the addition of p-TS suggest that a pre equilibrium step involving a process in which p-TS is one of the product.

10. Detection of free radical

By adding acrylamide solution, the generation of free radicals during the course of oxidation reaction was confirmed and no precipitation in the reaction mixture indicates that there is no free radical involvement in the pathway of reaction.

11. Effect of change in temperature and Computation of activation parameters

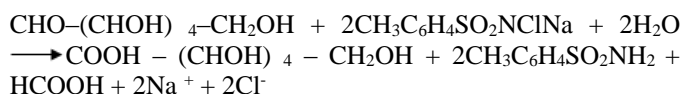
With the change in temperature from 303K to 323K the effect of temperature on reaction rate was studied. With the help of Arrhenius plot the values of activation energy (E_a^*) was calculated while the value of entropy of activation (ΔS^*), enthalpy of activation (ΔH^*), free energy of activation (ΔG^*), and frequency factor ($\log P_z$) were computed from Eyring equation. The fairly high positive value of enthalpy of activation and free energy of activation indicates that the transition state is highly solvated. The higher negative value of entropy of activation in the presence of CTAB indicates that more ordered activated complex is formed.

Table 3

Energy of Activation (E_a^*)	Entropy of Activation (ΔS^*)	Enthalpy of Activation (ΔH^*)	Free energy of Activation (ΔG^*)	Frequency factor ($\log P_z$)
53.46 KJ mol ⁻¹	-102.55 Jmol ⁻¹ K ⁻¹	44.65 KJ mol ⁻¹	83.47 KJ mol ⁻¹	$3.627 \times 10^6 \text{ mol}^{-1} \text{ dm}^{-3} \text{ sec}^{-1}$

12. Stoichiometry and Product analysis

Following stoichiometry of the reaction was observed –



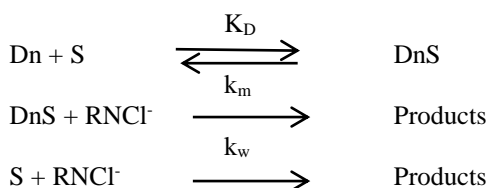
The products of oxidation reaction were analyzed by High Performance Liquid Chromatography and Spot test technique.

13. Reaction Mechanism

On the basis of experimental findings, product analysis,

reaction stoichiometry and thermodynamic parameters the following probable reaction mechanism has been proposed which is much consistent with the majority of the experimental results.

Oxidation in presence of surfactant –



Where D is surfactant molecule, DnS is substrate- surfactant micelle, RNCl is oxidant species and K_D , k_m and k_w are the constants.

The rate equation for this scheme may be given by –

$$\frac{k_{obs}}{S} = \frac{k_m + k_w \cdot K_D}{K_D + [D]^n}$$

Where k_{obs} is first order rate constant.

14. Conclusion

On the basis of above study of various effects and variation in concentrations of reactants during the course of reaction, it is well evident that cationic micelle of surfactant CTAB has an effective role as a catalyst for the oxidation of D-Allose by sodium N-chloro p-toluenesulphonamide in acidic medium. It has also found that the order of the reaction with respect to oxidant is first and with respect to substrate is fractional. The participation of an ion and a neutral molecule in the mechanistic steps of the reaction has well supported by the effects of solvent polarity and ionic strength.

15. References

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