



EFFECT OF SURFACTANT ON THE OXIDATION OF m-NITROPHENOL IN AQUEOUS ACETIC ACID MEDIUM BY CHLORAMINE-T : A KINETIC STUDY

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ABSTRACT

Oxidation of m-Nitrophenol by Chloramine-T has been investigated both in the presence and absence of the surfactant, Cetyl pyridinium bromide (CPBr). The reaction could be studied only at a moderate concentration of acid (acetic acid). Kinetic investigation revealed that the order of the reaction with respect to Chloramine-T is one in the absence of Cetyl pyridinium bromide (CPBr). But in the presence of surfactant, the values of first order rate constant increases with increasing concentrations of Chloramine-T. It is observed that the rate has almost ten times acceleration in the presence of cetyl pyridinium bromide due to the catalysis by micelle. The order with respect to substrate (m-nitrophenol) is found to be zero in the absence of the surfactant and fractional in the presence of the surfactant. The plot of $\log k$ versus $1/T$ for various values of temperature is a straight line, which proved the validity of Arrhenius equation. Activation parameters like ΔE^* , ΔH^* , ΔS^* , ΔG^* , are evaluated and a plausible mechanism is proposed.

Key Words: Surfactants, Chloramine-T, Cetyl pyridinium bromide.

INTRODUCTION

N-halo amides are versatile oxidising agents and their reactivity is a consequence of their ability to act as sources of

- (a) Halonium cation with halogen in + 1 oxidation state
- (b) Hypohalite species, and
- (c) N-anions

Sodium derivative of N-chloro p-toluene sulphonamide (Chloramine-T)¹⁻⁸ is a

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powerful oxidising agent and has been used for the estimation of several inorganic and organic compounds. The main reactive species between pH 3 and 11 are $\text{Ar-SO}_2\text{-NHCl}$, HOCl and OCI^- . The Chloramine-T system has a high value of redox potential in acidic medium. Research on oxidation of phenols and substituted phenols by various oxidants have been reported⁹⁻¹¹. Oxidation of m-nitrophenol by CAT has been studied kinetically both in the presence and absence of the surfactant cetyl pyridinium bromide (CPBr). Cetyl pyridinium bromide is selected as a surfactant because only a very few study has been undergone in the field of micellar catalysis by cetyl pyridinium bromide. The micelles formed from cetyl pyridinium bromide plays a vital role in this oxidation reaction. Generally micelles play an indispensable role in various systems like living systems¹²⁻²³. In this case even though before CMC, due to the formation of pre-micellar aggregates the rate of reaction enhances almost ten times as that without the surfactant. Here, Chloramine-T and m-nitrophenol interact in a molar ratio of 2 : 1 both in the presence and absence of cetyl pyridinium bromide (CPBr) in aqueous acetic acid medium. The reaction follows a first order kinetics in chloramine-T and zero order in m-nitrophenol in the absence of CPBr.

EXPERIMENTAL

All chemicals used were AR or GR level (grade). The reaction has been investigated in 10% acetic acid medium. Before using acetic acid, it was distilled. The reaction was conducted in brown bottles. Solution of chloramine-T was stored in bottles covered with black paper. Ostwald's isolation method is used to investigate the reaction. Effect of a particular reactant is studied by varying its concentration keeping the concentration of all other reactants constant. The reaction is started with the addition of thermostated solution of chloramine-T to the thermostated solution of mixture of the other reactants. The reaction was monitored by estimating the unreacted chloramine-T iodometrically. The first order rate constant values obtained are reproducible within $\pm 5\%$.

RESULTS AND DISCUSSION

Effect of [Chloramine-T] on the reaction rate

It is observed that the initial concentration of chloramine-T does not affect the rate of the reaction. The plot of k values versus concentration of [Chloramine-T] is a straight line graph parallel to X-axis (Series-1 in Fig. 1) showing the first order dependence of the reaction with respect to [Chloramine-T]. By the addition of surfactant, the reaction rate

increases due to the catalysis by micelles formed from the surfactant, cetyl pyridinium bromide (CPBr)²⁴ (Series-2 in Fig 1).

Table 1: Effect of [Chloramine-T]

[CAT] x 10 ⁻⁴ mol dm ⁻³	k x 10 ⁻⁵ sec ⁻¹ (in the absence of CPBr)	k x 10 ⁻⁵ sec ⁻¹ (in the presence of CPBr)
2.50	8.70	90.78
3.75	8.75	95.12
5.00	8.83	98.27
6.25	9.05	100.70
7.50	9.10	102.53

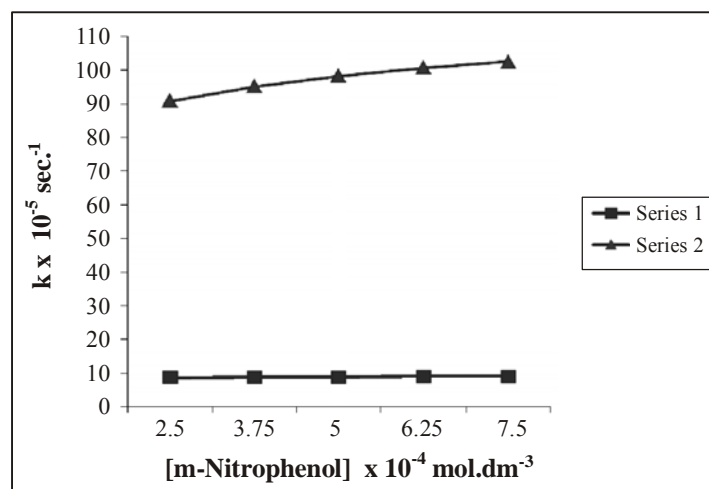


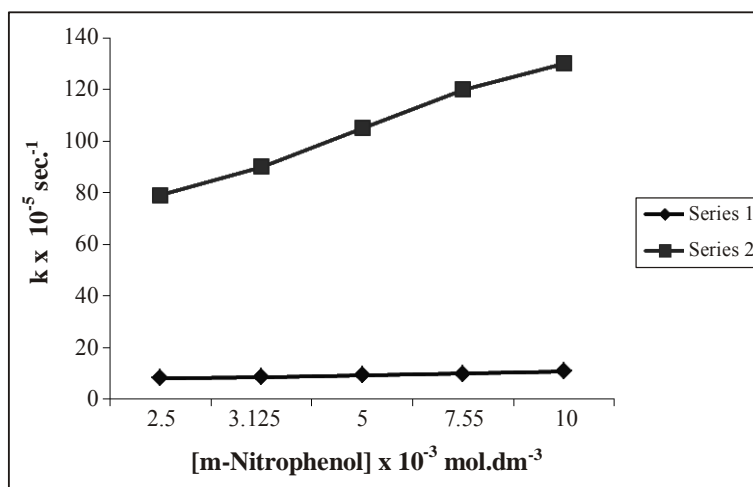
Fig. 1: Effect of [Chloramine-T]

Effect of [m-Nitrophenol]

The rate of the reaction does not depend on the initial concentration of m-nitrophenol in the absence of the surfactant (Table 2) but in the presence of the surfactant the rate increases with the increase in concentration of m-nitrophenol (Table 2). The plot of rate constant values versus [m-Nitrophenol] is a straight line shown as in Series-1 and Series-2 in Fig. 2. The order of the reaction with respect to m-nitrophenol is zero²⁵⁻²⁷ in the absence of the surfactant and fractional in the presence of the surfactant.

Table 2: Effect of [m-Nitrophenol]

[m-Nitrophenol] x 10 ⁻³ mol.dm ⁻³	k x 10 ⁻⁵ sec ⁻¹ (in the absence of CPBr)	k x 10 ⁻⁵ sec ⁻¹ (in the presence of CPBr)
2.50	8.33	79.00
3.125	8.70	90.00
5.00	9.42	105.00
7.50	10.00	120.00
10.0	10.85	130.00

**Fig. 2: Effect of [m-Nitrophenol]****Effect of [Acetic acid] on the reaction rate**

The effect of acetic acid is retarding²⁸ in both the cases studied i.e. as we increase the acid strength the rate of the reaction decreases to a minimum and then remains constant with the further addition of acid (Table 3 and Fig. 3).

Table 3: Effect of [Acetic acid]

[Acetic acid] % v/v	k x 10 ⁻⁵ sec ⁻¹ (in the absence of CPBr)	k x 10 ⁻⁵ sec ⁻¹ (in the presence of CPBr)
5	17.00	152.00
10	8.70	90.78
15	6.02	50.30
20	5.03	42.02
25	3.68	35.00

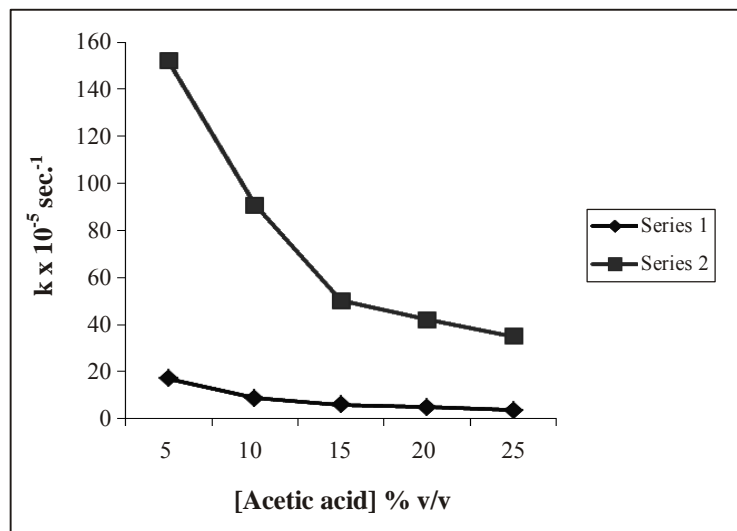


Fig. 3: Effect of [Acetic acid]

Effect of surfactant

The rate of the reaction has an interesting acceleration in the presence of the surfactant, cetyl pyridinium bromide (CPBr). Upto a concentration of $3.75 \times 10^{-4} \text{ mol.dm}^{-3}$, the rate of acceleration is moderate and above that the acceleration of reaction rate is very rapid showing the micellar activity of the surfactant (Table 4). The plot of rate constant values versus [CPBr] is given in Fig. 4. The accelerating activity of the surfactant below the CMC value is due to the formation of pre-micellar aggregates²⁹⁻³¹.

Table 4: Effect of Surfactant

[CPBr] x 10 ⁻⁴ mol.dm ⁻³	k x 10 ⁻⁵ sec ⁻¹
0.0	8.70
1.25	22.32
2.5	57.69
3.75	90.78
5.0	201.10
6.25	364.80

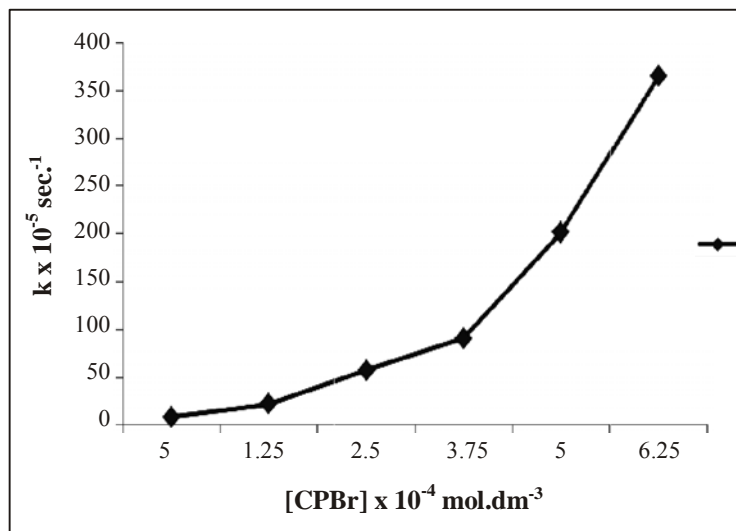


Fig. 4: Effect of surfactant

Effect of temperature

Effect of temperature has been studied for both the cases mentioned (Table 5). The activation parameters evaluated are given in Table 6. In presence of surfactant, the energy of activation is less than that in the absence of the surfactant.

The validity of Arrhenius plot has been verified by plotting $\log k$, versus reciprocal of temperature (Fig. 5). In the absence of surfactant, the effect of temperature is more.

Table 5: Effect of temperature

Temp. (k)	1/Temp.	$K_1 \times 10^{-5} \text{ sec}^{-1}$ (In the absence of CPBr)	5 + Log k_1	$k \times 10^{-5} \text{ sec}^{-1}$ (in the presence of CPBr)	5 + Log k
303	0.0033	5.20	0.7100	27.41	1.4380
308	0.00325	6.85	0.8357	40.60	1.6085
313	0.0032	8.70	0.9395	57.69	1.7618
318	0.003145	10.40	1.0170	85.52	1.9221
323	0.0031	12.20	1.0864	111.00	2.0453

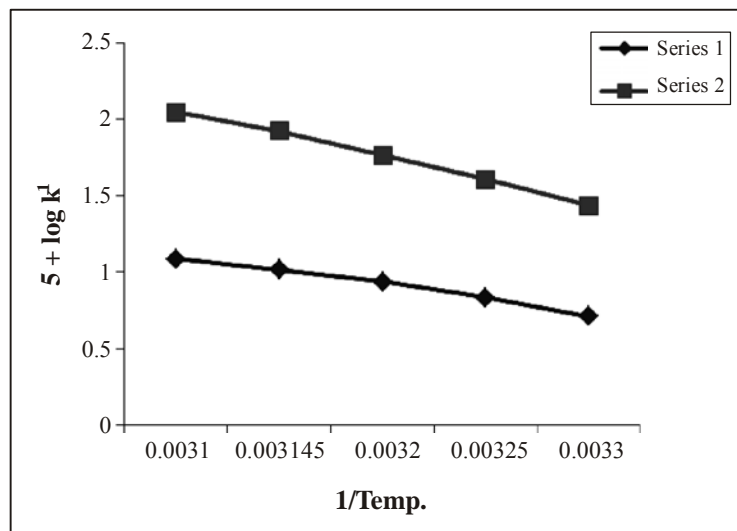


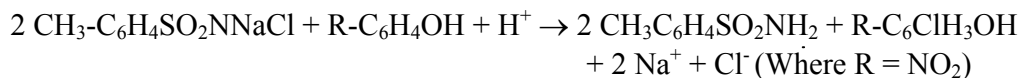
Fig. 5: Effect of temperature

Table 6: Activation parameters

Activation parameters	In the presence of CPBr	In the absence of CPBr
ΔE^* (KJ mol ⁻¹)	58.69	40.53
ΔH^* (KJmol ⁻¹)	56.08	37.98
ΔS^* (JK ⁻¹ mol ⁻¹)	-123.5	-197.1
ΔG^* (KJ mol ⁻¹)	94.74	99.53

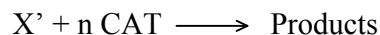
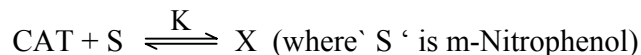
Stoichiometry

It is observed that two molecules of chloramine-T reacts with one molecule of m-nitrophenol. The final product is found to be the corresponding chloro substituted m-nitrophenol.



MECHANISM

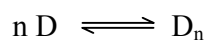
From the results of experimental work lead to the following reaction mechanism, which is much probable and well consistent with the experimental data.

Case – 1

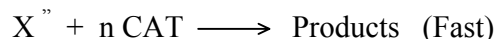
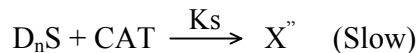
Therefore the reaction rate is –

$$\begin{aligned} -d[\text{CAT}] / dt &= K_w [\text{X}] \\ &= K_w k [\text{CAT}] [\text{S}] / 1 + k [\text{S}] \end{aligned}$$

Where K_w is the rate constant in the absence of the surfactant.

Case – II : Oxidation in the presence of the surfactant.

Where D_nS is the micelle associated with substrate



$$\text{Total rate, } \frac{-d[\text{CAT}]}{dt} = \frac{k_w k [\text{CAT}][\text{S}]}{1 + k [\text{S}]} + \sum K_s [\text{D}_n\text{S}] [\text{CAT}]$$

Where K_s is the rate constant in the presence of the micelle .

By doing appropriate approximation and rearrangement, the overall rate expression is –

$$K_{\text{obs}} = \frac{-d[\text{CAT}]}{dt} = \frac{K_w K_s K_d [D_n]}{1 + K_d [D_n]}$$

which is applicable to both the cases, i.e., in the absence and presence of the surfactant.

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