Micellar Catalyzed Oxidation of *p-Chlorophenol* by *Chloramine-T :* A Kinetic Study

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Abstract: *Oxidation of p-Chlorophenol by Chloramine-T has been investigated both in the presence and absence of the surfactant Cetylpyridinium bromide (CPBr). The reaction could be studied only at a moderate concentration of acetic acid and the rate is found to be decreasing with increasing concentrations of acetic acid. Kinetic investigation revealed that the order of the reaction with respect to Chloramine-T is one both in the presence and absence of the surfactant, Cetylpyridinium bromide (CPBr). It is observed that the rate has almost six times acceleration in the presence of Cetylpyridiniumbromide. The order with respect to substrate (p-Chlorophenol) is found to be zero both in the presence and absence of the surfactant. The effect of temperature has also been studied and the activation parameters like ΔE, ΔH, ΔS and ΔG, are evaluated and a plausible mechanism is proposed.*

Keywords: p-Chlorophenol, Chloramine-T), Cetylpyridinium bromide (CPBr)

1. Introduction

Chloramine-T)[1-8](Sodium derivative of N-Chloro p-toluene Sulphonamide) is a powerful oxidising agent and has been used for the estimation of several inorganic and organic compounds. The Chloramine-T system has a high value of redox potential in acidic medium. Various investigators have done research on the Oxidation of Phenols and substituted Phenols by different oxidants [9-10]. But the oxidation of p-Chlorophenol by Chloramine-T(CAT) has not yet been studied kinetically. Generally micelles play an indispensable role in various systems like living system[11-18].Micellar aggregates serve as an important bridge between microscopic and macroscopic chemical species in the development of new technologies. Micellar catalysis has become one of the major research topics nowadays. So in the present study the oxidation of p-Chlorophenol by CAT has been investigated kinetically in the presence and absence of the surfactant, Cetylpyridiniumbromide(CPBr). The enhancement of the reaction ratein thepresenceofthe surfactant, Cetylpyridinium bromide (CPBr) is due to the catalysis by micelles / pre-micellar aggregates and the rate of reaction enhances almost six times as that without the surfactant. The reaction follows a first order kinetics with respect to Chloramine-T and zero order with respect to p-Chlorophenol both in the presence and absence of the surfactant, Cetylpyridinium bromide (CPBr).

2. Experimental

The chemicals used were of Anala R / Guaranteed Reagent Grade. Ostwald's isolation method was used to investigate the reaction. In order to keep the medium acidic, 10% acetic acid(v/v) is used. Before using acetic acid, it is distilled. The effect of a reactant on the reaction rate is studied by varying its concentration keeping the concentrations of all other reactants constant. The reaction was monitored by estimating the unreacted Chloramine-T iodometrically. The first order rate constant values obtained are reproducible within 5%.

3. Results and Discussion

a) Dependence of reaction rate on [Chloramine –T]

The rate of the reaction is found to be independent of the initial concentrations of Chloramine-T(CAT). The plot of k values versus [Chloramine-T] is a straight line graph parallel to X-axis showing the first order dependence of the reaction with respect to [Chloramine-T][19].This is the trend observed for both the cases studied i.e. in the presence and absence of the surfactant(**Table-1&Fig-1).**

Table 1

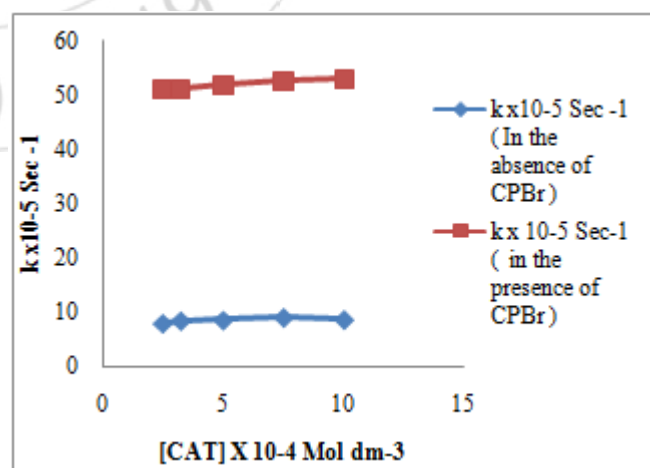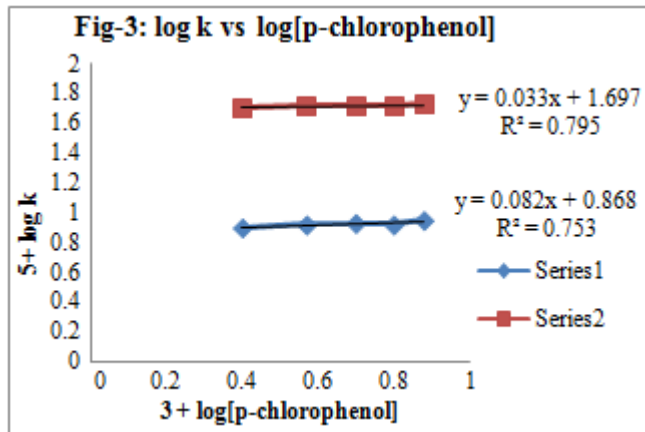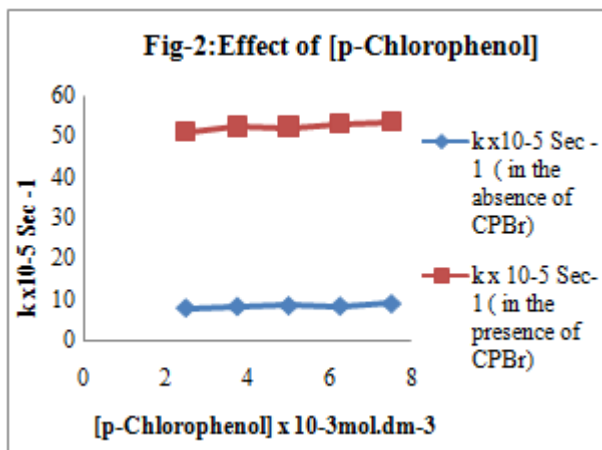| Sr. No.	[CAT] X 10^{-4} Mol dm^{-3}	k x10^{-5} Sec $^{-1}$ (In the absence of CPBr)	k x 10^{-5} Sec^{-1} (in the presence of CPBr)
1	2.5	7.9	51.2
2	3.25	8.4	51.1
3	5.0	8.5	51.8
4	7.5	9.0	52.5
5	10.0	8.6	53.0

Figure 1: Effect of [Chloramine -T]

b) Dependence of reaction rate on [p-Chlorophenol]

From the results it is clear that the reaction rate does not depend on the initial concentration of p- Chlorophenol both in the presence and absence of CPBr. The plot of values of rate constants versus [p- Chlorophenol] is a straight line

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parallel to X-axis showing the Zero order dependence of the reaction with respect to[p- Chlorophenol][20-22] in both the cases studied. The plot of log k versus log[p- Chlorophenol] is also straight line parallel to X-axis with almost zero slope showing the zero order dependence of the reaction with respect to[p- Chlorophenol] in the presence and absence of CPBr(**Table-2& Fig-2& 3).**

Table-2

Sr. No.	[p-Chlorophenol] x 10^{-3} mol.dm^{-3}	k x10^{-5} Sec $^{-1}$ (in the absence of CPBr)	k x 10^{-5} Sec^{-1} (in the presence of CPBr)
1	2.5	7.9	51.2
2	3.75	8.3	52.4
3	5.0	8.5	52.3
4	6.25	8.4	53.1
5	7.5	9.0	53.5

Fig-2:Effect of [p-Chlorophenol]

Fig-3: log k vs log[p-chlorophenol]

$y = 0.033x + 1.697$
$R^2 = 0.795$

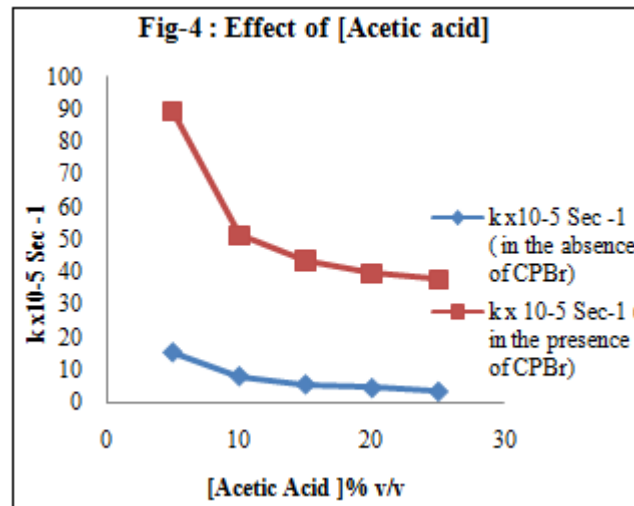$y = 0.082x + 0.868$
$R^2 = 0.753$

c) Dependence of reaction rate on [Acetic acid]
The effect of acetic acid is retarding[23] in both the cases studied. As we increase the acid strength the rate of the reaction decreases to a minimum and then remains constant with the further addition of acetic acid**Table-3 &Fig-4.**

Table 3

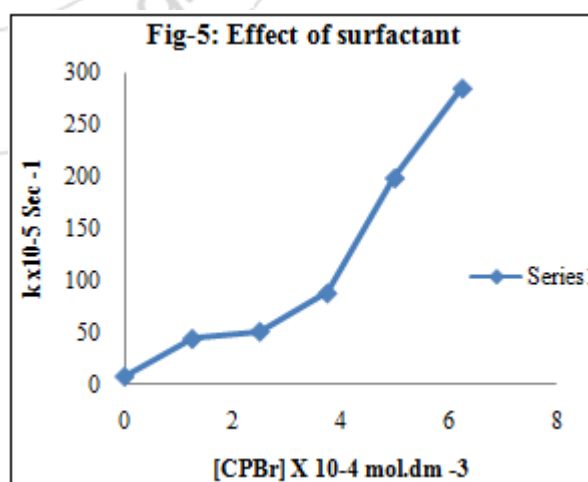| S. No	[Acetic Acid]% v/v	k x10^{-5} Sec $^{-1}$ (in the absence of CPBr)	k x 10^{-5} Sec^{-1} (in the presence of CPBr)
1	5	15.2	89.2
2	10	7.9	51.2
3	15	5.4	43.5
4	20	4.3	39.4
5	25	3.2	37.8

Fig-4 : Effect of [Acetic acid]

d) Dependence of reaction rate on[surfactant, CPBr]
To study the effect of surfactant, the reaction has been studied with the presence and absence of the surfactant, Cetylpyridinium bromide, CPBr. In this case the surfactant played a great role in enhancing the reaction rate. The rate of the reaction increases moderately upto a concentration of 3.75×10^{-4} mol.dm^{-3}and then increases drastically with the increase of [CPBr].This drastic increase in rate is due to the formation of micelles/ pre-micellar aggregates and hence by their catalysis(**Table-4**). The plot of rate constant values versus [CPBr] is given in **Fig-5**. The accelerating activity of the surfactant below the CMC value is due to the formation of pre-micellar aggregates[24-26].

Table 4

Sr. No.	[CPBr] x 10^{-4} mol.dm $^{-3}$	k x10^{-5} Sec $^{-1}$
1	0.0	7.9
2	1.25	44.3
3	2.5	51.2
4	3.75	88.2
5	5.0	199.2
6	6.25	285.7

Fig-5: Effect of surfactant

e) Dependence of reaction rate on Temperature
Effect of temperature has been studied for the two different cases mentioned (**Table-5**).The activation parameters evaluated are given in **Table-6**. In the absence of surfactant, the effect of temperature is more. In the presence of surfactant, the energy of activation is less than that in the

absence of the surfactant which shows the catalytic activity of the surfactant.The validity of Arrhenius equation is verified by plotting log k versus reciprocal of temperature.

Table 5

Sr. No.	Temp.	1/Temp.	$k \times 10^{-5} Sec^{-1}$ (in the absence of CPBr)	$k \times 10^{-5} Sec^{-1}$ (in the presence of CPBr)
1	303	0.0033	3.75	30.65
2	308	0.00325	5.53	38.23
3	313	0.0032	7.90	51.20
4	318	0.00315	10.89	62.85
5	323	0.0031	14.32	89.01

Fig-6 : Plot of log k vs 1/T

$y = -2.255x + 8.920$
$R^2 = 0.989$

$y = -2.887x + 10.11$
$R^2 = 0.996$
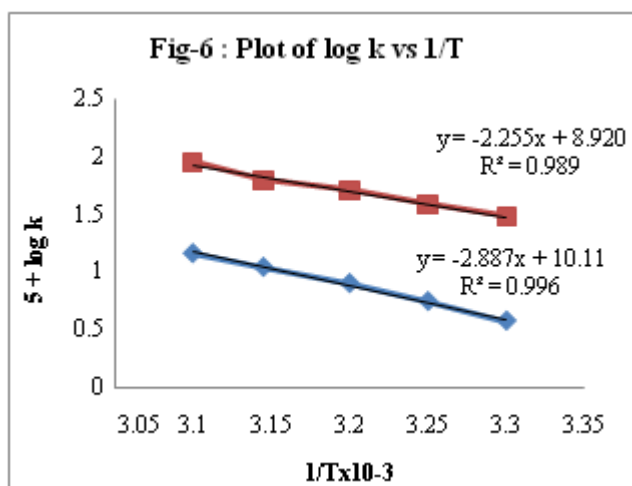
Table-6

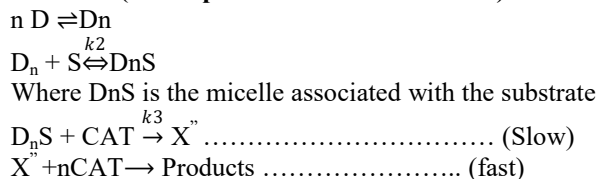| Activation Parameters	In the absence of CPBr	In the presence of CPBr
ΔE (KJ mol-1)	55.2	40.5
ΔS (JK-1 mol-1)	-150.3	-182.8
ΔH (KJ mol-1)	52.6	37.8
ΔG (KJ mol-1)	100.7	96.0

Mechanism

From the stoichiometric study, It is observed that two molecules of Chloramine-T reacts with one molecule of p-Chlorophenol. From the results of experimental work lead to the following reaction mechanism which is much probable and well consistent with the experimental data

Case – I (In the absence of the surfactant)

$CAT + S \overset{k}{\Longleftrightarrow} X$ ……………………………….. (fast)

$X \overset{k1}{\rightarrow} X'$ ………………………………….. (Slow)

$X' + n\ CAT \rightarrow Products$ ………………………...(fast)
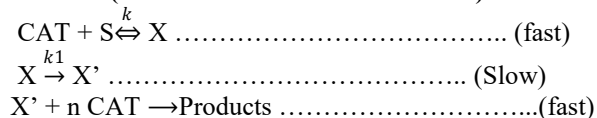
Case – II (In the presence of the surfactant)

$n\ D \rightleftharpoons Dn$

$D_n + S \overset{k2}{\Longleftrightarrow} DnS$

Where DnS is the micelle associated with the substrate

$D_nS + CAT \overset{k3}{\rightarrow} X''$ …………………………… (Slow)

$X'' + nCAT \rightarrow Products$ ………………….. (fast)

The total reaction rate can be expressed by

$$\frac{-d[CAT]}{dt} = \frac{k1k[S][CAT]}{1+k[S]} + \sum k3[DnS][CAT]$$

By doing appropriate approximation and rearrangement, the overall rate expression which is applicable to both the cases studied is,

$$k_{obs} = \frac{k1+k3k2[Dn]}{1+k2[Dn]}$$

4. Conclusion

From the rate expressions it is clear thatthe order of the reaction with respect to Chloramine-T is one both in the presence and absence of the surfactant Cetylpyridinium bromide (CPBr). The order with respect to substrate (p-Chlorophenol) is either zero or fractional both in the presence and absence of the surfactant. The experimental results clearly reveals that the rate of the reaction increases with the increase of [CPBr].This drastic increase in rate is due to the catalysis by micelles/ pre-micellar aggregates.

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