Asian Journal of Chemistry Vol. 15, No. 1 (2003), 133–138

Micellar Catalyzed Chlorination of Phenol by Chloramine-T

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The chlorination of phenol by chloramine-T (CAT) has been catalysed by cetyl pyridinium bromide (CPBr). The reaction was followed titrimetrically in acetic acid-water (20% v/v) medium at 313 K. The plot of observed rate constant *vs.* [CAT] proves the first order dependency of the reaction with respect to [CAT] both in presence and absence of the micelle. Though the rate with respect to CAT is one, the orders in phenol are fractional and zero in the presence and absence of the surfactant respectively. The rate of reaction increases with increase in concentration of surfactant. The positive cooperativity obtained indicates the possible interaction between micelle and substrate.

Key Words: Micellar, Catalyzed, Chlorination, Phenol, Chloramine-T.

INTRODUCTION

During the last two decades, the study of micellar catalysis has become an interesting subject of investigation. Some surfactants accelerate some reactions and some others retard the same reactions. The nature of surfactants plays an important role in the rate of reactions occurring in the micellar system. The present study is a kinetic investigation of chlorination of phenol by CAT[1–3] in the presence of cationic micelle and cetyl pyridinium bromide. The dependencey of the reaction rate on the concentration of CAT, phenol, surfactant, acetic acid and temperature has been investigated and a probable reaction mechanism is suggested.

EXPERIMENTAL

All chemicals used were of AnalaR and guaranteed reagent grades. The reactions were carried out in brown glass stoppered bottles. All the reactions were carried out in 20% acetic acid, 80% water (v/v) medium at 313 K. The reaction rate has been followed by estimating unreacted CAT iodometrically at various intervals of time. The specific rates are reproducible within ±5%.

RESULTS AND DISCUSSION

Dependence of rate on [CAT]: Dependence of rate on [CAT] has been determined by varying the initial concentration of CAT at given concentrations of the other reactants. The order with respect to [CAT] is first both in presence and absence of the surfactant.

Dependence of rate on [Phenol]: The order with respect to phenol is fractional[4] in the presence of the surfactant and zero in the absence of the surfactant. The values of first order rate constants are given in Table-1.

TABLE-1

[CAT] × 10^4 (mol. dm^{-3})	[Phenol] × 10^3 (mol. dm^{-3})	[HOAc] % (v/v)	[CPBr] × 10^4 (mol. dm^{-3})	Temp. (K)	k × 10^5 (sec^{-1})
3.25	10.00	10.00	—	313.00	12.40
4.00	10.00	10.00	—	313.00	12.64
5.00	10.00	10.00	—	313.00	12.82
6.75	10.00	10.00	—	313.00	12.75
10.00	10.00	10.00	—	313.00	13.05
3.25	10.00	10.00	3.75	313.00	74.27
4.00	10.00	10.00	3.75	313.00	74.23
5.00	10.00	10.00	3.75	313.00	74.28
6.75	10.00	10.00	3.75	313.00	74.43
10.00	10.00	10.00	3.75	313.00	74.66
2.50	10.00	10.00	—	313.00	12.40
2.50	15.00	10.00	—	313.00	12.48
2.50	20.00	10.00	—	313.00	12.60
2.50	30.00	10.00	—	313.00	13.05
2.50	40.00	10.00	—	313.00	14.20
2.50	10.00	10.00	3.75	313.00	74.27
2.50	15.00	10.00	3.75	313.00	90.19
2.50	20.00	10.00	3.75	313.00	107.70
2.50	30.00	10.00	3.75	313.00	135.40
2.50	40.00	10.00	3.75	313.00	173.50
2.50	10.00	5.00	—	313.00	26.71
2.50	10.00	10.00	—	313.00	12.40
2.50	10.00	15.00	—	313.00	10.07
2.50	10.00	20.00	—	313.00	5.05
2.50	10.00	25.00	—	313.00	3.10
2.50	10.00	10.00	3.75	313.00	74.27
2.50	10.00	15.00	3.75	313.00	72.43
2.50	10.00	20.00	3.75	313.00	69.80
2.50	10.00	25.00	3.75	313.00	68.70
2.50	10.00	30.00	3.75	313.00	67.63
2.50	10.00	10.00	1.25	313.00	26.31
2.50	10.00	10.00	2.50	313.00	54.01
2.50	10.00	10.00	3.75	313.00	74.27
2.50	10.00	10.00	5.00	313.00	176.20

[CAT] × 10^4 (mol. dm^{-3})	[Phenol] × 10^3 (mol. dm^{-3})	[HOAc] % (v/v)	[CPBr] × 10^4 (mol. dm^{-3})	Temp. (K)	k × 10^5 (sec^{-1})
2.50	10.00	10.00	6.25	313.00	271.40
2.50	10.00	10.00	—	303.00	5.41
2.50	10.00	10.00	—	308.00	8.34
2.50	10.00	10.00	—	313.00	12.40
2.50	10.00	10.00	—	318.00	17.52
2.50	10.00	10.00	—	323.00	23.52
2.50	10.00	10.00	3.75	303.00	27.16
2.50	10.00	10.00	3.75	308.00	42.47
2.50	10.00	10.00	3.75	313.00	74.27
2.50	10.00	10.00	3.75	318.00	127.10
2.50	10.00	10.00	3.75	323.00	177.70

Dependence of rate on detergent concentration: There is an increase in rate with increasing concentration of micelle. This can be assumed to be a possible interaction between the phenyl ring and the hydrocarbon core of the micelle.

The chlorinating species may be oriented in such a way that the attack on the micelle becomes more facile. Similar catalysis by anionic micelle NaLS has been observed in the chlorination of acetophenone, anilines and phenols by CAT.

The micellar catalysis before attaining the CMC (critical micelle concentration) value may be due to the formation of pre-micellar aggregates[5–7].

Temperature Dependence: The temperature dependence of the reaction rate has been studied in the range of 30 and 50°C. The activation parameters have been calculated from the results and summarized in Table-2.

TABLE-2

Temp. coeff.	ΔE* (kJ mol^{-1})	log PZ —	ΔS* (kJ^{-1} mol^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})
(a) *In the presence of the micelle:*					
2.10	60.46	6.17	130.8	57.81	99.46
(b) *In the absence of the Micelle:*					
3.00	89.26	11.76	23.74	86.62	94.05

Effect of solvent: The reaction rate decreases with increasing concentration of acetic acid. A plot of dielectric constant *vs.* log K gave a straight line with negative slope. This indicates the involvement of a negatively charged ion and a dipolar molecule in the reaction[8].

Stoichiometry: Stoichiometry of the reaction has been studied and it was obtained that one molecule of the substrate reacts with two molecules of the oxidant. The product of the reaction was found to be the corresponding chlorophenol.

Mechanism

$$nD \rightleftharpoons Dn$$

$$\mathrm{Dn + S \overset{K_D}{\rightleftharpoons} DnS}$$

$$\mathrm{Dns + CAT \overset{K_s}{\rightleftharpoons} X'}$$

$$\mathrm{X' + CAT \rightleftharpoons X''}$$

$$\mathrm{X'' \longrightarrow Products.}$$

The obtained rate constant K_{obs} can be expressed as

$$K_{obs} = \frac{-d}{dt}[\mathrm{CAT}]$$

$$= \frac{-d}{dt}[\mathrm{CAT}] \times \frac{1 + K[S]}{K[\mathrm{CAT}][S]}$$

$$= \frac{-d}{dt}[\mathrm{CAT}] \times \frac{K[S]}{K[S][\mathrm{CAT}]}$$

This explains all the experimental findings.

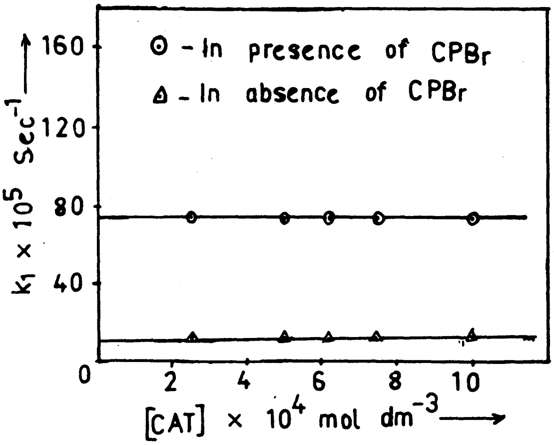


Fig. 1. Plot of k_1 *vs.* [CAT]

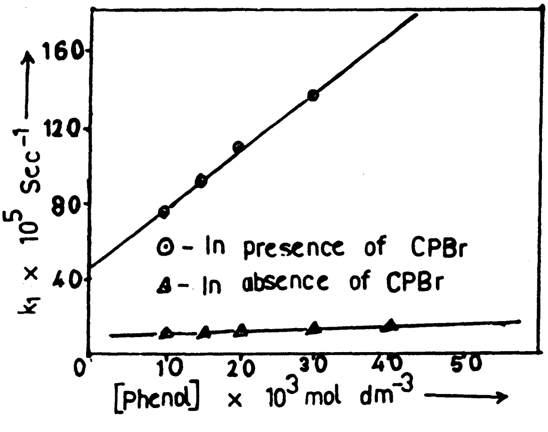


Fig. 2. Plot of k_1 *vs.* [SUBSTRATE]

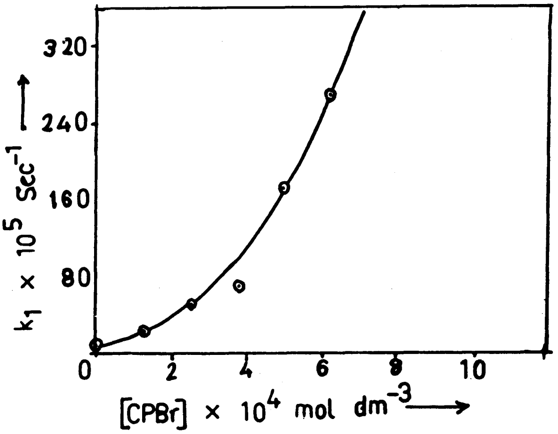


Fig. 3. Plot of k_1 *vs.* [CPBr]

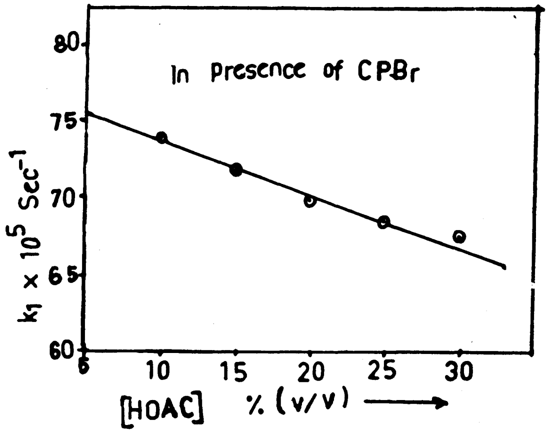


Fig. 4. Plot of k_1 *vs.* [HOAc]

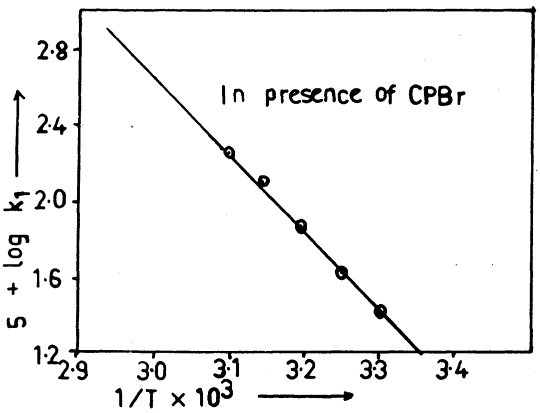


Fig. 5. Plot of log k_1 *vs.* 1/Temp. in presence of CPBr

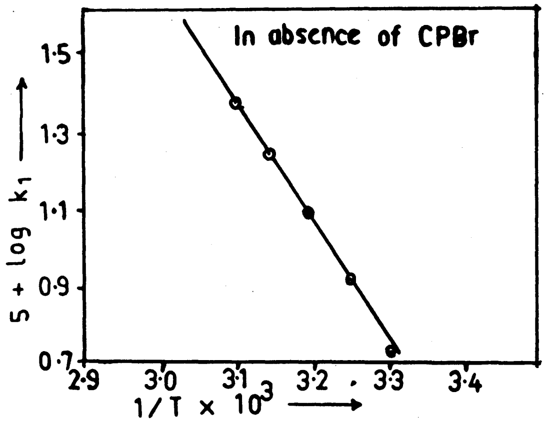
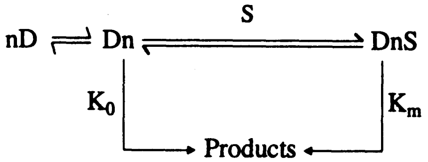


Fig. 6. Plot of log k_1 *vs.* 1/Temp. in absence of CPBr

Positive Cooperativity

According to the model proposed by Bruice *et al.*[6], n molecules of detergent associate to form Dn micelle and that combines with substrate molecules to form a substrate micelle complex.



The rate expression obtained is

$$\log[(K_{obs}-K_0)/(K_m-K_{obs})] = n\log[D]-\log K_D$$

and the graph between $\log[(K_{obs}-K_0)/(K_m-K_{obs})]$ and log [D] give a straight line whose slope is equal to 'n' which is 1.33 in the present case. This 'n' is considered as the index of cooperativity.

ACKNOWLEDGEMENT

I am highly indebted to my research superviser, Dr. S.K. Solanki, for his invaluable guidance provided to me from time to time.

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(*Received*: 17 May 2002; *Accepted*: 27 July 2002) AJC-2807