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Kinetics of Micellar Catalyzed Oxidation of *m*-Cresol by Chloramine-T

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The effect of micelles formed from the surfactant, cetyl pyridinium bromide (CPBr) on the oxidation of *m*-cresol by chloramine-T has been investigated kinetically. More over the effect of mercuric acetate on the reaction rate in the presence and absence of the surfactant has also been investigated. It is observed that the rate of the reaction has a rapid enhancement in the presence of the surfactant, showing the micellar catalytic action of the surfactant. The effect of mercuric acetate is also enhancing. It is found that the action of the surfactant is affected by the presence of mercuric acetate. The effect of acetic acid concentration on the reaction rate has also been studied. Its effect is retarding. As we increase the acid strength, the rate of the reaction decreases. The effect of temperature on this reaction is also studied and the activation parameters like ΔE^*, ΔH^*, ΔS^* and ΔG^* are evaluated. The effect of [CAT], [*m*-cresol], has also been studied. From the results obtained, a plausible mechanism is suggested.

Key Words: Surfactants, Micelle, *m*-Cresol, Chloramine-T, Cetyl pyridinium bromide.

INTRODUCTION

For the last few decades, micelles formed from surfactants have attracted the interest of many scientists[1-5]. Recently micellar catalysis has achieved the attention of many chemists[6-8]. The effect of micelles on polynuclear heterocyclic compounds have been reported recently[9-11]. Micellar systems have been recognized as potentially useful model matrices to study processes that occur in the complex plasma or cell membrane of living cells. These systems also play a vital role in pharmaceutical[12] industry and other industrial systems. The special significance of micelles in pharmacy is their ability to increase the solubility of sparingly soluble substances in water[13]. Surfactants generally known as detergents are amphiphilic molecules having distinct hydrophobic and hydrophilic regions. An important feature of micelles is its ability to solubilize a variety of compounds in its different regions[14]. Research on oxidation of phenols and substituted phenols[15] by various oxidants have been reported. The present study is the oxidation of *m*-cresol by chloramine-T[16-22] in the presence of cationic micelle formed from the surfactant cetyl pyridinium bromide (CPBr). The effect of mercuric acetate is also investigated. The reaction was carried out in acetic acid-water (20 % v/v) medium at 313 K. The effect of concentrations of chloramine-T, *m*-cresol, CPBr, acetic acid as well as mercuric acetate and the effect of temperature on the reaction rate have been studied.

EXPERIMENTAL

Chemicals used were AnalaR and Guaranteed Reagent Grades. The reactions were carried out in brown glass stoppered bottles in presence of acetic acid at 313 K. The unreacted chloramine-T was estimated iodometrically at various intervals of time. The rate constant values are reproducible within ± 5 %.

RESULTS AND DISCUSSION

Effect of chloramine-T, [CAT] on the reaction rate: The reaction rate does not depend on the initial concentration of CAT. But the order of the reaction with respect [CAT][23] is one both in the presence and absence of the micellar medium (Table-1). The plots of rate constant values *versus* [CAT] is shown in Figs. 1(2) and Fig. 1(1).

Effect of [*m*-cresol] on the reaction rate: The order of the reaction with respect to [*m*-cresol][24-26] is zero in the absence of the micelle and fractional in the presence of the micelle and also in the presence of mercuric acetate (Table-1). The plot of rate constant values *versus* [*m*-cresol] is shown in Fig. 1(5), 1(4) and 1(3) accordingly for, in the presence of micelle, in the presence of mercuric acetate and in absence of both.

Effect of [surfactant], [CPBr] on the reaction rate: It is very interesting to note that the reaction rate increases rapidly with the increase in concentration of surfactant Fig. 2(6). The effect of surfactant in presence of mercuric acetate is also

TABLE-1

[CAT] × 10^{-4} (mol dm^{-3})	[*m*-Cresol] × 10^{-3} (mol dm^{-3})	[CPBr] × 10^{-4} (mol dm^{-3})	[HOAc] (% v/v)	[$Hg(OAc)_2$] × 10^{-4} (mol dm^{-3})	Temp. (K)	K × 10^{-5} (s^{-1})
2.80	6.25	3.75	10	–	313	93.36
3.13	6.25	3.75	10	–	313	93.70
3.75	6.25	3.75	10	–	313	93.79
4.78	6.25	3.75	10	–	313	94.37
5.00	6.25	3.75	10	–	313	94.31
2.50	6.25	–	10	–	313	17.10
3.75	6.25	–	10	–	313	17.83
5.00	6.25	–	10	–	313	18.33
6.25	6.25	–	10	–	313	18.75
7.50	6.25	–	10	–	313	18.83
2.50	5.00	3.75	10	–	313	89.61
2.50	6.25	3.75	10	–	313	93.36
2.50	10.00	3.75	10	–	313	117.53
2.50	15.00	3.75	10	–	313	133.62
2.50	20.00	3.75	10	–	313	149.45
2.50	5.00	–	10	5.0	313	70.53
2.50	6.25	–	10	5.0	313	74.30
2.50	10.00	–	10	5.0	313	91.33
2.50	15.00	–	10	5.0	313	112.80
2.50	20.00	–	10	5.0	313	134.00
2.50	5.00	–	10	–	313	16.90
2.50	6.25	–	10	–	313	17.10
2.50	10.00	–	10	–	313	17.50
2.50	15.00	–	10	–	313	17.90
2.50	20.00	–	10	–	313	18.35
2.50	6.25	3.75	5	–	313	254.47
2.50	6.25	3.75	10	–	313	93.36
2.50	6.25	3.75	15	–	313	80.17
2.50	6.25	3.75	20	–	313	77.25
2.50	6.25	3.75	25	–	313	76.41
2.50	6.25	–	5	–	313	21.27
2.50	6.25	–	10	–	313	17.10
2.50	6.25	–	15	–	313	8.78
2.50	6.25	–	20	–	313	7.83
2.50	6.25	–	25	–	313	6.00
2.50	6.25	0.00	10	–	313	17.10
2.50	6.25	2.50	10	–	313	52.29
2.50	6.25	3.75	10	–	313	93.36
2.50	6.25	5.00	10	–	313	163.10
2.50	6.25	6.25	10	–	313	281.00
2.50	6.25	7.50	10	–	313	445.35
2.50	6.25	0.00	10	10.00	313	125.60
2.50	6.25	2.50	10	10.00	313	90.07
2.50	6.25	3.75	10	10.00	313	91.20
2.50	6.25	5.00	10	10.00	313	97.07
2.50	6.25	7.25	10	10.00	313	102.33
2.50	6.25	7.50	10	10.00	313	105.83
2.50	6.25	3.75	10	0.00	313	93.36
2.50	6.25	3.75	10	5.00	313	52.54
2.50	6.25	3.75	10	7.50	313	61.19
2.50	6.25	3.75	10	10.00	313	91.50
2.50	6.25	3.75	10	12.50	313	117.53
2.50	6.25	3.75	10	15.50	313	187.54
2.50	6.25	–	10	0.00	313	17.10
2.50	6.25	–	10	2.50	313	43.70
2.50	6.25	–	10	5.00	313	74.30
2.50	6.25	–	10	7.50	313	91.92
2.50	6.25	–	10	10.00	313	125.60
2.50	6.25	–	10	12.50	313	221.30
2.50	6.25	3.75	10	–	308	72.51
2.50	6.25	3.75	10	–	313	93.36
2.50	6.25	3.75	10	–	318	125.70
2.50	6.25	3.75	10	–	323	160.92
2.50	6.25	3.75	10	–	328	209.85
2.50	6.25	3.75	10	10.00	308	58.75
2.50	6.25	3.75	10	10.00	313	91.50
2.50	6.25	3.75	10	10.00	318	135.00
2.50	6.25	3.75	10	10.00	323	196.82
2.50	6.25	3.75	10	10.00	328	302.00
2.50	6.25	–	10	5.00	303	25.20
2.50	6.25	–	10	5.00	308	45.95
2.50	6.25	–	10	5.00	313	74.30
2.50	6.25	–	10	5.00	318	132.00
2.50	6.25	–	10	5.00	323	215.10

TABLE-2

Activation Parameters	In the presence of CPBr	In the presence of mercuric acetate	In the presence of both CPBr and mercuric acetate	In the absence of CPBr and mercuric acetate
ΔE^* (KJ mol^{-1})	44.8	85.9	67.8	60.6
$-\Delta S^*$ ($JK^{-1}mol^{-1}$)	163.0	33.0	90.8	112.0
ΔH^* (KJ mol^{-1})	42.2	83.3	65.1	58.0
ΔG^* (KJ mol^{-1})	94.0	94.0	94.0	93.6

studied and has shown in Table-1 and Fig. 2(7). The presence of mercuric acetate retard the catalytic activity of the micelle.

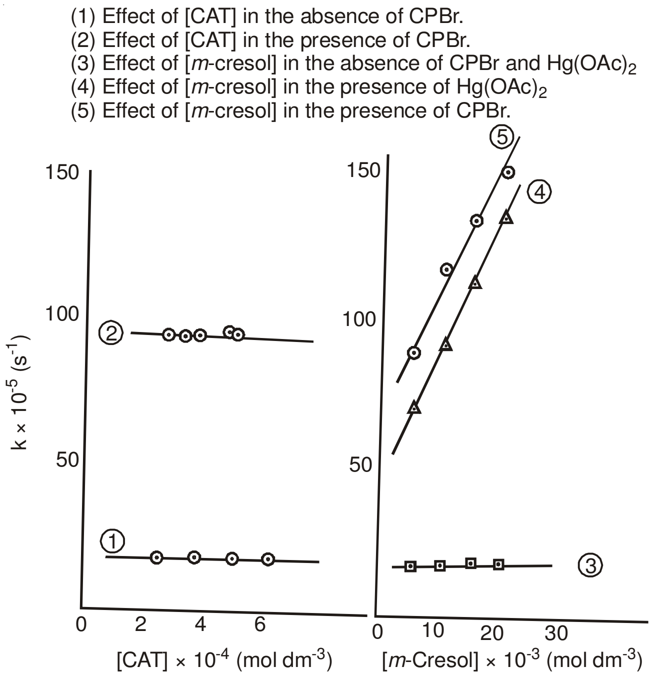

Fig. 1

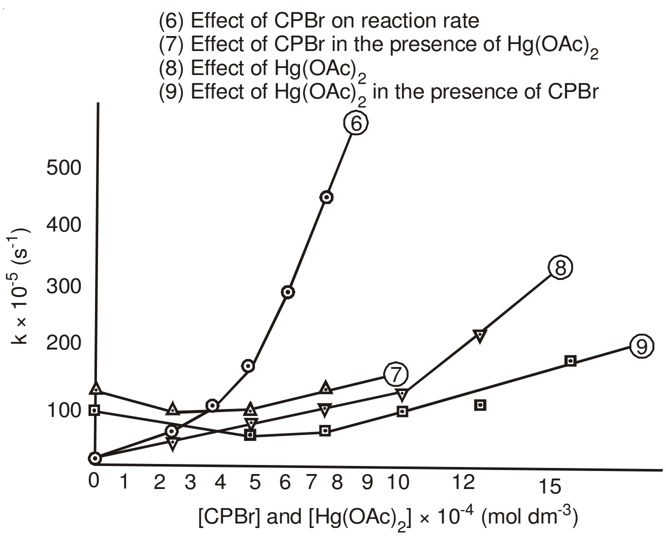

Fig. 2

The enhancement in the rate occurring before the CMC value of the micelle is due to the formation of pre-micellar aggregates[27-29].

Effect of mercuric acetate, [Hg(OAc)$_2$], on the reaction rate: The reaction rate increases with the increase of [Hg(OAc)$_2$] up to a concentration of 10×10^{-4} mol dim^{-3} and above this concentration a steep increase in rate is observed Fig. 2(8). The enhancement of reaction rate may be considered as the formation of an intermediate complex[30] between Hg^{2+} and CAT ion. It is also observed that the presence of Hg(OAc)$_2$ affect the catalytic activity of the pre-micellar aggregates due to the above mentioned complex formation (Table-1 and Fig. 2(7). The presence of surfactant also retard the activity of Hg(OAc)$_2$ up to a concentration of 6×10^{-4} mol dm^{-3} of Hg(OAc)$_2$ (Fig. 2(9) and then the rate increases with the increase in concentration of Hg(OAc)$_2$. But still the rate is less than that in the absence of surfactant (CPBr).

Effect of [CH_3COOH] on the reaction rate: The reaction rate decreases with the increase in concentration of acetic acid both in the presence and absence of the surfactant (Table-1 and Fig. 3) which shows the involvement of a negatively charged ion and a dipolar molecule in the reaction[31].

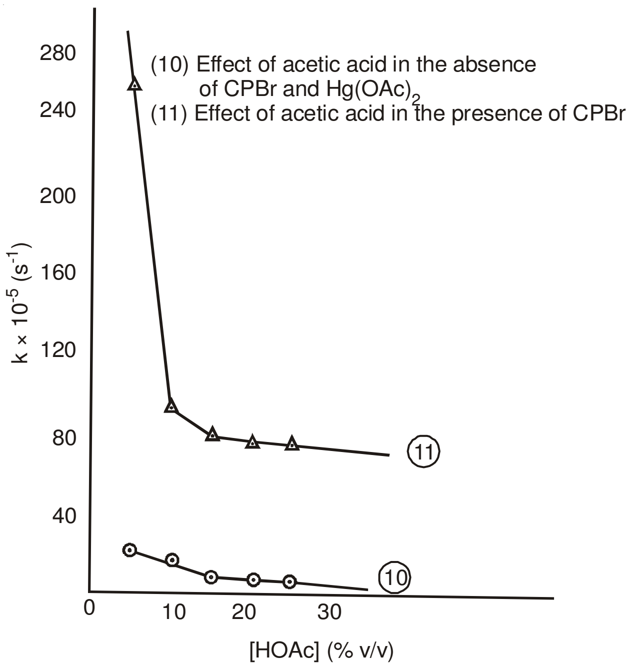

Fig. 3

Effect of temperature on the reaction rate: Effect of temperature on the reaction rate has been studied at different temperatures between 303 and 323 K. The temperature coefficient has a greater value in the absence of micelle than in the presence of it. The values of the various activation parameters calculated are given in Table-2.

Stoichiometry: Stoichiometry of the reaction is found that two molecules of chloramine-T react with one molecule of *m*-cresol. The products of the reaction were analyzed by

TLC[32] and spot tests[33]. It is found that the chloro-substituted *m*-cresol is the main product[34,35].

Mechanism

Case-I: Oxidation in the absence of the surfactant;

$$CAT + S \overset{K}{\rightleftharpoons} X \quad (Fast) \tag{1}$$

where S is the substrate (*m*-cresol).

$$X \xrightarrow{k_2} X^1 \quad (Slow) \tag{2}$$

$$X^1 + nCAT \longrightarrow Products \quad (Fast) \tag{3}$$

∴ The reaction rate is

$$= k_2[X]$$

$$= \frac{k_2 k[CAT][S]}{1 + k[S]} \tag{4}$$

Case-II: Oxidation in the presence of the surfactant:

$$nD \rightleftharpoons Dn \tag{5}$$

$$Dn + S \overset{k_o}{\rightleftharpoons} DnS$$

where DnS is the miceller associated with *m*-cresol.

$$DnS + CAT \xrightarrow{k_3} X'' \quad (Slow) \tag{6}$$

$$X'' + CAT \longrightarrow Products \quad (Fast) \tag{7}$$

The total reaction rate can be expressed as

$$\frac{-d[CAT]}{dt} = \frac{k_2 k[S][CAT]}{1 + k[S]} + \Sigma k_3[DnS][CAT] \tag{8}$$

By doing appropriate approximation the reaction rate can be shown as:

$$K_{obs} = \frac{k_2 + k_3 k_D[D_n]}{1 + k_D[D_n]} \tag{9}$$

The above rate expression is applicable to both the cases.

From the expression Nos. (8) and (9) we find (i) : The order of the reaction with respect to [CAT] is one. (ii) : The order with respect to [*m*-cresol] is either fractional or zero order. (iii) : The rate dependence of the reaction with respect to [surfactant] is clearly shown in the expression.

REFERENCES

1. R. Bayen, M. Islam and Asim K Das, *Indian J. Chem*., **48A**, 1055 (2009).
2. A.P. Mishra, K. Raj and R.P. Ravi, *Indian J. Chem*., **48A**, 1228 (2009).
3. C. Snigda and I. Kochi, *Indian J. Chem*., **48A**, 775 (2009).
4. M.K. Niyaz and I. Emran, *Indian J. Chem*., **48A**, 781 (2009).
5. P.K. Gupta, Shipra, and N.R. Dhamiwal, *Indian J. Chem*., **47A**, 1384 (2008).
6. V.W. Bhagwat, Mona, S.B. Jomalagada and B. Pare, *Indian J. Chem*., **42A**, 1644 (2003).
7. K. Ud-Oin, S.M. Shakeel and Z. Khan, *Indian J. Chem*., **42A**, 2455 (2005).
8. J. Pande and G.P. Panigrah, *Indian J. Chem*., **42A**, 1636 (2003).
9. S. Goyal and S. Acharya, *Orient. J. Chem*., **18**, 47 (2002).
10. S. Acharya and S. Mathur, *Int. J. Chem. Sci*., **3**, 433 (2005).
11. N. Nandi and I.N. Basurnallick, *J. Phys. Chem*., **97**, 3900 (1993).
12. S. Acharya and R. Jangid, *J. Ind. Council Chem*., **24,** 58 (2007).
13. S. Mall, G. Bucklon and D.A. Raulins, *J. Pharm. Sci*., **85**, 75 (1995).
14. K. Shinoda, J. Nalkagava, B. Tarnarnushi and T. Isemura, Colloidal Surfactant, Academic Press, New York.
15. B.S. Moodithaya and B.T. Gowda, *J. Indian Chem. Soc*., **79**, (2002).
16. P.S. Radhakrishnamurthy and S.C. Patil, *Indian J. Chem.*, **16A**, 541 (1978).
17. K. Selvraj, V. Venkateshwara and Ramarajan, *Indian J. Chem*., **36A**, 328 (1997).
18. Puttaswamy and D.S. Mahadevappa, *Indian J. Chem*., **32A**, 409 (1993).
19. V. Shukla and S.K. Upadhyay, *Indian J. Chem*., **47A**, 1032 (2008).
20. B. Pare, A. Manisha and S.B. Jonnalagadda, *Indian J. Chem*., **47A**, 1222 (2008).
21. Puttaswamy and N. Suresh, *Indian J. Chem*., **47A**, 1649 (2008).
22. K. Mohan and M.B. Jagadeesh, *Indian J. Chem*., **47A**, 1226 (2008).
23. Puttaswamy and A. Shukhdev, *Indian J. Chem*., **48A**, 339 (2009).
24. P.S. Radhakrishnamurthy and B.M. Sasmal, *Indian J. Chem*., **16A**, 884 (1978).
25. K.L. Mittal and B. Lindman, Surfactants in Solution, Plenum Press, New York, Vol. 2, p. 1015 (1984).
26 G. Sarasan, *J. Ind. Council Chem*., **24**, 79 (2007).
27 J.C. Bruce, J. Katzhendler and L. Fedor, *J. Am. Chem. Soc*., **90**, 1333 (1968).
28 B. Pare, V.W. Bhagwat and V.R. Shastry, *Asian J. Chem*., **13**, 1518 (2001).
29 G. Sarasan, *Asian J. Chem*., **15**, 133 (2003).
30 C.H. Bamford and C.F.H. Tipper, Comprehensive Chem., Kinetics, Elsevier Publishing Company, Amsterdam, London, New York, p. 290 (1972).
31 E.S. Amis, Solvent Effect on Reaction Rate and Mechanism, Academic Press New York and London, Ch. 2, p. 42 (1966).
32 U. Smith and J.W.T. Serkins, Chromatographic and Electrophoretic Techniques, William Heinamann Medical Books Ltd., p. 1 (1976).
33 F. Feigl, Spot Tests in Organic Analysis, Elsevier, Scientific Publishing Co., Amsterdam, Oxford, New York, p. 179 (1966).
34. K. Rangarajan, *Indian J. Chem*., **19A**, 79 (1980).
35. T. Higuchi and A. Hussain, *J. Chem. Soc. B*, 500 (1967).