

A Kinetic Study of Micellar Catalyzed Oxidation of Resorcinol by Chloramin-T

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Abstract

A kinetic study of oxidation of Resorcinol has been investigated in presence and absence of a cationic micelle, cetyl pyridium bromide (CPBr). It is observed that the rate was rapidly increased in the presence of surfactant. The rate was independent of the initial concentration of CAT, both in the presence and absence of surfactant. A first order kinetics is observed with respect to [CAT], both in presence and absence of micelle. Activation parameters for the reaction are evaluated and the plausible mechanism is suggested.

Key words: CAT, CPBr, Resorcinol, Micelle, Surfactant.

Introduction

Kinetic study in presence of micelles^{1,2} has become one of the very interesting subjects of investigation now a days. Research on oxidation of phenols^{3,4} by various oxidants has been reported. The present study is a kinetic study of oxidation of Resorcinol by CAT^{5,6,7} in the presence of surfactant, cetyl pyridium bromide (CPBr). The reaction was conducted in acetic acid-water (20% v/v) medium at 313 K and followed titrimetrically. The effect of concentration of chloramine-T, substrate, surfactant, acetic acid and mercuric acetate as well as effect of temperature on the reaction rate has been studied.

Experimental

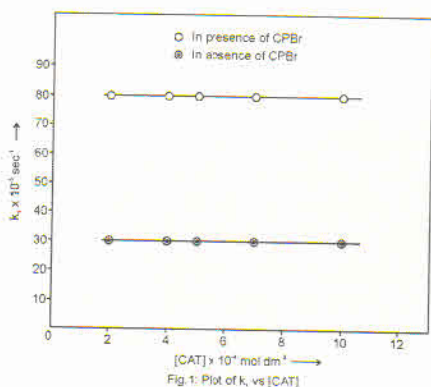
All the chemicals used were of AR Grade (E-Merck). The reactions were carried out in 20% acetic acid 80% water (v/v) medium in brown glass stoppered bottle at 313 K. The unreacted CAT was estimated iodometrically at various intervals of time. The rate constant values obtained are reproducible with in $\pm 5\%$.

Results and Discussion

A) Effect of [CAT] on reaction rate:

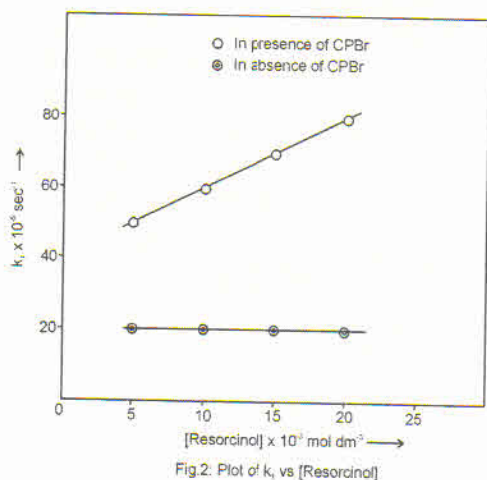
The effect of concentration of CAT on rate of reaction has been studied by varying the initial concentration of CAT keeping the

concentration of all other reactants constant. It is clear from the result that the rate is independent of the initial concentration of CAT. The plots of $\log(a-x)$ vs time gave linear graphs with almost same slopes which indicates the first order dependence of the reaction rate with respect to [CAT] both in presence and absence of surfactant (Fig.1).



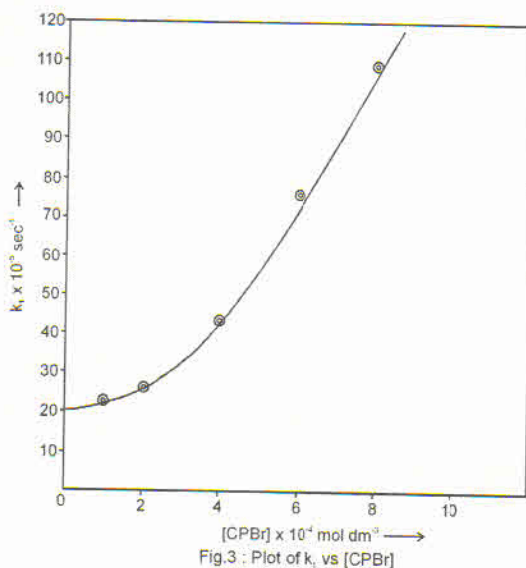
(B) Dependence of rate on [Resorcinol] :

The order with respect to Resorcinol in the presence of surfactant is fractional order and in its absence, it is zero order (Fig. 2).



(C) Dependence of rate on [Cetyl pyridium bromide, CPBr] :

As the concentration of CPBr increases the reaction rate also increases (Fig. 3). The catalytic efficiency of the surfactant is dependent on the position of the head group and the nature of charge bearing group. The nature of dependence of the reaction rate on surfactant concentration is one of the fundamental characteristics of micellar catalysis. Micelles are assumed to act as a separate phase, pseudo phase of constant properties independent of the composition of the medium⁸.



Here the reaction rate increases with the increase in concentration of CPBr. Micelles are supposed to have hydrocarbon like interior surrounded by a stern layer containing hydrated head group. The stern layer is the reaction site with in the micellar pseudo phase. In the present study, the formation of pre-micellar aggregates^{9,10,11} are responsible for the micellar catalysis.

(D) *Dependence of the reaction rate on the concentration of acetic acid :*

As the concentration of acetic acid increases, the rate of the reaction decreases both in the presence and absence of the surfactant. The plot of k (ordinate) vs [acetic acid] is shown in Fig. 4. The downward (negative) slope indicates that the involvement of a negatively charged ion as a dipolar molecule in the medium¹².

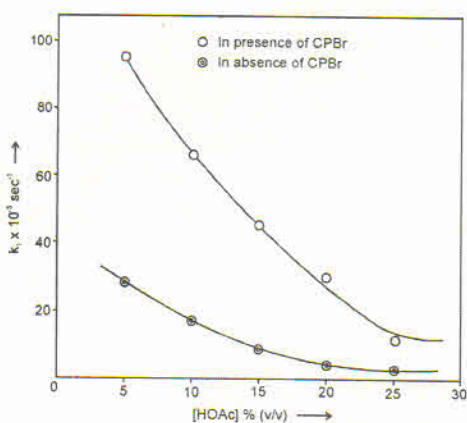


Fig.4: Plot of k , vs [HOAc]

(E) *Dependence of reaction rate on the concentration of mercuric acetate :*

The effect of mercuric acetate on the reaction rate is studied both in presence and absence of surfactant. In the absence of surfactant the reaction rate increases with increasing concentration of mercuric acetate. But in the presence of surfactant it is observed that the activity of the surfactant is affected by mercuric ions and due to this the reaction rate has a lower value as compared to the reaction rate only in the presence of the micelle.

(F) *Dependence of reaction rate on temperature :*

Effect of temperature on the reaction rate has been studied by carrying out the reaction both in presence and absence of micelle at different temperatures between 303 K and 323 K. The activation parameters calculated from the results are summarized in Table 1.

Table 1

	Temp. Coeff.	ΔE^* (KJ mol ⁻¹)	log PZ	ΔS^* (JK mol)	ΔH^* (KJ mol ⁻¹)	ΔG^* (KJ mol ⁻¹)
In the presence of micelle	1.72	46.23	3.92	159.0	47.52	92.21
In the absence of micelle	2.4	59.70	4.78	128.7	59.74	95.61

(G) *Stoichiometry :*

From the study of stoichiometry of the reaction, it is found that two molecules of CAT

react with one molecule of Resorcinol. The products of the reaction were analysed by TLC¹³ and spot test is found to be the chloro substituted Resorcinol is the main product.

(H) Mechanism :

Case 1: Oxidation in the absence of the surfactant:



where 'R' is Resorcinol



The reaction rate is

$$\frac{-d[\text{CAT}]}{dt} = \frac{k_w k [\text{CAT}][\text{R}]}{1 + k_w [\text{R}]} \quad (4)$$

Case-2 : Oxidation in presence of surfactant



where $\text{D}_n \text{R}$ is the micelle associated substrate (Resorcinol).

$$k_s$$


The overall rate is expressed by

$$\frac{-d[\text{CAT}]}{dt} = \frac{k_w k [\text{CAT}][\text{R}]}{1 + k [\text{R}]} + \sum k_s [\text{D}_n \text{R}] [\text{CAT}]$$

By doing appropriate approximation, the overall rate expression is

$$k_{\text{obs}} = \frac{k_w + k_s k [\text{Dn}]}{1 + k [\text{Dn}]}$$

This is applicable to both the cases i.e. oxidation in the presence and absence of the surfactant.

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