



Review Paper

Effect of Acetic Acid on Chlorination of some Phenols by Chloramine-T: A Kinetic Approach

Sarasan Geetha* and Pathak Namrata

Department of Chemistry, Govt. Holkar Science College, Indore, MP, INDIA

Available online at: www.isca.in, www.isca.me

Received 3rd March 2014, revised 11th March 2014, accepted 17th March 2014

Abstract

Chlorination of some phenols viz., *o*-Cresol, *m*-Cresol, *p*-Nitrophenol, Phenol, *p*-Cresol and *p*-Chlorophenol by Chloramine-T have been investigated in the absence and presence of the surfactant, Cetylpyridinium bromide (CPBr). The role of acetic acid in this oxidation reaction has been studied for all the phenols mentioned and summarised in this paper. It is very interesting to note that the reaction rate has a sudden fall by the increase of 5% to 10% acetic acid and further increase of acetic acid the rate of reaction becomes almost constant for all the phenols studied. The order of the reaction with respect to Chloramine-T is found to be one and that of with substrate is positive fractional. For the chlorination of phenols by chloramine-T, Acetic Acid plays a vital role. The experimental results reveals the importance of selection of optimum concentration of acetic acid for the chlorination of phenols by Chloramine-T in the absence and presence of Cetylpyridinium bromide (CPBr).

Keywords: Phenols, Chloramine-T, Acetic acid, Surfactant.

Introduction

Oxidation of phenol and substituted phenols by various oxidants under different solvent medium has been investigated by various researchers¹⁻⁴. But the chlorination of phenols by Chloramine-T in aqueous acetic acid medium and in the presence of surfactant has found to be a new field to be investigated. Chloramine-T is considered to be a mild oxidant, halogenating agent and many investigators have been conducted research with Chloramine-T⁵⁻¹¹. The oxidation potential of this system is pH dependent. As the solvent influences the specific reaction rate, many researchers have studied the effect of solvent in various reaction studies¹²⁻¹⁶. The most common solvent is water. Dielectric constant is not the only measure of solvent polarity still the polarity of a solvent is almost depends on the dielectric constant value. In the present study the effect of acetic acid on the rate of chlorination of *o*-Cresol, *m*-Cresol, *p*-Nitrophenol, Phenol, *p*-Cresol and *p*-Chlorophenol have been investigated in the absence and presence of Cetylpyridinium bromide (CPBr). The effect of acetic acid has been studied by varying the concentration of acetic acid keeping the concentration of all other reactants constant.

Material and Methods

The chemicals (Phenols, Chloramine-T, Cetylpyridinium bromide and Acetic acid) used were AR or GR level (grade) and all solutions were prepared in double distilled water. Acetic acid was distilled before using it. Ostwald isolation method is used to investigate the reaction. The reaction was conducted in brown bottles keeping the concentration of all reactants except acetic

acid constant. The reaction was monitored iodometrically and the first order rate constant values obtained is reproducible within $\pm 5\%$.

Results and Discussion

It is very interesting to note that in the absence of acid, the reaction was difficult to be studied. At low concentration of acetic acid, the reaction is fast and as the concentration of acetic acid increases, the reaction rate decreases and at higher concentration of acetic acid, the reaction rate remains almost constant both in the absence and presence of cetylpyridinium bromide (table 1 and 2, figure 1 and 2). In the presence of surfactant, the high rate constant values obtained are due to the micellar catalysis. The addition of acetic acid controls the reaction rate. From the result, it is clear that the presence of acid retards the reaction rate. Dielectric changes have a marked effect and the reactivity increases as the amount of water increases. The plot of $\log k$ versus reciprocal of dielectric constants (variation of acetic acid) gave straight line graph with negative slope. This indicates the involvement of a negatively charged ion and a dipolar molecule in the reaction¹⁷.

All phenols have shown almost same behaviour towards [Chloramine-T] in both the cases studied i.e. in the absence and presence of the surfactant. The values of pseudo first order rate constant remained constant at different initial concentrations of Chloramine-T for all phenols studied. The plots of $\log (a-x)$ versus time are linear graphs that indicate the first order dependence of the reaction with respect to [Chloramine-T]. (Results of this is not included in this paper).

The rate of the reaction was found to be increasing with increasing concentrations of phenols. The plots of first order rate constants versus [Phenol] are straight line graphs with positive slope which reveals the positive fractional order dependence of the reaction with respect to [Substrate] (This

result is also not included in this paper). The addition of cationic surfactant, cetylpyridiniumbromide, enhances the reaction rate due to micellar catalysis. In the presence of surfactant also the rate decreases with the increasing concentration of acetic acid.

Table-1
Effect of [Acetic Acid] in the Presence of Surfactant, (CPBr)

[Acetic Acid] % v/v.	k- values for phenols $\times 10^{-5} \text{ Sec}^{-1}$					
	Phenol	o-cresol	p-cresol	m-cresol	p-Nitro phenol	p-Chloro phenol
5	125	406	113	254	141	89
10	74	160	66	94	93	51
15	72	54	51	80	90	43
20	70	46	44	77	89	39
25	69	42	40	76	88	38

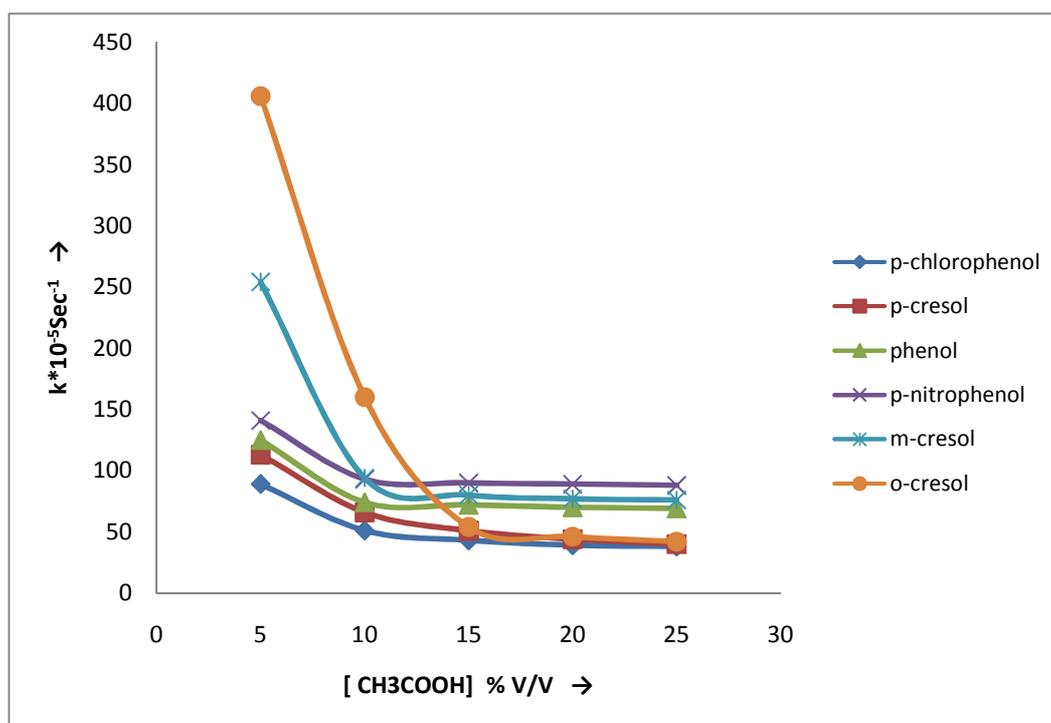


Figure-1
With Surfactant

Table-2
Effect of [Acetic Acid] in the Absence of Surfactant, (CPBr)

[Acetic Acid] % v/v.	k- values for phenols $\times 10^{-5} \text{ Sec}^{-1}$					
	Phenol	o-cresol	p-cresol	m-cresol	p-Nitro phenol	p-Chloro phenol
5	27	59	24	21	16	15
10	12	39	18	17	9	8
15	10	26	9	9	8	5
20	5	16	6	8	6	4
25	3	12	5	6	4	3

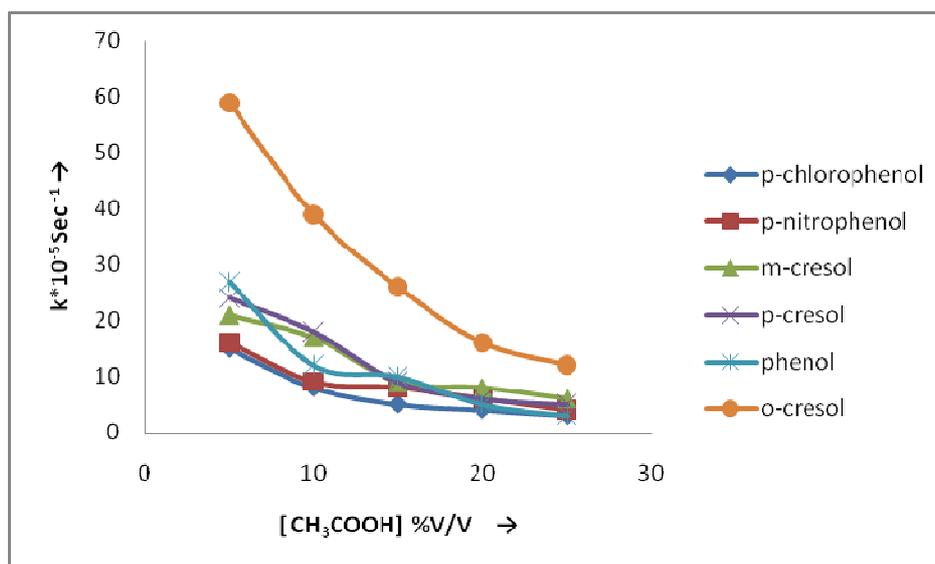


Figure-2
Without Surfactant

Stoichiometry: Stoichiometric investigation revealed two molecules of chloramine-T react with one molecule of phenol and the final product is found to be the corresponding chlorosubstituted phenol.

Conclusion

From the experimental results, it is clear that the effect of acetic acid is rate retarding and there is involvement of a negatively charged ion and a dipolar molecule in the reaction. By doing appropriate approximation and rearrangement, the overall rate expression is

$$K_{\text{obs}} = \frac{K_w + K_s K_d [\text{Dn}]}{1 + K_d [\text{Dn}]}$$

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

Where K_w is the rate constant for the slow and rate determining step in the absence of surfactant, K_d is the rate constant for the formation of complex between micelle and phenol, K_s is the rate constant for the slow and rate determining step in the presence of the surfactant and Dn is the micelle formed from the surfactant molecules.

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