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Effect of Mercuric acetate on the Oxidation of Some Phenols by Chloramine-T: A Kinetic Study

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Abstract: ***Oxidation of Phenol, o-Cresol, p-Cresol, m-Cresol, , and p-Chlorophenol byChloramine-T has been investigated in acidic medium. The present study includes the effect of mercuric acetate on the rate of oxidation of phenols by Chloramine-T. All phenols showed an increase in first order rate constant values with increase in mercuric acetate concentration. Among the phenols studied, the rate enhancement due to mercuric acetate is maximum in the case of m-Cresol. In order to determine various kinetic and activation parameters, reactions were conducted at different temperatures ranging from 303K to 328K. The values of various activation parameters determined are summarized and it is found that the values of various activation parameters in the absence of mercuric acetate is different from that in the presence of mercuric acetate for the oxidation of phenols by Chloramine-T. The values of ΔG* obtained for all phenols studied is almost same .This shows the mechanism of oxidation of all phenols studied by Chloramine-T in present case is same.***

Keywords: Chloramine-T, Mercuric acetate, o-Cresol, p-Cresol, m-Cresol, p-Nitro phenol, p-Chloro phenol

1. Introduction

Sodium derivative of N-Chloro p-toluene Sulphonamide(Chloramine-T) is a powerful oxidizing agent and has been used for the estimation of several inorganic and organic compounds.Various researchers have used Chloramine-T as an oxidant in their studies[1-10]. Chloramine-T system has a high value of redox potential in acidic medium. Research on Oxidation of Phenols and substituted Phenols by various oxidants have been reported[11,12] . Many researchers have studied the effect of mercuric acetate in various reactions [13-16].In the present study ,the role of mercuric acetate in the oxidation of some phenols by Chloramine-T has been carried out in acidic medium.

2. Experimental

All chemicals used were AnalaR or Guaranteed Reagent grade. The reaction was investigated in acetic acid medium. Acetic acid was distilled before using. Solution of Chloramine-T was stored in bottles covered with black paper and the reaction was conducted in brown bottles. Ostwald isolation method was used to investigate the reaction and the reaction was started with the addition of thermo-stated solution of Chloramine-T to the thermo-stated solution of other reactants. Effect of a particular reactant was studied by changing the initial concentration of the reactant keeping the concentration 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

Oxidation of some phenols(Phenol, o-Cresol, m-Cresol, p-Cresol, & p-Chloro phenol) by chloramine-T has been carried out, both in the presence and absence of mercuric acetate.The reaction follows a first order kinetics in Chloramine-T [17] and zero order in phenols [18,19] both in the absence and presence of mercuric acetate. The effect of acetic acid for the reaction has been found to be rate retarding[20].

It is observed that in the absence of mercuric acetate the oxidation rate is very slow and by the addition of mercuric acetate, the rate of the reaction increases with increase in concentration of mercuric acetate for all phenols studied. Among the phenols, the rate enhancement is maximum for m-Cresol with mercuric acetate,then for o-Cresol, p-Chlorophenol,Phenol and the least rate enhancement is for p-Cresol (Table-1 & Fig -1) . Effect of temperature on the oxidation of these phenols by Chloramine –T has been studied by conducting the reaction in the presence and absence of mercuric acetate at temperatures ranging from 303-328K. The values of activation parameters calculated for the oxidation of phenols by Chloramine –T in the presence and absence of mercuric acetate are summarised in Table -2 & 3

Table 1

$[Hg(OAC)_2]*10^{-3}$ mol dm^{-3}	$K*10^{-5}$ Sec^{-1} (Phenol)	$K*10^{-5}$ Sec^{-1} (o-Cresol)	$K*10^{-5}$ Sec-1 (P-Cresol)	$K*10^{-5}$ Sec-1 (m-Cresol)	$K*10^{-5}$ Sec-1 (p-ChloroPhenol)
0	12.4	38.6	18.1	17.1	7.9
0.25	14	40.2	19.8	43.7	14
0.5	16	44.2	21.2	74.3	25.2
0.75	18	49	24.3	91.9	27
1	20.2	54.6	27.3	125.6	31.5
1.25	24	60	29	221.3	33
1.5	30.6	66	30.5		37
1.75	34	70.4	32		40.5
2	39.5	76.1	37.4		47.1
2.5	49.3	82	40.4		61.4
3	60.4	96	45.6		

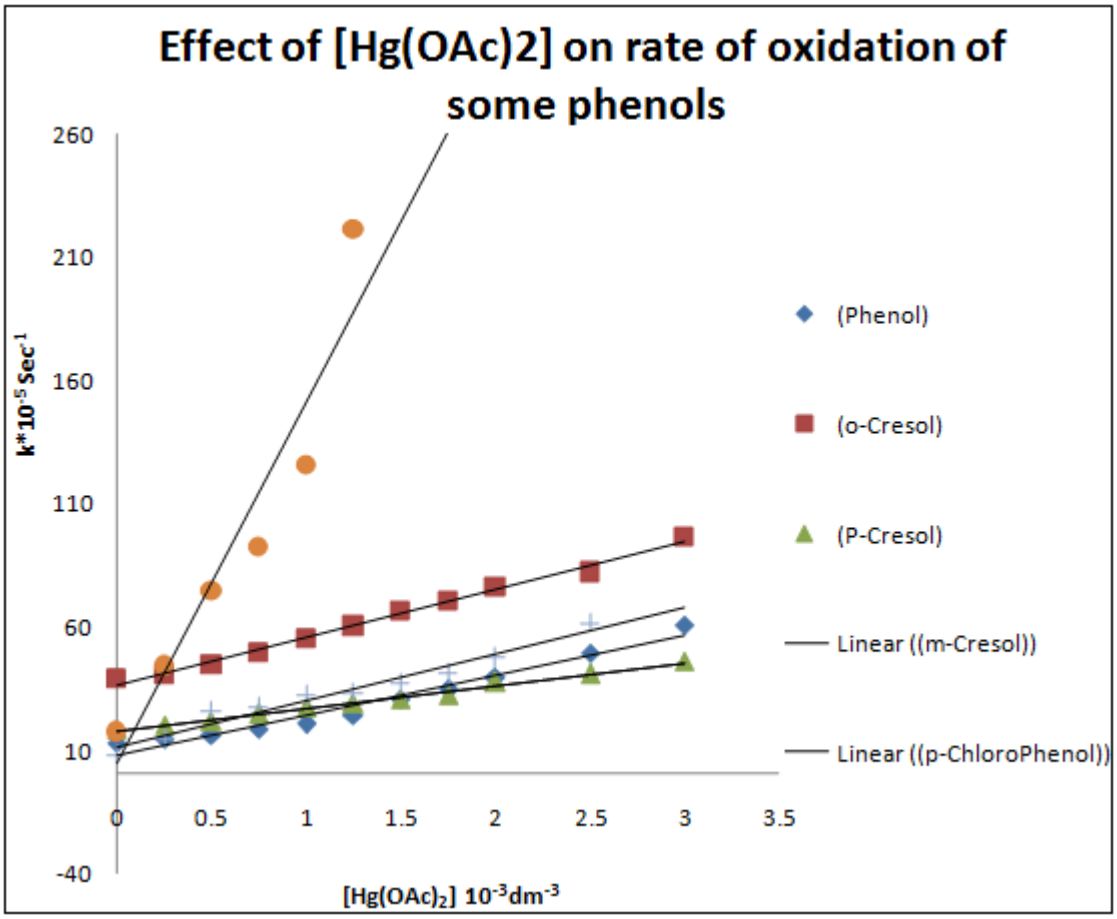

Table 2

Activation parameters	Value of activation parameters (In the absence of Mercuric Acetate)				
	Phenol	o-Cresol	m-Cresol	p-Cresol	p-Chloro phenol
ΔE^* $KJmol^{-1}$	60.5	42.8	60.6	60.6	55.2
ΔH^* $KJmol^{-1}$	57.8	40.3	58	58	52.2
$-\Delta S^* JK^{-1}mol^{-1}$	130.8	177	112	126	151
log PZ	6.2	3.8	7.2	6.4	5.1
ΔG^* $KJmol^{-1}$	99.5	96	93.6	97.7	100.7

Table 3

Activation parameters	Value of activation parameters (In the presence of Mercuric Acetate)				
	Phenol	o-Cresol	m-Cresol	p-Cresol	p-Chloro phenol
ΔE^* $KJmol^{-1}$	-	63.4	85.9	56.6	47.7
ΔH^* $KJmol^{-1}$	-	60.8	83.3	54	45
$-\Delta S^* JK^{-1}mol^{-1}$	-	109	33	136	165.8
log PZ	-	3.87.3	11.2	5.9	4.3
ΔG^* $KJmol^{-1}$	-	94.9	94	96.6	97.7

Stoichiometry

It is observed that two molecules of Chloramine-T reacts with one molecule of substrate(phenols). The product analysis revealed that the corresponding chloro-substituted phenol is the main product.

Mechanism

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

$CAT + S \rightleftharpoons X$

$X \rightarrow X'$ (Slow)

$X' + n\ CAT \rightarrow$ Products (fast)

Case – II

$M + S \rightleftharpoons MS$

Where M is mercuric acetate , S is substrate and MS is the mercuric acetate

associated with the substrate

$M''S + CAT \rightarrow X$ (Slow)

$X + CAT \rightarrow$ Products

Total reaction rate can be expressed by:

$-d[CAT]/dt = \{k_w k [S] [CAT] /1+k [S]\} + k_s[MS] [CAT]$

Where k_w is the rate constant in the absence of mercuric acetate and k_s is therate constant in the presence of mercuric acetate.

4. Conclusion

All Phenols selected for the study andChloramine-T react in a molar ratio of 2:1 both in the presence and absence of mercuric acetate in aqueous acetic acid medium. The reaction follows a first order kinetics in Chloramine-T and zero order in phenols both in the absence and presence of mercuric acetate.The role of mercuric acetate is found to berate enhancing. The rate of oxidation of m-Cresol by Chloramine – T is highly enhanced by the presence of mercuric acetate.The order of rate enhancement by mercuric acetate for phenols is as m-Cresol > o-Cresol > p-Chlorophenol > Phenol > p-Cresol. The values of ΔG* obtained for all phenols studied is almost same .This shows the mechanism of oxidation of all phenols by Chloramine-T is same.

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