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Research Article

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A comparative study of oxidation of Phenol and *o*-Cresol by Chloramine-T: A kinetic approach

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ABSTRACT

Oxidation of phenol and o- cresol by Chloramine- T has been investigated in acetic acid medium using Ostwald isolation method. The plots of log (a-x) versus time for [Chloramine- T] gave straight line graphs which shows the first order dependence of the reaction rate with respect to[Chloramine- T]. The order of the reaction with respect to [phenol/o- Cresol] is found to be zero. It is observed that as the acid strength increases the rate of oxidation of phenol as well as that of o- Cresol decreases. The effect of temperature has also been studied. The activation parameters calculated are summarized. The value of energy of activation is found to be more in the case of phenol which reveals that o- Cresol is more reactive towards Chloramine- T. From the results obtained a plausible mechanism is proposed.

Key words: Chloramine-T, Kinetic study, Phenols.
Abbreviations : CAT (Chloramine-T).

INTRODUCTION

Sodium derivative of N-Chloro p-toluene sulfonamide (Chloramine –T)[1-8]is a powerful oxidizing agent and the system has a high value of redox potential in acid medium. Oxidation of phenols by various oxidants have been investigated by various researchers[9,10]. The present study isan attempt to compare the rates of oxidation of phenol and o-cresol by Chloramine- T (CAT) in acid medium.

EXPERIMENTAL SECTION

The chemicals used were of AnalaR / Guaranteed reagents grade. All reactions were conducted in brown glass bottles and the unreacted Chloramine –T was estimated titrimetrically at regular intervals of time.

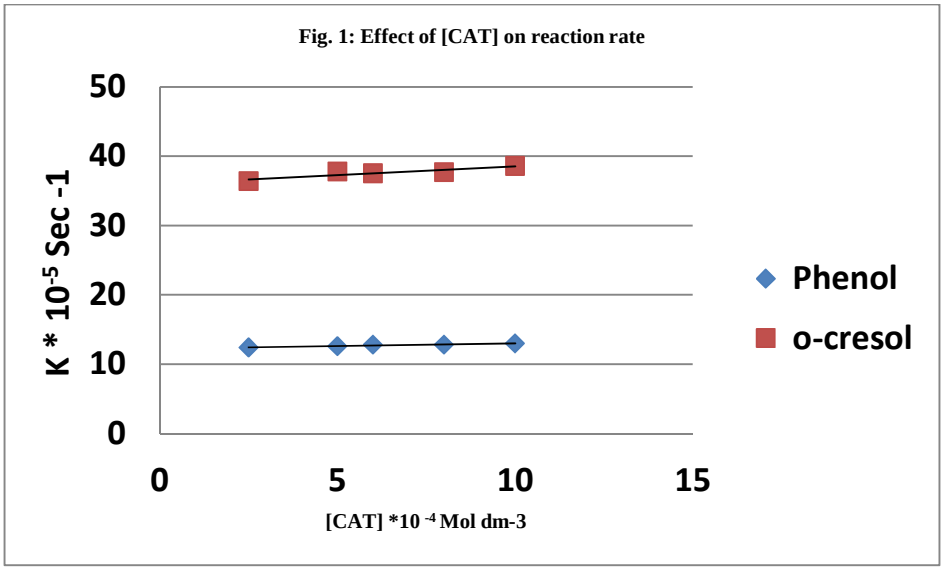
RESULTS AND DISCUSSION

1. Effect of [CAT] on reaction rate.
To study the effect of [CAT] on the reaction rate, experiments were conducted at different initial concentrations of CAT keeping the concentrations of all other reactants constant. The plots of log (a-x) versus time are straight lines with negative slopes indicate the first order dependency of the reaction with respect to[CAT]. The plots of rate constant versus concentration of CAT[11]is a straight line parallel to X-axis(Table1&Fig.1).

Table-1

[CAT]*10^{-4} Mol dm^{-3}	k*$10^{-5}$$Sec^{-1}$ (phenol)	k*10^{-5}Sec-1 (o-cresol)
2.5	12.4	36.4
5.0	12.6	37.8
6.0	12.8	37.5
8.0	12.8	37.7
10.0	13.0	38.6

Fig. 1: Effect of [CAT] on reaction rate



2.Effect of [substrate] on reaction rate.

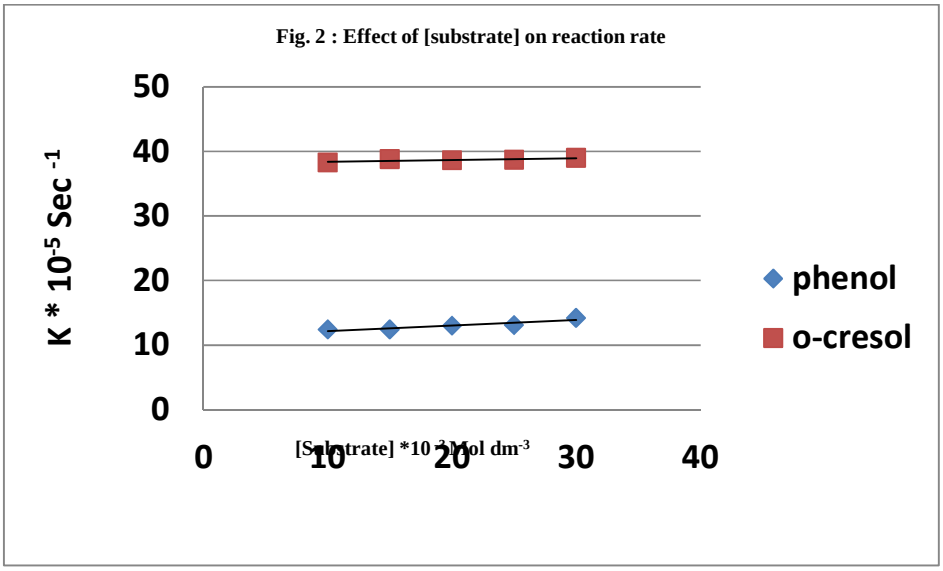
Effect of substrate concentration on the reaction rate was studied by determining the rate constant values at various initial concentrations of phenol/o-cresol.It is observed that the rate constant values remained constant for various initial concentrations of phenol/o-cresol. For both phenol and o-cresol, the slopes of plots of log k versus log c is found to be almost zero. Hence the reaction shows a zero order dependence with respect to [substrate][12,13] (Table 2, 3&Fig: 2, 3).

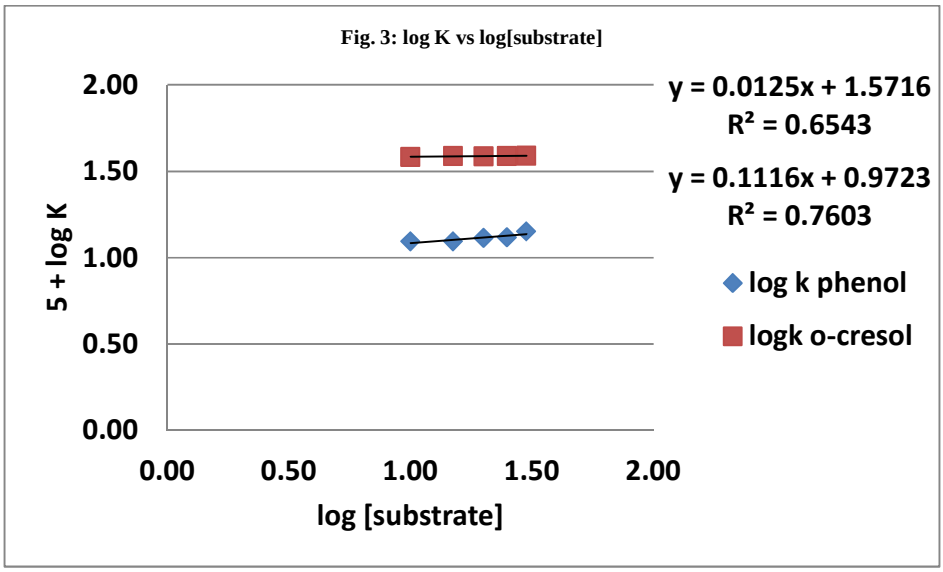
Table-2

[phenol/o-cresol]*10^{-3} Mol dm^{-3}	k*$10^{-5}$$Sec^{-1}$ (phenol)	k*$10^{-5}$$Sec^{-1}$ (o-cresol)
10.0	12.4	38.3
15.0	12.4	38.8
20.0	13.0	38.6
25.0	13.1	38.7
30.0	14.2	39.0

Table-3

Log [phenol/o-cresol]	log k (phenol)	Log k (o-cresol)
1.00	1.09	1.58
1.18	1.09	1.59
1.30	1.11	1.59
1.40	1.12	1.59
1.48	1.15	1.59



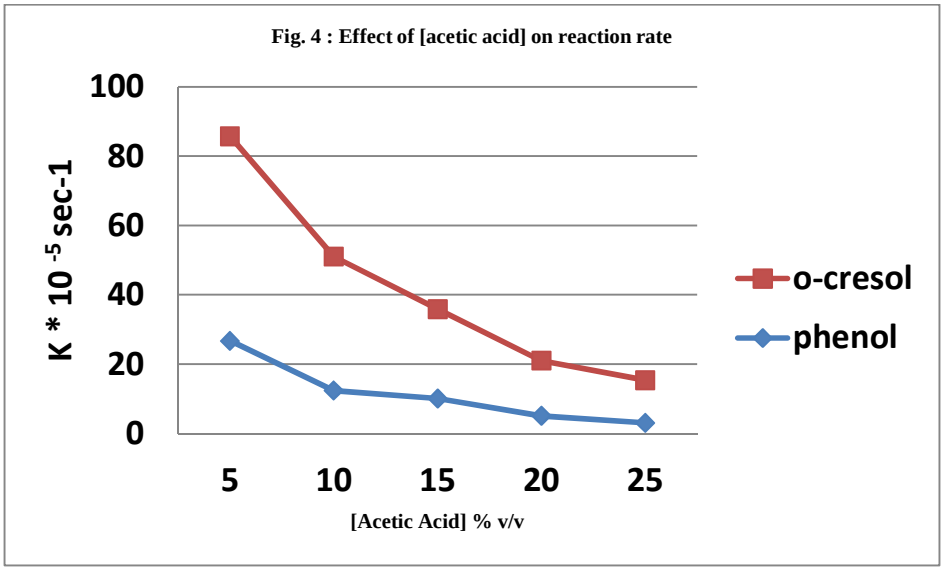


3.Effect of [acetic acid] on the reaction rate

For both phenol and o-cresol, the rate constant values decreases with increasing values of acetic acid[14],(Table4&Fig.4). The slope of the plot between k and [acetic acid] is negative.

Table-4

[Acetic acid] % v/v	k*10^{-5}Sec^{-1} (phenol)	k*10^{-5}Sec^{-1} (o-cresol)
5.0	26.7	59.0
10.0	12.4	38.6
15.0	10.1	25.8
20.0	5.1	15.9
25.0	3.1	12.3



4. Effect of Temperature on the reaction rate

To study the effect of temperature on the oxidation of phenol &o-cresol, reactions were carried out at different temperatures ranging from 303-323^{0}K keeping the concentrations of all reactants same. Activation parameters like ΔE*, ΔH*, ΔS*,&ΔG* are calculated and summarized (Table 6). The value of energy of activation is found to be more for phenol than o-cresol which clearly proves chloramine –T is more reactive towards o-cresol. The plots of log k versus 1/ T for phenol and o-cresol are straight line graphs with negative slopes which proves the validity of Arrhenious equation(Table 5 & Fig.5)

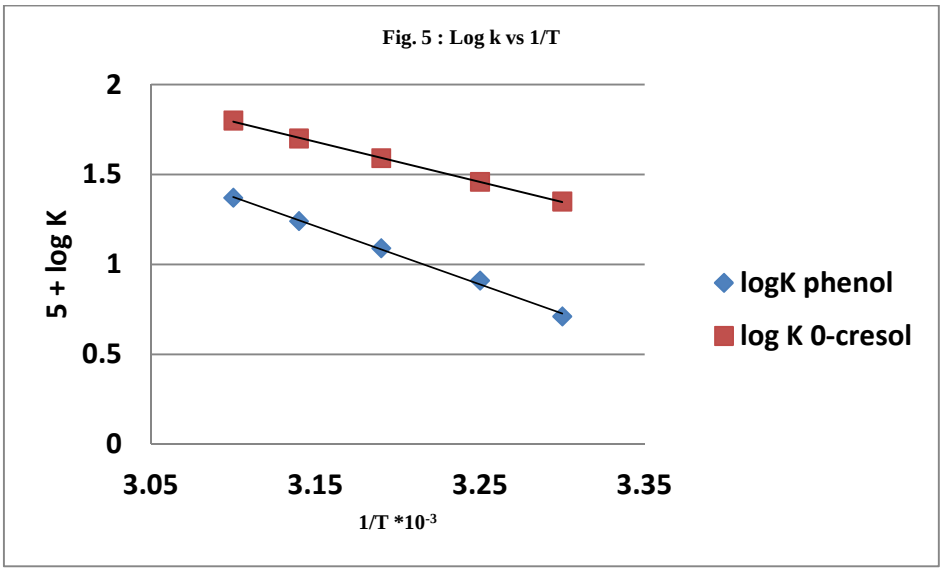


Table-5

1/T^{0}K	log k (phenol)	log k (o-cresol)
3.30	0.71	1.35
3.25	0.91	1.46
3.19	1.09	1.59
3.14	1.24	1.70
3.10	1.37	1.80

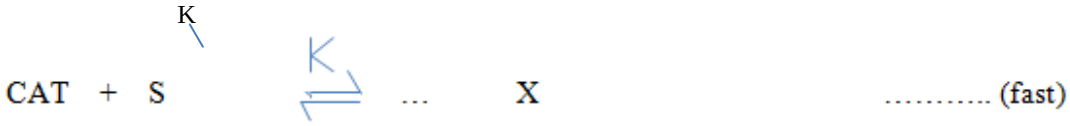
Table - 6

Activation parameters	Value of activation parameters (phenol)	Value of activation parameters (o-cresol)
ΔE^* KJmol^{-1}	60.5	42.9
ΔH^* KJmol^{-1}	57.8	40.3
$-\Delta S^*$JK^{-1}mol^{-1}	130.8	177.4
log PZ	6.2	3.7
ΔG^* KJmol^{-1}	99.5	95.8

Product Analysis

The products of oxidation were analysed by TLC and spot tests and it was found that the corresponding chloro-substituted phenol was the main product. From the stoichiometry study it was found that two molecules of chloramine-T react with one molecule of the substrate.

Mechanism



Where S is the phenolic compound (substrate)

Therefore the reaction rate is

$-d[CAT]/dt = k_1[X]$

On substitution

$-d[CAT]/dt = k_1 K [CAT] [S] / 1+ K [S]$

CONCLUSION

The rate of the reaction with respect to [CAT] is one and that of the substrates (phenol and o-cresol) is zero. The rate of the reaction decreases with increase of acid strength which shows the involvement of a negatively charged ion and a dipolar molecule in the reaction. The values of activation parameters reveals that o-cresol is more reactive than phenol with Chloramine-T.

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