RESEARCH ARTICLE

Rapid Kinetics of Bromination of the regioisomers of Cresol in aqueous medium by the competition technique: A quantitative elucidation of the reactivity of Cresols

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Manuscript Details	ABSTRACT

Cite this article as:
Bhore JB, Dangat VT*, Bonde SL and Borkar VT. Rapid Kinetics of Bromination of the regioisomers of Cresol in aqueous medium by the competition technique: A quantitative elucidation of the reactivity of Cresols, *Int. Res. J. of Sci. & Engg.*, 2014; 2 (4):142-144.

ABSTRACT

The kinetic **s**tudy for the bromination of the regioisomers of cresol in aqueous medium by molecular bromine has been carried out using the competition technique. These reactions are rapid and are found to be of the second order. The specific reaction rates determined at 26.0^o C are 1.5 x 10^4, 3.0 x 10^4 and 50.0 x $10^4\,M^{-1}\,s^{-1}$ for the *ortho, para* and *meta* isomers respectively. These values quantitatively justify the relative reactivity of these regioisomers in aqueous medium which has been qualitatively speculated hitherto for these rapid bromination reactions.

KEYWORDS: Bromination , Cresols , Competition, Iodometry

INTRODUCTION

Bromination by molecular bromine is the fastest among halogenations (Dangat, 1984). The reactions investigated herein are electrophilic substitutions and are very rapid in aqueous medium necessitating a special technique for this study. This technique is based on a competition for bromine by cresol and iodide ions. The reaction between potassium iodide and bromine is very rapid, the kinetics of which has been studied by Rao et al. (1979) the velocity constant being 77.0 x $10^4\,M^{-1}\,s^{-1}$ at 26.0 ^{0}C. When an aqueous solution of a large excess of both, potassium iodide and cresol in known concentrations is treated with a small concentration of bromine, there is a competition for bromine between potassium iodide and cresol according to the following equations.

I.   Bromination of *o*-cresol by molecular bromine
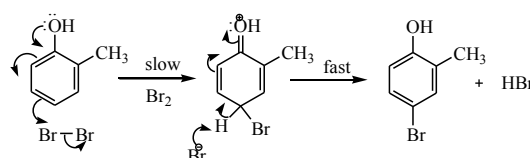
II. Displacement of iodine from potassium iodide by bromine

$$2 KI + Br_2 \longrightarrow KBr + I_2$$

Cresol does not react with potassium iodide or iodine at any significant rate under these conditions.

The amount of iodine liberated v, in the competition is determined iodometrically and compared with that, V liberated in the absence of the competition by an equal amount of bromine. Rates of the two competing reactions are thus compared and after establishing the order of the reaction under study (I), its specific reaction rate is evaluated having known that for (II).

In order to ascertain the order of the reaction under study, the competition for bromine is carried out with different ratios of cresol and potassium iodide concentrations. Order determines the dependence of the reaction rate on reactant concentrations hence variation in the competitor concentration ratio elucidates the reaction order (Dangat, 2011).

MATERIALS AND METHODS

Preparation Chemicals:
AR grade samples of the cresol isomers, potassium iodide and bromine are used to prepare the required stock solutions in conductivity water. The bromine solution is standardized using iodometry.

Determination of the specific reaction rate:
v cm³of sodium thiosulphate in the iodometric titration corresponds to the bromine reacted with potassium iodide and (V-v) cm³corresponds to that reacted with cresol in the competition. The ratio v/(V-v) is the competition ratio (Dangat, 2011).

Set I:
10 cm³ 0.0025 M Br₂ + 40 cm³ 0.005 M KI + 50 cm³ H₂O Vs 0.005 M Na₂S₂O₃ = V cm³

Set II:
10 cm³ of 0.0025 M Br₂ + 40 cm³ 0.005 M KI + 50 cm³ 0.200 M *o*-cresol Vs 0.005 M Na₂S₂O₃ = v cm³
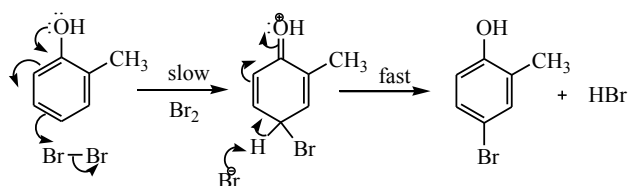Set III:
10 cm³ of 0.0025 M Br₂ + 40 cm³ 0.005 M KI + 50 cm³ 0.050 M *p*-cresol Vs 0.005 M Na₂S₂O₃
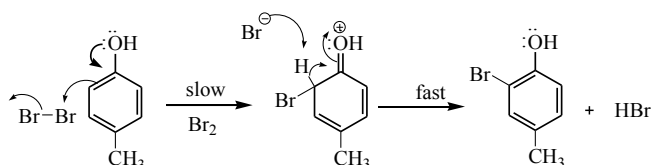
Set IV:
10 cm³ of 0.0025 M Br₂ + 40 cm³ 0.005 M KI + 50 cm³ 0.003 M *m*-cresol Vs 0.005 M Na₂S₂O₃

Reactions:

I. Bromination of *o*-cresol by molecular bromine

II . Bromination of *p*-cresol by molecular bromine

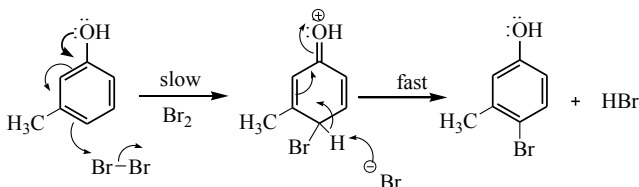III. Bromination of *m*-cresol by molecular bromine

Table 1: Bromination of *o*-cresol: Initial conc. of the reactants in 100 cm³ reaction mixture.

Sr. No.	Reactant	Concentration/M
1	Bromine	0.00025
2	*o*-cresol	0.10
3	potassium iodide	0.002

Titre values   V = 10.0 cm³   v = 5.05 cm³

Table: 2 Bromination of *p*-cresol : Initial conc. of the reactants in 100 cm³ reaction mixture

Sr. No.	Reactant	Concentration/M
1	Bromine	0.00025
2	*p*-cresol	0.05
3	potassium iodide	0.002

Titre values   V = 10.0 cm³   v = 5.05 cm³

Table: 3 Bromination of *m*-cresol : Initial conc. of the reactants in 100 cm³ reaction mixture

Sr. No.	Reactant	Concentration
1	Bromine	0.00025 M
2	*m*-cresol	0.003 M
3	potassium iodide	0.002 M

Titre values   V = 10.0 cm³   v = 5.05 cm³

RESULTS AND DISCUSSION

The competition ratio [V-v]/v is arranged to be near to unity as the error in it is then minimum. This is achieved by the prudent choice of the concentrations of the competitors in the reaction mixture ensuring precise determination of the velocity constant. In this study, we have used the appropriate concentration of each of the three regio-isomers of cresol in the three competition reactions studied with the aim of maintaining the competition ratio nearly 1 and in view of the observed rapidity of the reactions. The concentrations of both the competitors are large and almost constant compared to that of bromine in the competition. Under these conditions,

$$\frac{K_1[cresol]^x\,[Br_2]^y}{K_2[K\,I]\,[Br_2]} = \frac{V-v}{v}$$

When x and y are both taken as 1, over a variation of the concentration range of cresol, the velocity constant values k_1 obtained for the bromination of cresol are found to be constant suggesting an overall order of 2 for the reaction in all the three reactions studied. The velocity constant values obtained are presented in Table 4.

Table 4: The relative reactivity of cresols evidenced from kinetic data for bromination

Regioisomer	Velocity constant for bromination /$10^4 M^{-1} s^{-1}$
o-cresol	1.5
p-cresol	3.0
m-cresol	50.0

Green chemistry principles are inherent in this study since microgram chemicals are used in these rapid reactions besides all solutions being aqueous and very dilute.

CONCLUSION

The velocity constant values obtained in this study for the bromination of the regioisomers of cresol quantitatively justify the speculated relative reactivity of cresols in aqueous solution in electrophilic aromatic substitution reactions (Clayden et al., 2009). The rate of bromination of *m*-cresol is the greatest followed by *p*-cresol, that of *o*-cresol being the slowest. The monobromo product is formed at the position *para* to the -OH group with greatest ease in the case of *m*-cresol while in *o*-cresol, the aromaticity is markedly less due to steric hindrance, considerably slowing the approach of the electrophile.

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