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ENERGETICS OF 2,3,5 TRIMETHYL PHENOL – FORMALDEHYDE REACTION

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Abstract—*A kinetic study of the reaction of 2,3,5 trimethyl phenol with formaldehyde has been made at 345, 350, 355 and 360K and at pH values of 9.8, 10.3, 11.0 and 11.5 using sodium hydroxide as catalyst. An overall second order rate law with the formation of 4,6 dimethylol 2,3,5 methyl phenol. Activation energy, $\Delta E^{\neq}$ and entropy of activation, $\Delta S^{\neq}_{obs}$ values were calculated using the linear plots of log k versus 1/T. Effect of the polar nature of solvents i.e. methanol, ethanol, isopropanol and 1,4 dioxan show that rate of the reaction is highest in 1,4 dioxan. Catalysis by Lewis bases, ethylamine (MEA), diethylamine (DEA) tri ethylamine and tetra ethyl ammonium hydroxide (TEAH) exihibit that MEA acts as weak Lewis base and TEAH as a strong base. A comparative study of the reactivities of different phenols viz 2,4 xylenol, phenol, m-cresol and saligenin-formaldehyde reactions reveal that rate is lowest in the case of 2-tertiary butyl 3-methyl phenol -formaldehyde reaction and highest in saligenin-formaldehyde reaction. The calculated and experimental values of second order rate constant at different temperatures and at pH value of 11.0 agree well within the experimental error.*

Keywords*: Kinetic; Deprotonation; Activated complex; and Entropy of activation.*

INTRODUCTION

The resinous and non-resinous products formed by the reactions of different phenols with formaldehyde find large number of industrial applications. Therefore, a comprehensive kinetic studies of the reactions of 2,3,5 trimethyl phenol with formaldehyde, undoubtedly would reveal useful information regarding the factors controlling the properties and production of phenol-aldehyde product and in elucidating the exact mechanism of these reactions. A review of literature reveals that research works were mainly concerned with the detection of major components formed during the reaction and preparation of the phenolic resins.[1-6] The kinetics study of the reaction of 2, 3, 5 trimethyl phenol with formaldehyde has been the subject of slower growth[7-14]. In present work a comprehensive kinetic and mechanistic study of 2,3,5 trimethyl phenol with formaldehyde has been made at 345, 350, 355 and 360K and pH values of 9.8,10.3,11.0 and 11.5 taking into account the functionality (n) i.e., the number of available reactive positions on reacting phenol. Temperature and pH ranges for kinetic studies are chosen in such a way that the reaction can be studied moderately in the laboratory. At low temperature and pH, reaction is very slow to study the progress and at high temperature and pH polymerisation of product can occur.

Experimental

Materials: Ethylamine(MEA), diethylamine(DEA) and triethylamine(TEA) were from Sigma-Aldrich chemicals. Potassium iodide, AR, was an E. Merck products, 2,3,5 trimethyl phenol and tetraethyl ammonium hydroxide(TEAH) used for kinetic study was a Fluka AG Buchs G (Switzerland) products. 1,4 Dioxan and isopropanol were of spectroscopic grade (E Merck). Other chemicals sodium hydroxide and 4-nitroaniline used were AR grade CDH (India) products. A German thermostat (model NBE) was used for rate studies. Thermostat consists of a circular type steel bath and is provided with a tubular heating element. An electric motor was used for stirring the water. The sensitivity of the thermostat was ± 0.05°C.

Method:

100 ml of the 2, 3, 5 trimethyl phenol in 1:1, methanol –water mixture, was taken in a 250 ml round bottom flask .To this flask requisite amount of sodium hydroxide solution was added to give the desired pH. In a separate flask 100 ml of standardized formaldehyde solution was taken and suspended the flask in the same thermostat. After 5 minutes, when both the flasks attained the temperature of the bath, the solutions were mixed carefully and fitted with a water condenser. After a definite interval of time 10 ml of reaction mixture was withdrawn and placed in an ice-bath to freeze the reaction. Kinetic study in terms of the estimation of reactants i.e. 2-tertiary butyl 3-methyl phenol and formaldehyde was made at different temperatures and pHs.

2, 3, 5 trimethyl phenol was separated from the other reactants by preparatory TLC and estimated spectrophotometrically. Yellowish orange colour developed by the interaction of phenol and diazotised p-nitroaniline was utilised in the estimation. λ_{max} of 550 mμ was used for the estimation[15].

Prepration of diazotised p-nitroaniline : 0.5% solution of p-nitroaniline was prepared in 2N HCl and 5ml of this solution was diazotised by adding 0.5 ml of 5.0% aqueous sodium nitrite solution to get required indicator. Because of the unstability, every time a fresh sample of the indicator solution was prepared.

Estimation of formaldehyde : 10.0 ml approximately 1.0% solution of formaldehyde was taken in a conical flask. This was run into 5.0 ml of standardised sodium bisulphite solution. The flask was corked and kept at room temperature for 15 minutes. During this time 5.0 ml of sodium bisulphite solution was titrated with standardised (N/10) iodine solution. This is equivalent to the initial concentration of formaldehyde (a). Sodium bisulphite left unreacted in the bisulphite-formaldehyde was estimated by titrating with N/10 iodine solution. This will give amount of formaldehyde reacted at a given time (y). The difference between initial concentration of formaldehyde (a) and the amount of formaldehyde reacted (y) at a given time (t) gives the amount of unreacted formaldehyde left i.e. (a-y)[16-19].

Results and Discussion : The study has been summarised as given below:

1) Effect of Temp. and pH on The 2,3,5 Methyl Phenol HCHO Reaction :

Reaction : 2, 3, 5 trimethyl phenol reacts with formaldehyde in the presence of OH^- to form 4-methylol derivative:

$$(CH_3)_3.C_6H_3.OH + HCHO \rightarrow (CH_3)_3.C_6H_2.OH.CH_2OH$$

The experimental observations indicate second order rate law for the reaction.

The equation for the reaction rate is: ,

$$dy/dt = k\,(na-y)\,(b-y) \quad ---(1)$$

where a and b are the initial concentrations of and formaldehyde, y is the amount of formaldehyde reacted at time t and n = 1, is the functionality of 2,3,5 tri methyl ol l phenol. k is an overall t. The integration of equation (1) gives the following expression (2).

$$k = [2.303 / t\,(a-b)]\,[(\log b / a)\{(a-y) / (b-y)\}] \quad ----(2)$$

Results of kinetic studies are carried out at different temperatures and different pH values using sodium hydroxide as catalyst . A plot of [log b/a . (a-y) / (b-y)] versus time (t) gives straight line, showing that reaction follows an overall second order rate law . The overall second order rate constant values at pH 10.0, 10.4, 10.8 and 11.2 and at temperature 338 K are given in table1[20-23]. As the pH of the system increases, the rate of 2,3,5 trimethyl phenol – formaldehyde reaction also increases (Table 1). It shows that rate of the reaction directly depends upon the hydroxyl ions concentration. The experimental correctness of the methyl phenol-formaldehyde reaction is verified by calculating the rate constantst a pH of 11.0 and temperature of 345, 350, 355 and 360K and comparing the same with the experimental values.The values of Arrhenius parameters along with the entropy of activation can be calculated by plotting log k vs. 1/ T (Table 2).

Table 1. Overall Rate Constants k, at Different Temperature^s and at Different Concentrations of NaOH$^{.-}$

S.N	[NaOH].103 (mol.dm-3)	Θ (0C)	Initial [HCHO] (mol.dm-3)	K, IInd order rate constant 3.mol—1.s-1-)
1.	4.20	65	0.4017	3.22 x 10-6
2.	10.20	65	0.4123	66.15x 10-6
3.	16.20	65	0.4225	1.94 x 10-5
4.	22.20	65	0.4076	4.47 x 10-5
5	4.20	70	0.4222	6.25 x10-6
6	10.20	70	0.4231	9.25 x 10-6
7	16.2	70	0.4317	3.41 x 10-6
8	22.2	70	0 .4025	9.6 x 10-5

2) Effect of Different Lewis Bases and TEAH as Catalysts

Changing the nature of catalysts have been studied in the presence Lewis bases i.e. ethylamine (MEA), diethylamine (DEA), triethylamine (TEA) and the base tetraethylammonium hydroxide at 345K and pH value of 9.8 were calculated.

Due to the inductive effect, MEA, DEA and TEA behave as weak Lewis bases in comparison to tetraethylammonium hydroxide (TEAH) and the rate of the 2, 3, 5 tri methyl phenol – formaldehyde reaction is highest in the latter case. Rate can be arranged in the following order :

TEAH > TEA > DEA > MEA

←

Rate in increasing order

3) Effect of the Polarity of Different Media

A study of the effect of different solvents was made on 2, 3, 5 trimethyl phenol- formaldehyde reaction at pH value of 11.2 and temperature of 345K using methanol, ethanol, isopropanol and 1,4 dioxan as solvents in the ratio of 1:1

(v/v) solvent- water mixture. It can be seen from table 5 that rate is high in the polar solvent 1,4 dioxan and it decreases as the polarity of the medium decreases. The second order rate constants could be arranged in the following order :

1,4 Dioxan > Isopropanol > Ethanol > Methanol

←

Rate in increasing order

4) Comparative Rate Study of 2,3,5 Trimethyl Phenol-Formaldehyde Reactions :

A comparative rate study of the overall second order rate constant values for 2, 3, 5 trimethyl methyl phenol, 2,4-xylenol, m-cresol and saligenin- formaldehyde [24] at 345, 350, 355 and 355K reveals that rate of reaction is lowest with 2, 3, 5 trimethyl methyl phenol-formaldehyde reaction due to the reason that tertiary butyl group is more electron releasing in comparison to methyl group, so the electron density at the phenol nucleus is greatly increased, that will not favour the easy removal of H^+ from the phenol nucleus. Due to ortho and para directing effects of methyl group, the approaching electrophile will be directed toward the meta position of the phenol nucleus and which is not susceptible for an electrophilic attack. The tertiary butyl group, the steri hindrance by this group will be large. The electrophilic center and hence rate would be slow.

Rate of different phenols-formaldehyde reaction can be arranged in the following order:

2, 3, 5 Trimethyl < 2, 4-Xylenol < Phenol < m-Cresol < Saligenin
phenol

←

Rate in decreasing order

Mechanism: Due to inductive and mesomeric effects 2,3,5 methyl phenol in the presence of OH^- acquires a negative charge at the p- position and exists as 2,3,5 methyl phenolate ion and form the activated complex with the formaldehyde molecule.

This is a slow reaction and hence the rate determining step. Activated complex formed rearranges to give monomethylol 2,3,5 tri methyl phenolate ion and reacts with a water molecule to give monomethylol 2, 3, 5 tri methyl phenol and OH^- is set free to further catalyse the reaction. In the mechanism suggested above, net entropy of activation ($\Delta S^{\neq}_{obs}$) is the sum of the entropy of deprotonation of 2,3,5 methyl phenol ($\Delta S^{\neq}_{ph}$) and entropy required for the formation of activated complex ($\Delta S^{\neq}_{AC}$) given by the equation (3):

$$\Delta S^{\neq}_{obs} = \Delta S^{\neq}_{ph} + \Delta S^{\neq}_{AC} \qquad \text{----- (3)}$$

$\Delta S^{\neq}_{ph}$ of 2,3,5 tri methyl phenol and formaldehyde, is invariably negative and its value becomes more and more negative as pH of the reaction increases.

Table 2. Various Activation Parameters for the 2, 3, 5 trimethylphenol-Farmaldehyde Reaction

S.N.	$[NaOH]\times10^3$	$\Delta E \times10^{-3}$	$\Delta S\times10$
	$mol.dm^{-3}$	$J.mol^{-1}$	$JK^{-1}.mol^{-1}$
1	4.20	13.77	+05.52
2	10.20	12.85	+03.48
3	16.20	08.56	- 08.26
4	22.20	06.88	-02.59

Activated complex formed is unstable and distorted and its value is assumed to remain constant. Since $\Delta S^{\neq}_{ph}$ for 2,3,5 tri methyl phenolate ion is becoming increasingly negative with of increase of pH and $\Delta S^{\neq}_{AC}$ has large postive value. The net result would be that the entropy of activation ($\Delta S^{\neq}_{Obs}$) would decreases with increase of pH. The larger values of energy of activation (ΔE) at lower pH show that OH^- play an important role in the reaction.

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