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KINETICS OF ACID CATALYSED CATECHOL FORMALDEHYDE REACTION

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A kinetic study of catechol-formaldehyde reaction has been made at temperatures 65, 70, 75 and 80 °C and at different concentrations of hydrochloric acid and taking the functionality of catechol into consideration. The reaction follows second order rate kinetics. The rate of the reaction increases with increase of temperature and concentration of hydrochloric acid. The overall rate constant k, has been resolved into the stepwise rate constants k_1 and k_2. Entropy of activation and Arrhenius parameters have been calculated.

Key Words : Kinetics; Acid Catalysed Catechol-Formaldehyde Reaction; Entropy of Activation; Arrhenius Parameters

INTRODUCTION

PHENOLS combine with aldehydes forming a variety of products. The rate of the reaction and nature of the products formed depend upon the type of the substituents present in a phenol, on the nature of the catalyst used and on the medium of the reaction. Phenol-formaldehyde reactions have been studied by various authors.[1–12] A review of the literature reveals that not even a single kinetic study on catechol-formaldehyde reaction has been reported.[1–14] In this communication, a comprehensive kinetic study of acid catalysed catechol-formaldehyde reaction has been carried out at temperatures 65 ± 0.05, 70 ± 0.05, 75 ± 0.05 and 80 ± 0.05 °C using different concentrations of hydrochloric acid as catalyst.

EXPERIMENTAL

Materials and Method

(*a*) *Materials* : Catechol used for rate studies was a E. Merck product. Formaldehyde, sodium hydroxide, oxalic acid were B. D. H. products. Hydrochloric acid and methanol were A. R. or C. P. quality, *p*-nitroaniline used for the preparation of the indicator was a Thomas Baker and Co. product.

A German thermostat (model NBE) was used for rate studies. The temperature control of the thermostat was within ± 0.05 °C.

(*b*) *Method* : The solution of catechol was prepared in 50 per cent methanol. Formaldehyde solution was prepared in doubly distilled water. Reaction mixture consisting of 20ml of 0.897M solution of catechol, 20ml nearly similar concentration of formaldehyde and 6ml of hydrochloric acid of varying concentration (determined using Leeds Northrup conductivity bridge) were taken in a round bottom flask fitted with a water condenser and suspended in the thermostat maintained at the desired temperature. After a definite interval of time 4ml of the reaction mixture was withdrawn and placed in an ice bath to freeze the reaction. Formaldehyde was estimated by Ripper's sodium bisulphite method and the catechol was determined spectrophotometrically. Diazotisation reaction[9] of catechol with *p*-nitroaniline was utilised to determine the concentration of catechol.

RESULTS AND DISCUSSION

Acid catalysed catechol-formaldehyde reaction proceeds according to following equation :

$$C_6H_4(OH)_2 + CH_2O \xrightarrow{k_1} C_6H_3(OH)_2 \,.\, CH_2OH \qquad \text{...(A)}$$

$$C_6H_3(OH)_2 \,.\, CH_2OH + C_6H_4(OH)_2 \xrightarrow{k_2} C_6H_3(OH)_2{-}C_6H_2{-}(OH)_2 \times C_6H_3 + H_2O \qquad \text{...(B)}$$

The overall rate expression for the formation of products is given by :

$$\frac{dx}{dt} = k(a - x)\,(b - y), \qquad \text{...(1)}$$

where a and b are the initial concentrations of catechol and formaldehyde, x and y are the amounts of catechol and formaldehyde reacted during 't' time interval.

It has been found that ratio of the catechol and formaldehyde reacted at any time in the reaction were

$$x = 1.80y \qquad \text{...(2)}$$

Putting the value of x in equation (1) and upon integration, we get :

$$k = \frac{2.303 \times 1.80}{t(1.80b - a)} \log \frac{a}{b} \frac{(b - y)}{(a - 1.80y)} \qquad \text{...(3)}$$

Results of the kinetic study have been given in Tables I and II.

A linear plot of $\log a/b \,.\, (b-y)/(a-1.80y)$ versus time confirms the second order kinetics of the reaction (Fig. 1). Arrhenius parameters and entropy of activation have been calculated using transient kinetics by plotting $\log k/T$ versus $1/T$ (Fig. 2). These values are given in Table III. Activation energy and entropy of activation values are found to decrease with increase in concentration of hydrochloric acid.

Calculation of Stepwise Rate Constants

From reactions (A) and (B), the rate of formation of mono methylol catechol is :

$$\frac{dy}{dt} = k_1(na - y - z)\,(b - y). \qquad \text{...(4)}$$

TABLE I

Second order rate constants for various HCl concentrations

Initial [Catechol] = 0.39M; Temp. = 65 ± 0.05 °C

Run No.	[HCl] $\times10^{-3}$N	Initial [HCHO] (M)	Time (sec)	[HCHO] reacted (moles/litre)	[Catechol] reacted (moles/litre)	Second order rate constant (litre/mole-sec)	Average second order rate constant (litre/mole-sec)
1	2.45	0.4237	14400	0.0115	0.0209	9.21×10^{-6}	
			21600	0.0160	0.0289	9.11×10^{-6}	
			28800	0.0220	0.0389	9.00×10^{-6}	
			36000	0.0285	0.0519	9.70×10^{-6}	$(9.25 \pm 0.30)\times10^{-6}$
2	7.35	0.4331	10800	0·0240	0.0431	2.05×10^{-5}	
			18800	0.0350	0.0628	2.25×10^{-5}	
			25200	0.0493	0.0896	2.55×10^{-5}	
			32400	0.0628	0.1144	2.68×10^{-5}	$(2.51 \pm 0.38)\times10^{-5}$
3	12.25	0.4431	7200	0.0341	0.0615	5.61×10^{-5}	
			12600	0.0536	0.0978	5.54×10^{-5}	
			19800	0.0754	0.1376	5.48×10^{-5}	
			27000	0.1004	0.1817	6.03×10^{-5}	$(5.66 \pm 0.40)\times10^{-5}$
4	17.15	0.4251	5400	0.0401	0.0729	9.46×10^{-5}	
			9000	0.0619	0.1103	9.45×10^{-5}	
			12600	0.0783	0.1401	9.25×10^{-5}	
			16200	0.1011	0.1809	9.86×10^{-5}	$(9.50 \pm 0.25)\times10^{-5}$

TABLE II

Second order rate constants for various HCl concentrations

Initial [Catechol] = 0.39M; Solvent = Methanol-water (1:1, v/v)

Temp. °C	[HCl] $\times10^{-3}$M	[HCHO] (M)	Second order rate constant (litre/mole-sec)
70	2.45	0.4186	$(2.03 \pm 0.07)\times10^{-5}$
	7.35	0.4210	$(3.28 \pm 0.12)\times10^{-5}$
	12.25	0.4662	$(6.55 \pm 0.21)\times10^{-5}$
	17.15	0.4537	$(1.10 \pm 0.12)\times10^{-4}$
75	2.45	0.4586	$(3.79 \pm 0.06)\times10^{-5}$
	7.35	0.4174	$(1.05 \pm 0.05)\times10^{-4}$
	12.25	0.3895	$(1.46 \pm 0.14)\times10^{-4}$
	17.15	0.4541	$(2.68 \pm 0.24)\times10^{-4}$
80	2.45	0.3907	$(7.67 \pm 0.14)\times10^{-5}$
	7.35	0.4064	$(1.29 \pm 0.13)\times10^{-4}$
	12.25	0.4089	$(2.35 \pm 0.32)\times10^{-4}$
	17.15	0.4452	$(4.74 \pm 0.21)\times10^{-4}$

The concentration of catechol, formaldehyde and monomethylol catechol would be $(a - x)$, $(b - y)$ and $(y - z)$ respectively at any time interval t, where x, y and z are the respective amounts of catechol, formaldehyde and monomethylol catechol

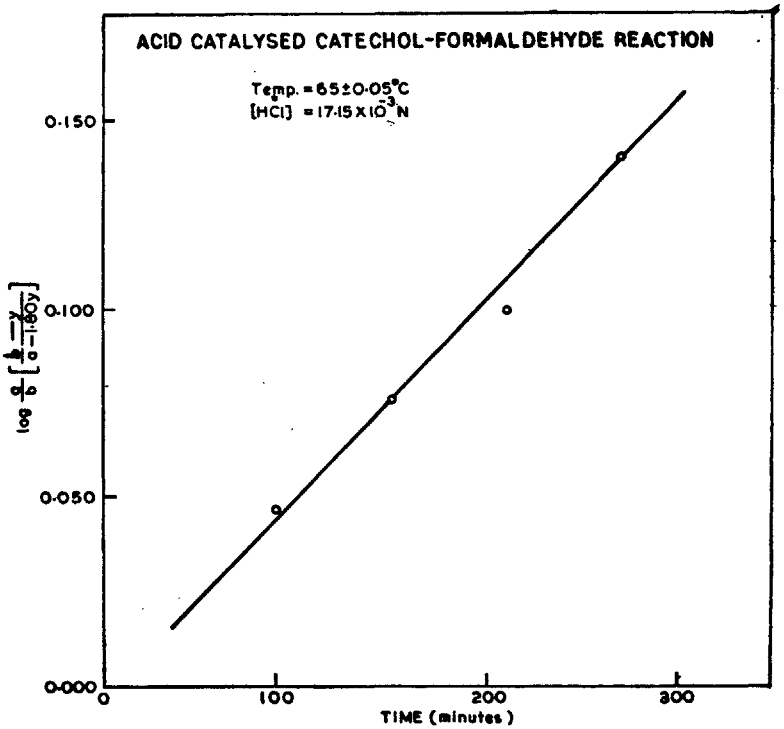

FIG 1

TABLE III

Overall Arrhenius parameters for the catechol-formaldehyde reaction

[HCl] $\times 10^{-3}$N	ΔE (k cal/mole)	ΔS (cal/deg-mole)
2.45	37.43	28.72
7.35	29.91	8.15
12.25	20.33	−18.00
17.15	16.66	−42.12

reacted at time t, n is the functionality of catechol. The rate of formation of tetrahydroxydiphenyl methane is :

$$\frac{dz}{dt} = k_2(na - y - z)(y - z), \qquad \ldots(5)$$

where $(na - y - z)$ is the concentration of catechol at any time t. The amount of catechol reacted at any stage of the reaction is equal to the sum of the amounts of formaldehyde and monomethylol catechol reacted.

i.e., $$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}, \qquad \ldots(6)$$

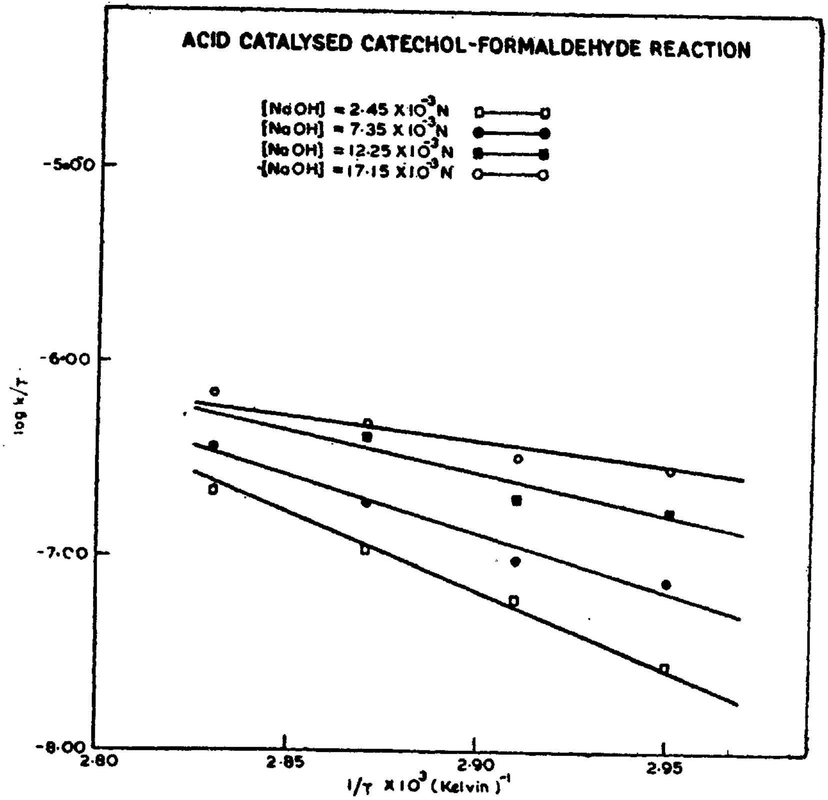

FIG 2

It follows from equation (1), (4) and (5) :

$$k = k_1 + k_2\left(\frac{2y - z}{b - y}\right). \qquad \ldots(7)$$

Utilizing the values of x, y and k from Tables I and II in equation (7), we obtained values for k_1 and k_2. The average values of k_1 and k_2 at different temperatures and concentrations of hydrochloric acid are given in Table IV.

As can be seen from Table IV, $k_2/k_1 = 66\text{–}69$.

A Comparative Study of the Reactivity of Acid Catalysed Catechol-Formaldehyde Reaction with that of 2-Methyl Resorcinol and 2-Tertiory Butyl 4-Methyl Phenol-Formaldehyde Reaction

We have extended our work on the kinetics of 2-methyl resorcinol and 2-tertiary butyl 4-methyl phenol-formaldehyde reaction under similar experimental conditions. Data have been summarized in Table V. A comparative study shows that rate of the reaction is the highest with 2-methyl resorcinol-formaldehyde and the lowest with 2-tertiary butyl 4-methyl phenol-formaldehyde.

TABLE IV

Stepwise rate constants at various HCl concentration and at different temperatures

Temp. °C	[HCl] $\times 10^{-3}$N	Stepwise rate constants (litre/mole-sec)		
		k_1	k_2	$m = k_2/k_1$
75	2.45	1.67×10^{-5}	1.15×10^{-3}	68.86
	7.35	3.04×10^{-5}	2.03×10^{-3}	66.77
	12.25	4.04×10^{-5}	2.76×10^{-3}	68.32
	17.15	6.67×10^{-5}	4.53×10^{-3}	67.91
80	2.45	2.78×10^{-5}	1.97×10^{-3}	70.86
	7.35	4.08×10^{-6}	2.76×10^{-3}	67.64
	12.25	5.32×10^{-5}	3.57×10^{-3}	67.11
	17.15	7.90×10^{-5}	5.28×10^{-3}	66.84

TABLE V

Comparison of overall rate constant

[HCl] $\times 10^{-3}$ (N)	Overall second order rate constant (l/mole-sec)		
	Catechol-formaldehyde reaction	2-Tertiary butyl 4-methyl phenol-formaldehyde reaction	2-methyl resorcinol-formaldehyde reaction
	Temp. = 65 ± 0.05 °C		
2.45	9.25×10^{-6}	1.90×10^{-6}	2.28×10^{-5}
7.35	2.51×10^{-5}	2.46×10^{-6}	5.30×10^{-5}
12.25	5.66×10^{-5}	8.70×10^{-6}	9.31×10^{-5}
17.15	9.50×10^{-5}	1.90×10^{-5}	3.17×10^{-4}
	Temp. = 70 ± 0.05 °C		
2.45	2.03×10^{-5}	4.16×10^{-6}	4.07×10^{-5}
7.35	3.28×10^{-5}	7.58×10^{-6}	8.68×10^{-5}
12.25	6.65×10^{-5}	1.81×10^{-5}	2.28×10^{-4}
17.15	1.11×10^{-4}	3.63×10^{-5}	6.62×10^{-4}
	Temp. = 75 ± 0.05 °C		
2.45	3.79×10^{-5}	1.31×10^{-5}	7.65×10^{-5}
7.35	1.05×10^{-4}	2.18×10^{-5}	1.37×10^{-4}
12.25	1.46×10^{-4}	4.46×10^{-5}	4.53×10^{-4}
17.15	2.68×10^{-4}	7.58×10^{-5}	9.32×10^{-4}
	Temp. = 80 ± 0.05 °C		
2.45	7.67×10^{-5}	2.29×10^{-5}	1.48×10^{-4}
7.35	1.29×10^{-4}	4.01×10^{-5}	3.09×10^{-4}
12.25	2.35×10^{-4}	7.58×10^{-5}	7.30×10^{-4}
17.15	4.74×10^{-4}	1.38×10^{-4}	1.46×10^{-4}

Due to the presence of two hydroxyl groups in *ortho* positions in catechol, the removal of H^+ becomes difficult and retards the formation of catecholate ion. Rate of the reaction will, therefore, be lower in comparison to 2-methyl resorcinol-formaldehyde reaction.

Rate of the reaction is the lowest with 2-tertiary butyl 4-methyl phenol-formaldehyde reaction because of strong *ortho* and *para* directing methyl and 2-tertiary butyl 4-methyl groups, which will direct the approaching formaldehyde molecule towards the *meta* position of 2-tertiary butyl 4-methyl phenol, not susceptible to attack. Steric hindrance due to tertiary butyl group will be large and the formaldehyde molecule will not easily reach the reactive centres of phenol.

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REFERENCES

1. M M Sprung and M T Gladstone *J Am chem Soc* **71** (1949) 2907
2. S R Finn and G J Lewis *J Soc Chem Ind* **69** (1950) 129
3. J H Freeman and C W Lewis *J Am chem Soc* **76** (1954) 2080
4. M Toshiro and A Tadanao *Kagyo Kagaku Zasshi* **60** (1957) 1078
5. S Shoji and H Horiuchi *Kagyo Kagaku Zasshi* **62** (1959) 1921
6. L M Yeddanapalli and D J Francis *Markromol Chem* **55** (1962) 74
7. A A Zavitasas R D Beaulien and J R Leblanc *J Polym Sci Part A* **6** (1968) 2541
8. A G Ryabukhin *Vysokomol Soedin Ser A* **11** (11) (1969) 2562
9. H C Malhotra and Avinash *Indian J Chem* **13** (1975) 1159
10. H C Malhotra and Avinash *J Appl Polym Sci* **20** (1976) 2461
11. H C Malhotra and V K Gupta *J Appl Polym Sci* **22** (1978) 343
12. H C Malhotra and V P Tyagi *J macromol Sci Chem A* **15** (5) (1980) 675
13. L M Debing G E Murray and R J Schatz *Ind Engng Chem* **44** (1952) 356
14. J I De Jong and J De Jonge *Rec Traw Chem* **72** (1953) 497