

## Kinetics of the Acid-Catalyzed Phenol-Formaldehyde Reaction

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### Synopsis

A kinetic study of the reaction of phenol with formaldehyde has been carried out at temperatures of  $65^{\circ} \pm 0.05^{\circ}\text{C}$ ,  $70^{\circ} \pm 0.05^{\circ}\text{C}$ ,  $75^{\circ} \pm 0.05^{\circ}\text{C}$ , and  $80^{\circ} \pm 0.05^{\circ}\text{C}$  using hydrochloric acid as catalyst. The pH maintained was 1.14, 1.32, 2.20, and 3.00. The reaction follows a second-order rate law. The rate is found to increase with decrease in pH. The overall rate constants are resolved into step rate constants. The values of the Arrhenius parameters and the entropy of activation for the overall reaction as well as for the step reactions have been calculated. A mechanism conforming to the energies and entropies of activation of the reaction has also been suggested.

### INTRODUCTION

The kinetics of the acid-catalyzed reaction of various phenols with formaldehyde has been the subject of various studies.<sup>1-10</sup> Earlier workers, with the exception of Yeddanapalli,<sup>8</sup> were concerned mainly with the evaluation of the overall rate constants, first order or second order, or with the detection of various components formed during the reaction. The present investigation is a continuation of our findings on the alkali-catalyzed phenol-formaldehyde reaction.<sup>10</sup> In the present communication, the kinetics of the phenol-formaldehyde reaction at pH values 1.14, 1.32, 2.20, and 3.00 and at temperatures of  $65^{\circ} \pm 0.05^{\circ}\text{C}$ ,  $70^{\circ} \pm 0.05^{\circ}\text{C}$ ,  $75^{\circ} \pm 0.05^{\circ}\text{C}$ , and  $80^{\circ} \pm 0.05^{\circ}\text{C}$  using hydrochloric acid as catalyst was investigated.

### EXPERIMENTAL

#### Materials

Phenol, formalin (37.5% formaldehyde), iodine, sodium thiosulfate, potassium iodide, sodium bisulfite, and potassium bromate used were B.D.H. products. Phenol was further purified by recrystallization. Hydrochloric acid and methanol were A.R. or C.P. quality; *p*-nitroaniline used for the preparation of the indicator was a Thomas Baker & Co. product.

An oil thermostat was employed for rate studies. The temperature of the bath was controlled by a toluene-mercury regulator which was connected to

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TABLE I  
Results of Kinetic Studies:  
Initial Phenol Concentration, 0.390 mole; Temperature,  $65^\circ \pm 0.05^\circ\text{C}$

Run no.	pH	Initial formaldehyde concentration, moles	Time, sec	Formaldehyde reacted, moles/liter	Phenol reacted, moles/liter	Second-order rate constant, l./mole-sec	Average rate constant, l./mole-sec
1	1.14	0.340	3600	0.174	0.282	$1.59 \times 10^{-3}$	$1.605 \times 10^{-3} \pm 0.013$
			5200	0.193	0.315	$1.60 \times 10^{-3}$	
			6000	0.201	0.332	$1.60 \times 10^{-3}$	
			6600	0.206	0.350	$1.63 \times 10^{-3}$	
2	1.32	0.394	5880	0.130	0.214	$0.43 \times 10^{-3}$	$0.470 \times 10^{-3} \pm 0.026$
			6060	0.137	0.228	$0.46 \times 10^{-3}$	
			6840	0.154	0.257	$0.52 \times 10^{-3}$	
3	2.20	0.420	9600	0.0151	0.0245	$1.68 \times 10^{-5}$	$1.697 \times 10^{-5} \pm 0.038$
			13200	0.0206	0.0336	$1.69 \times 10^{-5}$	
			18600	0.0282	0.0465	$1.69 \times 10^{-5}$	
			25200	0.0416	0.0707	$1.73 \times 10^{-5}$	

the mains through a magnetic relay, which was the main temperature-controlling unit. The thermostat was fitted with a thermometer and an electrical stirrer. The temperature control of the thermostat was within  $\pm 0.05^\circ\text{C}$ .

### Kinetic Measurements

Experiments were carried out in a 500-ml R.B. flask fitted with a water condenser. The flask containing the reaction mixture was suspended in a thermostat maintained at the desired temperature. After 10 min, when the reaction vessel attained the temperature of the thermostat, 10 ml of the reaction mixture was taken out and placed in an ice bath to freeze the reaction.

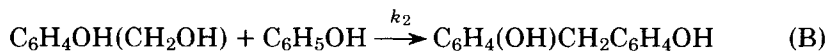
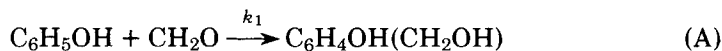
Formaldehyde was estimated by the usual sodium bisulfite method. Phenol, which was separated from the reaction mixture by thin-layer chromatography, was estimated colorimetrically.

## RESULTS AND DISCUSSION

Results of the kinetic studies carried out at various pH's and temperatures are presented in Tables I to IV.

### Calculations of Overall Rate Constants

The reaction of phenol with formaldehyde in acid medium proceeds according to the equations



The rate expression for the formation of the products is

$$\frac{dx}{dt} = k(a-x)(b-y) \quad (1)$$

TABLE II  
Results of Kinetic Studies:  
Initial Phenol Concentration, 0.390 mole; Temperature,  $70^\circ \pm 0.05^\circ\text{C}$

Run no.	pH	Initial formaldehyde concentration, moles	Time, sec	Formaldehyde reacted, moles/liter	Phenol reacted, moles/liter	Second-order rate constant, l./mole-sec	Average rate constant, l./mole-sec
1	1.14	0.340	1080	0.076	0.125	$0.12 \times 10^{-2}$	$0.222 \times 10^{-2} \pm 0.075$
			1680	0.146	0.239	$0.23 \times 10^{-2}$	
			1980	0.152	0.251	$0.21 \times 10^{-2}$	
			2280	0.184	0.307	$0.33 \times 10^{-2}$	
2	1.32	0.420	4230	0.136	0.222	$0.70 \times 10^{-3}$	$0.675 \times 10^{-3} \pm 0.051$
			5700	0.165	0.271	$0.67 \times 10^{-3}$	
			6000	0.172	0.286	$0.70 \times 10^{-3}$	
			6420	0.180	0.301	$0.74 \times 10^{-3}$	
3	2.20	0.420	23400	0.064	0.102	$0.35 \times 10^{-4}$	$0.408 \times 10^{-4} \pm 0.04$
			25800	0.074	0.120	$0.38 \times 10^{-4}$	
			28860	0.087	0.143	$0.43 \times 10^{-4}$	
			29940	0.090	0.151	$0.43 \times 10^{-4}$	
			30780	0.094	0.161	$0.45 \times 10^{-4}$	
4	3.00	0.400	17460	0.004	0.001	$0.25 \times 10^{-5}$	$0.25 \times 10^{-5} \pm 0.005$
			30780	0.007	0.012	$0.25 \times 10^{-5}$	
			51840	0.012	0.019	$0.26 \times 10^{-5}$	

TABLE III  
Results of Kinetic Studies:  
Initial Phenol Concentration, 0.390 mole; Temperature,  $75^\circ \pm 0.05^\circ\text{C}$

Run no.	pH	Initial formaldehyde concentration, moles	Time, sec	Formaldehyde reacted, moles/liter	Phenol reacted, moles/liter	Second-order rate constant, l./mole-sec	Average rate constant, l./mole-sec
1	1.14	0.384	960	0.080	0.130	$0.127 \times 10^{-2}$	$0.237 \times 10^{-2} \pm 0.068$
			1410	0.148	0.241	$0.238 \times 10^{-2}$	
			1740	0.170	0.282	$0.267 \times 10^{-2}$	
			2100	0.192	0.325	$0.316 \times 10^{-2}$	
2	1.32	0.400	2640	0.134	0.217	$1.050 \times 10^{-3}$	$1.085 \times 10^{-3} \pm 0.060$
			2940	0.138	0.225	$1.050 \times 10^{-3}$	
			3240	0.146	0.242	$1.060 \times 10^{-3}$	
3	2.20	0.384	3540	0.153	0.259	$1.180 \times 10^{-3}$	$0.7855 \times 10^{-4} \pm 0.02$
			12060	0.061	0.098	$0.706 \times 10^{-4}$	
			13500	0.070	0.113	$0.752 \times 10^{-4}$	
			14280	0.077	0.128	$0.809 \times 10^{-4}$	
4	3.00	0.400	14400	0.082	0.141	$0.875 \times 10^{-4}$	$0.5496 \times 10^{-5} \pm 0.02$
			17460	0.008	0.013	$0.551 \times 10^{-5}$	
			22140	0.012	0.020	$0.544 \times 10^{-5}$	
			42000	0.020	0.033	$0.579 \times 10^{-5}$	
			52680	0.024	0.044	$0.524 \times 10^{-5}$	

where  $a$  and  $b$  are the initial concentrations of phenol and formaldehyde, respectively, and  $x$  and  $y$  are the respective amounts of phenol and formaldehyde reacted at time  $t$ .

As seen from equations (A) and (B), phenol is being used up in both steps. Therefore, at any stage in the reaction, the phenol consumed will be more than that of formaldehyde. This can be seen from Tables I to IV. The average proportion of phenol and formaldehyde reacted was actually found to be

$$x = 1.65y \quad (2)$$

Substituting the value of  $x$  in eq. (1) and integrating, we get

TABLE IV  
Results of Kinetic Studies:  
Initial Phenol Concentration, 0.390 mole; Temperature,  $80^\circ \pm 0.05^\circ\text{C}$

Run no.	pH	Initial formaldehyde concentration, moles	Time, sec	Formaldehyde reacted, moles/liter	Phenol reacted, moles/liter	Second-order rate constant, l./mole-sec	Average rate constant, l./mole-sec
1	1.14	0.348	780	0.141	0.228	$0.447 \times 10^{-2}$	$0.517 \times 10^{-2} \pm 0.057$
			860	0.157	0.259	$0.510 \times 10^{-2}$	
			963	0.175	0.294	$0.593 \times 10^{-2}$	
2	1.32	0.316	1140	0.062	0.102	$0.960 \times 10^{-3}$	
			1800	0.116	0.189	$1.545 \times 10^{-3}$	
			1860	0.128	0.214	$1.793 \times 10^{-3}$	
			2040	0.135	0.223	$1.820 \times 10^{-3}$	
3	2.20	0.347	6360	0.081	0.130	$0.219 \times 10^{-3}$	$1.53 \times 10^{-3} \pm 0.35$
			7380	0.099	0.161	$0.253 \times 10^{-3}$	
			7830	0.108	0.180	$0.275 \times 10^{-3}$	
4	3.00	0.340	13800	0.012	0.019	$6.35 \times 10^{-6}$	$0.2595 \times 10^{-3} \pm 0.028$
			17400	0.018	0.030	$7.68 \times 10^{-6}$	
			21000	0.020	0.033	$7.11 \times 10^{-6}$	
							$7.05 \times 10^{-6} \pm 0.47$

$$k = \frac{2.303 \times 1.65}{t(1.65b - a)} \log \frac{a}{b} \frac{(b - y)}{(a - 1.65y)} \quad (3)$$

The results of the overall rate constants are given in Tables I to IV.

The rate of the reaction of phenol with formaldehyde in acidic medium is found to obey a second-order rate law. A linear dependence of  $\log a/b(b - y)/(a - 1.65y)$  on time (Fig. 1) further illustrates this point.

By plotting  $\log k$  versus  $1/T$  (Fig. 2), the values of the Arrhenius parameters and entropy of activation for the overall reaction were calculated. These values are summarized in Table V.

It is seen that the activation energy increases with increase in pH. It is suspected that what is happening is a transition between the catalyzed reaction and the uncatalyzed reaction, which should have an increased activation energy. A straight line is observed when  $\log k$  is plotted against pH (Fig. 4). The values of the frequency factors and entropy of activation increase as the pH of the reaction mixture increases from 1.14 to 3.00, the significance of which is discussed later along with the reaction mechanism.

### Calculations of Step Rate Constants

From reactions (A) and (B), the rate of formation of monomethylol phenol is

$$\frac{dy}{dt} = k_1(na - y - r)(b - y) \quad (4)$$

The concentrations of phenol, formaldehyde, and monomethylol phenol would be  $(a - x)$ ,  $(b - y)$ , and  $(y - r)$ , respectively, at any time interval  $t$ , where  $x$ ,  $y$ , and  $r$  are the respective amounts of phenol, formaldehyde, and monomethylol phenol reacted at time  $t$ ;  $n$  is the functionality of phenol.

The rate of formation of dihydroxydiphenylmethane is

$$\frac{dr}{dt} = k_2(na - y - r)(y - r) \quad (5)$$

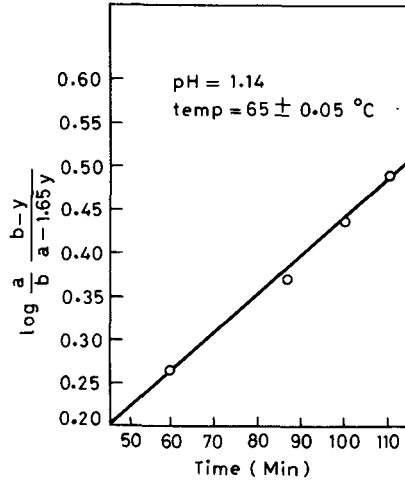


Fig. 1. Linear dependence of  $\log \frac{a}{b} \frac{b-y}{a-1.65y}$  on time.

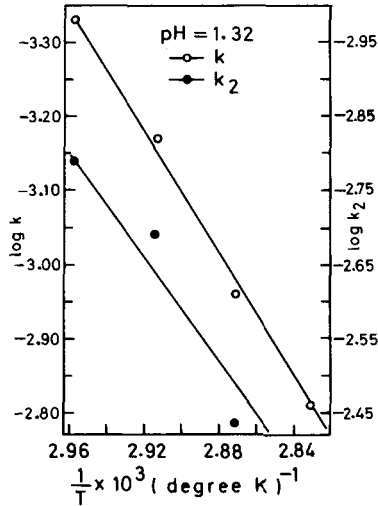


Fig. 2. Plots of logarithm of rate constant vs.  $1/T(^{\circ}K)^{-1}$ : (O-O-O) plot of overall rate constants vs.  $1/T(^{\circ}K)^{-1}$ ; (●-●-●) plot of step rate constant  $k_2$  vs.  $1/T(^{\circ}K)^{-1}$ .

where  $(na - y - r)$  is the concentration of phenol at any time  $t$ .

The amount of phenol reacted at any stage of the reaction is equal to the sum of the amount of formaldehyde and monomethylol phenol reacted at any time  $t$ , i.e.,

$$-\frac{dx}{dt} = -\frac{dy}{dt} - \frac{dr}{dt} \tag{6}$$

Therefore, from eqs. (4), (5), and (6),

$$-\frac{dx}{dt} = -nk_1(a-x)(b-y) - nk_2(a-x)(y-r) \tag{7}$$

It follows from eqs. (1) and (7) that

$$k(a-x)(b-y) = nk_1(a-x)(b-y) + nk_2(a-x)(y-r) \tag{8}$$

TABLE V  
Overall Arrhenius Parameters for the Phenol-Formaldehyde Reaction

pH	<i>E</i> , kcal	log <i>A</i> , l./mole-sec	Δ <i>S</i> , cal/degree-mole
1.14	14.3	6.6	-33.2
1.32	18.9	8.9	-22.3
2.20	38.9	20.4	+36.4
3.00	45.4	23.0	+42.1

TABLE VI  
Step Rate Constants at Different pH Values and Temperatures

pH	<i>k</i> <sub>1</sub> , l./mole-sec	<i>k</i> <sub>2</sub> , l./mole-sec	<i>k</i> <sub>2</sub> / <i>k</i> <sub>1</sub>
Temperature, 65° ± 0.05° C			
1.14	4.20 × 10 <sup>-4</sup>	45.20 × 10 <sup>-4</sup>	10.2
1.32	1.60 × 10 <sup>-4</sup>	16.20 × 10 <sup>-4</sup>	10.1
2.20	0.09 × 10 <sup>-4</sup>	1.10 × 10 <sup>-4</sup>	12.8
Temperature, 70° ± 0.05° C			
1.14	5.60 × 10 <sup>-4</sup>	63.10 × 10 <sup>-4</sup>	11.2
1.32	2.05 × 10 <sup>-4</sup>	20.50 × 10 <sup>-4</sup>	10.0
2.20	2.00 × 10 <sup>-5</sup>	24.60 × 10 <sup>-5</sup>	12.3
3.00	1.50 × 10 <sup>-6</sup>	19.50 × 10 <sup>-6</sup>	13.0
Temperature, 75° ± 0.05° C			
1.14	7.00 × 10 <sup>-4</sup>	70.20 × 10 <sup>-4</sup>	10.0
1.32	3.70 × 10 <sup>-4</sup>	36.70 × 10 <sup>-4</sup>	10.0
2.20	3.80 × 10 <sup>-5</sup>	48.90 × 10 <sup>-5</sup>	12.7
3.00	2.50 × 10 <sup>-6</sup>	30.00 × 10 <sup>-6</sup>	12.0
Temperature, 80° ± 0.05° C			
1.14	12.60 × 10 <sup>-4</sup>	134.0 × 10 <sup>-4</sup>	10.6
1.32	5.24 × 10 <sup>-4</sup>	50.12 × 10 <sup>-4</sup>	12.0
2.20	1.03 × 10 <sup>-4</sup>	10.91 × 10 <sup>-4</sup>	10.9
3.00	4.70 × 10 <sup>-6</sup>	50.00 × 10 <sup>-6</sup>	10.6

or

$$k = nk_1 + nk_2 \frac{y-r}{b-y} \quad (9)$$

Now,  $(y+r) = x$ , or  $r = x - y$ , and the functionality of phenol ( $n$ ) = 1,

$$\therefore k = k_1 + k_2 \frac{2y-x}{b-y} \quad (10)$$

Substituting the values of  $x$ ,  $y$ , and  $k$  (from Tables I-IV) at two different time intervals, two simultaneous equations for  $k_1$  and  $k_2$  at a given temperature and pH were obtained. These equations were then solved for  $k_1$  and  $k_2$ . The average values of  $k_1$  and  $k_2$  thus obtained at various temperatures and pH's are given in Table VI.

By plotting log  $k$  (step rate constants) versus  $1/T$  (Figs. 2 and 3), the values of the Arrhenius parameters for the step reactions were obtained. These values have been tabulated in Table VII.

As can be seen from Table VI, the rate of formation of dihydroxydiphenylmethane is 10-13 times the rate of formation of monomethylol phenol, i.e.,

$$k_2/k_1 \approx 10-13$$

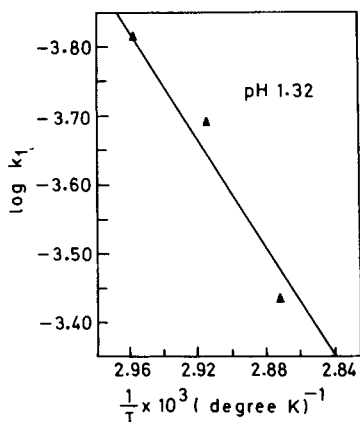


Fig. 3. Plot of logarithm of step rate constant  $k_1$  against  $1/T(^{\circ}\text{K})^{-1}$ .

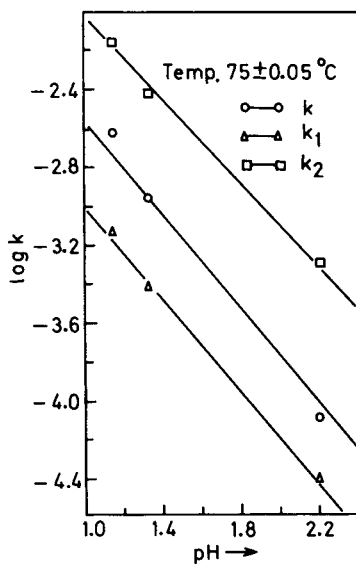


Fig. 4. Plots of the logarithms of the overall rate constants vs. pH.

An attempt was also made to evaluate the ratio  $k_2/k_1$  from purely theoretical considerations of the acid-catalyzed phenol-formaldehyde reaction as suggested by Ryabukhin.<sup>9</sup>

From eqs. (4) and (5) we obtain

$$\frac{d(y+r)}{dt} = k_1(b-y)(na-y-r) + k_2(y-r)(na-y-r) \quad (11)$$

Dividing eq. (11) by (7),

$$\frac{d(y+r)}{dx} = \frac{k_1(b-y)(na-y-r) + k_2(y-r)(na-y-r)}{nk_1(a-x)(b-y) + nk_2(a-x)(y-r)} \quad (12)$$

or

$$\frac{d(y+r)}{dx} = \frac{na-y-r}{n(a-x)}$$

TABLE VII  
Arrhenius Parameters for the Step Reactions

pH	<i>E</i> , kcal	log <i>A</i> , l./mole-sec	$\Delta S$ , cal/degree-mole
		<i>k</i> <sub>1</sub>	
1.14	13.78	5.53	-37.51
1.32	17.56	7.54	-28.26
2.20	35.56	20.07	+19.35
3.00	40.10	20.50	+28.80
		<i>k</i> <sub>2</sub>	
1.14	13.78	6.58	-32.87
1.32	16.23	7.70	-27.54
2.20	34.45	21.16	+21.12
3.00	39.80	21.80	+30.50

or

$$\frac{d(y+r)}{na-y-r} = \frac{1}{n} \cdot \frac{dx}{a-x} \quad (13)$$

Integrating, we obtain

$$\log(na-y-r) = \frac{1}{n} \log(a-x) + \log c \quad (14)$$

Putting the conditions at  $t = 0$ ,  $y = 0$ , and  $r = 0$ ,

$$\begin{aligned} \log na &= \frac{1}{n} \log a + \log c = \log a^{1/n} + \log c \\ \log c &= \log na^{n-1/n} \end{aligned}$$

Putting the value of this constant in eq. (14), we get

$$\log(na-y-r) = \frac{1}{n} \log(a-x) + \log na^{n-1/n} \quad (15)$$

$$na-y-r = na^{n-1/n}(a-x)^{1/n} \quad (16)$$

$$\therefore y+r = na - na^{n-1/n}(a-x)^{1/n} \quad (17)$$

To establish the relation between the amount of reacted phenol and formaldehyde, excluding the concentration of reacted methylol groups, subtract eq. (5) from eq. (4):

$$\frac{d(y-r)}{dt} = k_1(b-y)(na-y-r) - k_2(y-r)(na-y-r) \quad (18)$$

Dividing eq. (18) by eq. (4) yields

$$\frac{d(y-r)}{dy} = 1 - \frac{k_2}{k_1} \cdot \frac{y-r}{b-y} \quad (19)$$

If  $k_2/k_1 = u$ , (20)

$$\therefore \frac{d(y-r)}{dy} = 1 - u \cdot \frac{(y-r)}{(b-y)} \quad (21)$$

Integrating, we obtain



$$\frac{y-r}{(b-y)^u} = -\frac{1}{1-u} \cdot \frac{1}{(b-y)^{u-1}} + c \tag{22}$$

Putting the limits at  $t = 0, y = 0,$  and  $r = 0,$

$$0 = -\frac{1}{1-u} \cdot \frac{1}{b^{u-1}} + c$$

$$c = \frac{1}{1-u} b^{1-u}$$

Putting this value of constant in eq. (22), we obtain

$$\frac{y-r}{(b-y)^u} = \frac{1}{1-u} b^{1-u} - \frac{1}{1-u} (b-y)^{1-u}$$

$$y-r = \frac{1}{u-1} (b-y) - \frac{1}{u-1} (b-y)^u b^{1-u} \tag{23}$$

Adding of eqs. (17) and (23) results in

$$2y = na - na^{n-1/n}(a-x)^{1/n} + \frac{1}{u-1} (b-y) - \frac{1}{u-1} b^{1-u}(b-y)^u \tag{24}$$

which can be represented by

$$x = a - \left\{ \frac{a^{1-n/n}}{n} \left[ na - 2y + \frac{1}{u-1} (b-y) - \frac{1}{u-1} b^{1-u}(b-y)^u \right] \right\}^n \tag{25}$$

Knowing the amounts of phenol and formaldehyde reacted at a given time interval, the value of  $u$  can be obtained using eq. (25). We have actually calculated the values of  $u$  at temperatures 70°C and 75°C and pH value 2.20. These values of  $u$  obtained at different time intervals are given in Table VIII.

It should be pointed out that, in obtaining the values of  $k_2/k_1$  (Table VIII), the relation ( $x = 1.65y$ ) has nowhere been used, whereas the ratio  $k_2/k_1$  given in Table VI involves indirectly the fact that  $x = 1.65y$ . The average values of  $k_2/k_1$  (Table VIII) are in good agreement with values as given in Table VI.

This confirms that the approximation used in obtaining the second-order rate expression (3) regarding the proportions of phenol and formaldehyde reacted in acid-catalyzed reaction at a given time interval is very much in order.

This has further been confirmed by making a comparison of the values of the overall rate constant obtained using eq. (3) with the overall rate constant values as obtained purely from the theoretical considerations of the reaction, i.e., substituting the values of  $(y-r)$  from eq. (23) in the overall rate expression (8), which gives

$$k(b-y) = k_1(b-y) + \frac{k_2}{u-1} [(b-y) - b^{1-u}(b-y)^u]$$

or

$$k = k_1 + \frac{k_2}{u-1} \left[ 1 - \left( \frac{b-y}{b} \right)^{u-1} \right] \tag{26}$$

From eq. (26) and utilizing the values of the step rate constants at temperatures 70°C and 75°C and at a pH value 2.20 from Table VI, the values of the

TABLE VIII  
Calculated Values of  $k_2/k_1$

Time, sec	Calculated values of $k_2/k_1 = u$	Average value
Temperature, $70^\circ \pm 0.05^\circ\text{C}$ ; pH 2.20		
23400	14.70	12.3
25800	13.35	
28860	11.75	
30780	13.10	
Temperature, $75^\circ \pm 0.05^\circ\text{C}$ ; pH 2.20		
12060	14.25	13.9
13500	12.60	
14280	12.80	
14400	16.10	

TABLE IX  
Comparison of Overall Rate Constants

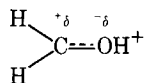
Temperature $\pm 0.05^\circ\text{C}$	pH	Average value of overall rate constant, l./mole-sec	
		from eq. (3)	from eq. (26)
$70^\circ$	2.20	$0.410 \times 10^{-4}$	$0.396 \times 10^{-4}$
$75^\circ$	2.20	$0.787 \times 10^{-4}$	$0.755 \times 10^{-4}$

overall rate constant have been calculated; they are given in Table IX along with the values obtained from eq. (3).

From the comparison given in Table IX, it is confirmed that the values of the overall rate constants for the acid-catalyzed phenol-formaldehyde reaction reported by us are very much in order.

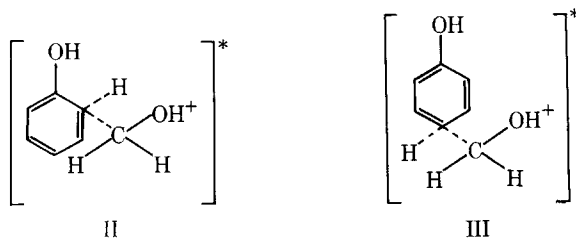
### MECHANISM

In the presence of  $\text{H}^+$  ions, protonation of the formaldehyde takes place at the oxygen atom as the electron cloud density is greater around oxygen than around the carbon atom.

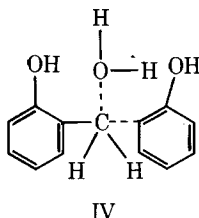


I

Due to inductive and mesomeric effects, the electron density is greater at the ortho and para positions in the phenol nucleus than at the meta position. The protonated formaldehyde (I) then attacks at the ortho or para position of the phenol to form the activated complexes II and III:



This is a slow reaction and the rate-determining one. The activated complex then breaks up to liberate  $H^+$  ions to form monomethylol phenol. The carbonyl group of the formaldehyde in monomethylol phenol takes up a proton, and the carbon atom of the carbonium ion thus acquires a positive charge, forming the activated complex IV with another phenol molecule at the ortho or para position:



This complex then rearranges and breaks up to give dihydroxydiphenylmethane with the liberation of a molecule of water and hydrogen ion.

According to the suggested mechanism for the formation of monomethylol phenol, the reaction takes place in two steps. The net entropy of activation will be the sum of the entropy of protonation and the entropy required for the formation of the activated complex:

$$\Delta S^*(\text{obs}) = \Delta S^*_p + \Delta S^*$$

The entropy of protonation is invariably positive, since the protonation is required only at the fixed site. The fact that the entropy of activation, i.e.,  $\Delta S^*(\text{obs})$ , is increasing with increase in pH (Table V) and becomes positive at pH 2.20 and 3.00 indicates that  $\Delta S^*_p$  is numerically less than  $\Delta S^*$ , up to pH 1.32, but becomes larger than  $\Delta S^*$  at pH 2.20 and 3.00, with the result that the net entropy of activation at pH 2.20 and 3.00 is positive.

The larger values of energies of activation at higher pH's (Table V) indicate that the  $H^+$  ions play an important role in the reaction. The rate of the reaction decreases with increase in pH, the rate constants being lower at pH 3.00 than at pH 1.14 (Tables I-IV).

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