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H. C. Malhotra^a; Vinod Kumar^a

^a Department of Chemistry, University of Delhi, Delhi, India

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Energetics of the Acid-Catalyzed o-Cresol-Formaldehyde Reaction

H. C. MALHOTRA* and VINOD KUMAR

Department of Chemistry
University of Delhi
Delhi 110007, India

ABSTRACT

The acid-catalyzed reaction of o-cresol with formaldehyde follows second-order kinetics. The reaction was carried out at 65, 70, 75, and 80°C and at pH values of 1.30, 1.80, 2.00, 2.50, and 3.00, using hydrochloric acid as a catalyst. The rate was found to increase with decreasing pH. The overall rate constant (k) has been resolved into stepwise rate constants (k_1 and k_2) for the formation of monomethylol and methylene derivatives. Values of Arrhenius parameters and of the entropy of activation for the overall reaction were also calculated. A mechanism consistent with our kinetic data is given.

INTRODUCTION

Several investigators [1-10] have studied the kinetics of various phenols with formaldehyde. A detailed study of the kinetics of phenol-formaldehyde reaction in acid medium was reported by Malhotra and Avinash [11]. However, no comprehensive study on the kinetics of

*To whom correspondence should be addressed.

the *o*-cresol-formaldehyde reaction catalyzed by acid appears to have been carried out. The present investigation is a continuation of our findings on the alkali-catalyzed *o*-cresol-formaldehyde reaction [12]. The present study was carried out at temperatures of 65 ± 0.06 , 70 ± 0.05 , 75 ± 0.05 , and $80 \pm 0.05^\circ\text{C}$ and at pH values of 1.30, 1.80, 2.00, 2.50, and 3.00 using hydrochloric acid as the catalyst.

EXPERIMENTAL

Materials

The *o*-cresol, formalin (37.5% formaldehyde), and hydroxylamine hydrochloride used were BDH products. Sodium hydroxide and methanol were AR or CP quality. *o*-Cresol was distilled twice before use.

An immersion-type thermostat (German Model E3E) having a temperature control of $\pm 0.05^\circ\text{C}$ was employed for rate studies.

Procedure

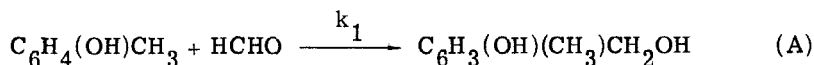
The experiments were carried out in a 250-mL round-bottomed flask fitted with a water condenser. The flask was suspended in a thermostat maintained at the desired temperature. After 10 min, when the reaction mixture attained the temperature of the thermostat, an aliquot (10 mL) of the reaction mixture was taken and placed in an ice bath to freeze the reaction.

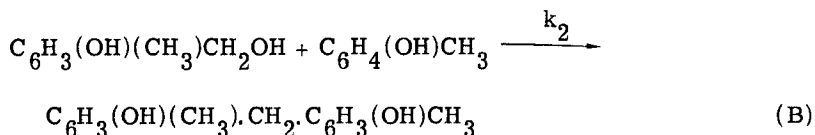
Formaldehyde was estimated by the hydroxylamine hydrochloride method. *o*-Cresol was separated from the reaction mixture by thin-layer chromatography and estimated colorimetrically.

RESULTS AND DISCUSSION

Calculation of Overall Rate Constants

o-Cresol reacts with formaldehyde in acid medium to form the methylol derivatives which immediately combine with another molecule of *o*-cresol to form methylene derivatives.





where k_1 and k_2 are the stepwise rate constants.

The rate of formation of monomethylol-o-cresols and dihydroxy-dimethyldiphenylmethane can be written as

$$dx/dt = k(a - x)(b - y) \quad (1)$$

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

It is clear from Eqs. (A) and (B) that at any stage of the reaction the amount of o-cresol consumed is more than that of formaldehyde. The average proportion of o-cresol and formaldehyde reacted was experimentally found to be

$$x = 1.80y \quad (2)$$

Substituting this value of x in Eq. (1), the integrated rate equation works out to be

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

The results of the kinetic studies carried out at different temperatures and pH values are given in Table 1. The reaction follows a second-order rate law. The rate of the reaction was further found to increase with an increase of temperature if the concentration of hydrogen ions is maintained constant.

The values of the Arrhenius parameters and the entropy of activation are given in Table 2. It is noticed from Table 1 that there is an increase in the rate of a reaction as pH decreases from 3.00 to 1.30, confirming the catalytic effect of H^+ ions.

Calculations of the Stepwise Rate Constants

From Reactions (A) and (B), the concentrations of o-cresol, formaldehyde, monomethylol-o-cresol, and functional groups in o-cresol would be $(a - x)$, $(b - y)$, $(y - z)$, and $(na - y - z)$, respectively,

TABLE 1. Overall Rate Constant k at Different Temperatures and pH Values

pH	Temperature (°C)	Initial [HCHO] (mol/L)	Initial [o-cresol] (mol/L)	Second-order rate constant k (L/mol·s)
1.30	65	0.4000	0.3918	$(2.14 \pm 0.14) \times 10^{-4}$
1.80	65	0.4300	0.4111	$(0.55 \pm 0.02) \times 10^{-4}$
2.00	65	0.4350	0.4138	$(3.21 \pm 0.14) \times 10^{-5}$
2.50	65	0.4450	0.4166	$(4.36 \pm 0.22) \times 10^{-6}$
1.30	70	0.3900	0.3918	$(5.97 \pm 0.16) \times 10^{-4}$
1.80	70	0.4325	0.4111	$(1.16 \pm 0.02) \times 10^{-4}$
2.00	70	0.4344	0.4138	$(7.30 \pm 0.05) \times 10^{-5}$
2.50	70	0.4450	0.4166	$(1.51 \pm 0.10) \times 10^{-5}$
3.00	70	0.4550	0.4176	$(2.50 \pm 0.08) \times 10^{-6}$
1.30	75	0.3850	0.3918	$(1.04 \pm 0.06) \times 10^{-3}$
1.80	75	0.4337	0.4111	$(2.38 \pm 0.08) \times 10^{-4}$
2.00	75	0.4350	0.4138	$(1.40 \pm 0.08) \times 10^{-4}$
2.50	75	0.4550	0.4166	$(2.64 \pm 0.14) \times 10^{-5}$
3.00	75	0.4575	0.4176	$(7.52 \pm 0.13) \times 10^{-6}$
1.30	80	0.4038	0.3918	$(1.52 \pm 0.07) \times 10^{-3}$
1.80	80	0.4375	0.4111	$(3.51 \pm 0.13) \times 10^{-4}$
2.00	80	0.4425	0.4138	$(2.54 \pm 0.06) \times 10^{-4}$
2.50	80	0.4475	0.4166	$(5.65 \pm 0.07) \times 10^{-5}$
3.00	80	0.4550	0.4176	$(1.52 \pm 0.12) \times 10^{-5}$

at any time t , where x , y , and z are the respective amounts of *o*-cresol, formaldehyde, and monomethylol-*o*-cresol reacted at time t ; n is the functionality of *o*-cresol.

The rate of formation of monomethylol-*o*-cresol is

$$dy/dt = k_1(na - y - z)(b - y) \quad (4)$$

TABLE 2. Activation Parameters for the o-Cresol-Formaldehyde Reaction

pH	E (kcal/mol)	log A (L/mol·s)	ΔS^\ddagger (cal/mol·degree)
1.30	25.25	12.86	-0.001
1.80	31.20	15.96	+14.15
2.00	33.58	17.19	+19.78
2.50	45.39	23.92	+50.58
3.00	51.66	27.31	+66.09

and the rate of formation of dihydroxydimethyldiphenylmethane is

$$dz/dt = k_2(na - y - z)(y - z) \quad (5)$$

where $(na - y - z)$ is the concentration of o-cresol at any time t .

At any time t the amount of o-cresol reacted would be equal to the sum of the amount of formaldehyde and monomethylol reacted, i.e.,

$$-\frac{dx}{dt} = -\frac{dy}{dt} - \frac{dz}{dt} \quad (6)$$

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

$$-dx/dt = -nk_1(a - x)(b - y) - nk_2(a - x)(y - z) \quad (7)$$

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

$$k = nk_1 + nk_2 \frac{y - z}{b - y} \quad (8)$$

Now $y + z = x$ and the functionality of o-cresol $(n) = 1$. Therefore

$$k = k_1 + k_2 \frac{2y - x}{b - y} \quad (9)$$

Substituting the values of x , y , and k (from Tables 1 and 3) and using the method of successive approximation, the values of k_1 and k_2 were

TABLE 3. Reacted Amounts of o-Cresol (x) and Formaldehyde (y) at Different Temperatures at pH = 1.80

Time (s)	Temperature (°C)	Formaldehyde reacted (mol/L)	o-Cresol reacted (mol/L)
3,600	65 ± 0.05	0.0175	0.0313
6,000		0.0300	0.0538
9,000		0.0425	0.0765
12,000		0.0550	0.0992
9,000	70 ± 0.05	0.0750	0.1315
10,200		0.0850	0.1520
11,100		0.0900	0.1625
12,600		0.0975	0.1760
4,500	75 ± 0.05	0.0762	0.1344
5,400		0.0875	0.1575
6,300		0.0987	0.1780
7,200		0.1087	0.1981
3,000	80 ± 0.05	0.0800	0.1420
3,600		0.0900	0.1620
4,200		0.1000	0.1820
5,400		0.1150	0.2120

obtained at different temperatures and pH's. These values are given in Table 4.

As can be seen from Table 4, the rate of formation of dihydroxydimethyldiphenylmethane is 18 to 21 times the rate of formation of monomethylol-o-cresol, i.e., $k_2/k_1 \approx 18$ to 21.

An attempt was also made to evaluate the ratio k_2/k_1 purely from theoretical considerations.

Adding Eqs. (4) and (5) and dividing the resulting equation by Eq. (7) and integrating, we obtain

$$y + z = na - na^{(n-1)/n} (a - x)^{1/n} \quad (10)$$

TABLE 4. Stepwise Rate Constants at Different pH Values and Temperatures

pH	Temperature (°C)	Rate constant (L/mol·s)		
		k ₁	k ₂	k ₂ /k ₁
1.30	65 ± 0.05	0.12 × 10 ⁻³	2.42 × 10 ⁻³	20.16
1.80		0.38 × 10 ⁻⁴	7.52 × 10 ⁻⁴	19.78
2.00		0.25 × 10 ⁻⁴	4.65 × 10 ⁻⁴	18.60
2.50		0.40 × 10 ⁻⁵	7.45 × 10 ⁻⁵	18.62
1.30	70 ± 0.05	0.28 × 10 ⁻³	5.48 × 10 ⁻³	19.57
1.80		0.59 × 10 ⁻⁴	1.11 × 10 ⁻³	18.81
2.00		0.48 × 10 ⁻⁴	9.05 × 10 ⁻⁴	18.85
2.50		1.13 × 10 ⁻⁵	2.25 × 10 ⁻⁴	19.91
3.00		2.45 × 10 ⁻⁶	4.93 × 10 ⁻⁵	20.12
1.30	75 ± 0.05	0.40 × 10 ⁻³	7.40 × 10 ⁻³	18.50
1.80		1.15 × 10 ⁻⁴	2.20 × 10 ⁻³	19.17
2.00		0.89 × 10 ⁻⁴	1.67 × 10 ⁻³	18.82
2.50		2.20 × 10 ⁻⁵	4.30 × 10 ⁻⁴	19.56
3.00		0.65 × 10 ⁻⁵	1.30 × 10 ⁻⁴	20.03
1.30	80 ± 0.05	0.53 × 10 ⁻³	1.05 × 10 ⁻²	19.81
1.80		1.74 × 10 ⁻⁴	3.39 × 10 ⁻³	19.51
2.00		0.12 × 10 ⁻³	2.33 × 10 ⁻³	19.41
2.50		0.38 × 10 ⁻⁴	7.65 × 10 ⁻⁴	20.13
3.00		1.38 × 10 ⁻⁵	2.75 × 10 ⁻⁴	19.92

Subtracting Eq. (5) from Eq. (4), dividing the resulting equation by Eq. (4) and then integrating it, we obtain

$$y - z = \frac{1}{m - 1} (b - y) - \frac{1}{m - 1} (b - y)^m b^{1-m} \quad (11)$$

Adding Eqs. (10) and (11) and rearranging, we obtain

$$x = a - \left[\frac{a^{(1-n)/n}}{n} \left\{ na - 2y + \frac{1}{m-1} (b-y) - \frac{1}{m-1} b^{1-m} (b-y)^m \right\} \right]^n \quad (12)$$

By knowing the amounts of *o*-cresol and formaldehyde reacting in a given time interval, the value of *m* was obtained using Eq. (12). The values of *m* thus calculated at 65, 70, 75, and 80°C and at a pH value of 1.80 are given in Table 5.

In calculating the values of k_2/k_1 given in Table 5, the relation $x = 1.80y$ has nowhere been used whereas the ratio k_2/k_1 given in Table 4 indirectly involves the fact that $x = 1.80y$. The average values of k_2/k_1 (Table 5) are in excellent agreement with values given in Table 4.

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

The values of *k* (overall rate constant) have also been calculated theoretically by substituting the values of (*y* - *z*) from Eq. (11) in the overall rate expression (8) which gives

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

or

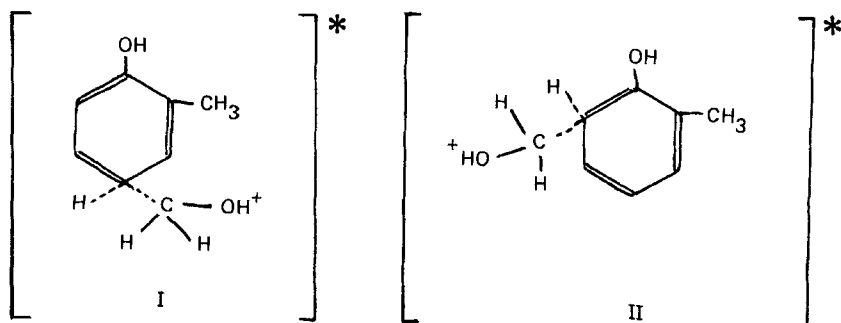
$$k = k_1 \left[\frac{k_2}{m-1} \left[1 - \left(\frac{b-y}{b} \right)^{m-1} \right] \right] \quad (13)$$

Using the above equation, the values of the overall rate constant have also been calculated at various temperatures and pH's utilizing the values of the stepwise rate constants from Table 3. These values are given in Table 6 along with the values obtained from Eq. (3).

The excellent agreement between the overall rate constant values reported in Table 6 confirms the authenticity of our kinetic data.

MECHANISM

In the presence of H^+ ions, the formaldehyde molecule becomes protonated at the oxygen atom, which then attacks at the ortho or para position of the *o*-cresol to form the activated Complexes I and II.

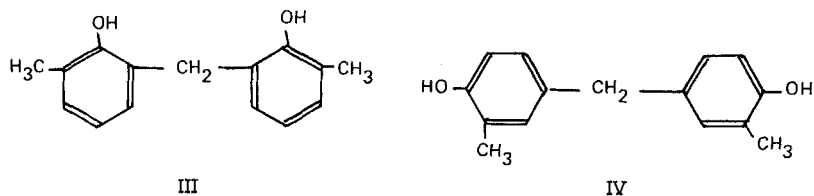
TABLE 5. Calculated Values of k_2/k_1 (m) at pH Values 1.80

Time (s)	Temperature (°C)	Calculated values of k_2/k_1	Average values
3,600	65 ± 0.05	22.12	
6,000		20.80	
9,000		19.25	
12,000		18.00	20.04
9,000	70 ± 0.05	20.32	
10,200		20.30	
11,100		20.57	
12,600		18.63	19.95
4,500	75 ± 0.05	20.50	
5,400		19.88	
6,300		18.90	
7,200		18.50	19.50
3,000	80 ± 0.05	20.86	
3,600		20.30	
4,200		19.75	
5,400		18.91	19.95

TABLE 6. Comparison of Overall Rate Constants

pH	Temperature (°C)	Average value of overall rate constant (L/mol·s)	
		From Eq. (3)	From Eq. (13)
1.30	65 ± 0.05	2.14×10^{-4}	1.92×10^{-4}
1.80		5.50×10^{-5}	5.20×10^{-5}
2.00		3.21×10^{-5}	3.07×10^{-5}
2.50		4.36×10^{-6}	4.27×10^{-6}
1.30	70 ± 0.05	5.97×10^{-4}	5.58×10^{-4}
1.80		1.16×10^{-4}	1.17×10^{-4}
2.00		7.30×10^{-5}	7.13×10^{-5}
2.50		1.51×10^{-5}	1.29×10^{-5}
3.00		2.50×10^{-6}	2.57×10^{-6}
1.30	75 ± 0.05	1.04×10^{-3}	1.14×10^{-3}
1.80		2.38×10^{-4}	2.34×10^{-4}
2.00		1.40×10^{-4}	1.49×10^{-4}
2.50		2.64×10^{-5}	2.67×10^{-5}
3.00		7.52×10^{-6}	7.32×10^{-6}
1.30	80 ± 0.05	1.52×10^{-3}	1.54×10^{-3}
1.80		3.51×10^{-4}	3.52×10^{-4}
2.00		2.54×10^{-4}	2.42×10^{-4}
2.50		5.65×10^{-5}	5.50×10^{-5}
3.00		1.52×10^{-5}	1.55×10^{-5}

This is a slow reaction and the rate-determining one. The activated complex thereafter breaks up to form monomethylol-o-cresol with the liberation of H^+ ions. In the presence of H^+ ions, the monomethylol-o-cresols will exist in the form of carbonium ions which will attack at the ortho or para positions of another molecule of o-cresol to give the corresponding methylene Compounds III and IV.



According to the suggested mechanism for the formation of mono-methylol derivatives, the reaction takes place in two steps:

1. Protonation of the formaldehyde
2. Formation of the activated complex

Therefore, the net entropy of activation will be the sum of the entropy involved in the protonation and the entropy involved in the formation of the activated complex, i. e.,

$$\Delta S^{\ddagger} = \Delta S_p + \Delta S^*$$

The entropy involved in the protonation will always be positive, and because the activated complex has a more ordered molecular configuration than those of the reactant molecules, the entropy involved in the formation of the activated complex (ΔS^*) will be negative and its value is assumed to remain constant. Table 2 shows that entropy of protonation is numerically less than the entropy of the activated complex up to pH 1.30, but becomes more as the catalyst concentration decreases, with the result that the observed entropy of activation becomes positive.

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