Kinetics and Mechanism of the Alkali-Catalyzed
p-Cresol–Formaldehyde Reaction

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Synopsis

The kinetics of the reaction of p-cresol with formaldehyde in relation to the functionality of p-cresol using NaOH as catalyst has been studied at temperatures of $(65 \pm 0.05)°C$, $(70 \pm 0.05)°C$, $(75 \pm 0.05)°C$, and $(80 \pm 0.05)°C$. The pH maintained was 7.0, 8.0, 9.0, 9.4, and 10.0. The reaction follows a second-order rate law. The rate was found to increase with increase in pH. The stepwise rate constants (k_1 and k_2) for the formation of monomethylol-p-cresol and dimethylol-p-cresol, respectively, were calculated from the overall rate constant k. The values of Arrhenius parameters and the entropy of activation for the overall as well as the stepwise reactions were calculated. The experimental and calculated values of k at pH 10.0 and temperatures 65, 70, 75, and 80°C were found to agree well within experimental errors. A mechanism conforming to the energies and entropies of activation of the reaction is suggested.

INTRODUCTION

Several investigators[1-11] have studied the kinetics of the reaction of various phenols with formaldehyde in alkaline medium. However, the kinetics of the m-cresol–formaldehyde reaction in relation to the functionality of m-cresol in alkaline medium was studied in detail by Malhotra and Gupta.[12] The kinetics of the o-cresol–formaldehyde reaction was also studied in detail by Malhotra and Vinod.[13] With regard to the kinetics of the p-cresol–formaldehyde reaction in alkaline medium, no comprehensive study has been done. The present work was carried out to study the kinetics of the p-cresol–formaldehyde reaction using sodium hydroxide as catalyst at $(65 \pm 0.05)°C$, $(70 \pm 0.05)°C$, $(75 \pm 0.05)°C$, and $(80 \pm 0.05)°C$. The pH maintained was 7.0, 8.0, 9.0, 9.4, and 10.0.

EXPERIMENTAL

Materials

p-Cresol, formalin (37.5% formaldehyde), iodine, sodium thiosulfate, potassium iodide, sodium bisulfite, and potassium bromate used were B.D.H. products. p-Cresol was distilled twice before use. The methanol used was A.R. grade.

An oil thermostat, in which the temperature of the bath was controlled within $\pm0.05°C$ by a toluene mercury regulator through a magnetic relay, was used for the rate studies.

Procedure

A 500-ml R.B. flask containing the reaction mixture prepared in methanol–water mixture (1:1 v/v) at the desired pH, and fitted with a water condenser was suspended in the thermostat maintained at the desired temperature. After 10 min, when the reaction mixture attained the temperature of the bath, an aliquot (10 ml) of the reaction mixture was taken out and placed in an ice bath to freeze the reaction. Formaldehyde was estimated by the bisulfite method.

RESULTS AND DISCUSSION

The results of the kinetic studies at different temperatures and pH values are given in Table I. The overall reaction has been found to obey a second-order rate law. The values of the activation energies (ΔE), frequency factors (A), and the entropies of activation (ΔS^*) for the overall reaction are given in Table II. The Arrhenius parameters and the entropies of activation for the stepwise reactions were found to be the same. It has been observed that with an increase in pH (a) the rate of the reaction increases, and (b) the energy of activation (ΔE) and entropy of activation (ΔS^*) decrease appreciably.

Calculation of Stepwise Rate Constants

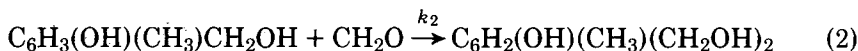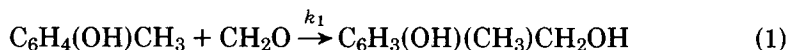p-Cresol reacts with formaldehyde in alkaline medium according to the scheme

$$C_6H_4(OH)CH_3 + CH_2O \xrightarrow{k_1} C_6H_3(OH)(CH_3)CH_2OH \qquad (1)$$

$$C_6H_3(OH)(CH_3)CH_2OH + CH_2O \xrightarrow{k_2} C_6H_2(OH)(CH_3)(CH_2OH)_2 \qquad (2)$$

TABLE I
Overall Rate Constant k at Different Temperatures and pH Values

pH	Temperature (± 0.05), °C	Initial [p-cresol]	Initial [HCHO]	k, l/mol·sec
8.0	65	0.4668	0.510	$(1.73 \pm 0.07) \times 10^{-7}$
9.0	65	0.4620	0.505	$(1.31 \pm 0.12) \times 10^{-6}$
9.4	65	0.4607	0.504	$(4.41 \pm 0.22) \times 10^{-6}$
10.0	65	0.4371	0.520	$(1.52 \pm 0.04) \times 10^{-5}$
8.0	70	0.4668	0.510	$(6.85 \pm 0.15) \times 10^{-7}$
9.0	70	0.4607	0.495	$(3.46 \pm 0.20) \times 10^{-6}$
9.4	70	0.4607	0.500	$(7.55 \pm 0.20) \times 10^{-6}$
10.0	70	0.4371	0.500	$(2.40 \pm 0.15) \times 10^{-5}$
7.0	75	0.4671	0.500	$(1.96 \pm 0.10) \times 10^{-7}$
8.0	75	0.4668	0.515	$(1.07 \pm 0.10) \times 10^{-6}$
9.0	75	0.4620	0.505	$(6.82 \pm 0.30) \times 10^{-6}$
9.4	75	0.4607	0.514	$(9.98 \pm 0.20) \times 10^{-6}$
10.0	75	0.4465	0.520	$(3.33 \pm 0.10) \times 10^{-5}$
7.0	80	0.4671	0.496	$(3.44 \pm 0.20) \times 10^{-7}$
8.0	80	0.4668	0.500	$(1.87 \pm 0.23) \times 10^{-6}$
9.0	80	0.4324	0.516	$(1.07 \pm 0.10) \times 10^{-5}$
9.4	80	0.4496	0.500	$(2.14 \pm 0.30) \times 10^{-5}$
10.0	80	0.3928	0.436	$(5.72 \pm 0.13) \times 10^{-5}$

TABLE II
Various Activation Parameters for the *p*-Cresol–Formaldehyde Reaction

pH	ΔE, kcal/mol	$\log A$, l/mol·sec	ΔS^*, cal/deg·mol
10.0	19.08	7.75	−23.41
9.4	23.46	9.73	−14.35
9.0	33.50	15.86	+13.70
8.0	42.15	20.50	+34.93

where k_1 and k_2 are the stepwise rate constants for the formation of mo-nomethylol–*p*-cresol and dimethylolol–*p*-cresol, respectively. The overall rate expression is given by

$$kt = \frac{2.303}{(na - b)} \log \left(\frac{b}{na}\right) \left(\frac{na - y}{b - y}\right) \tag{3}$$

where a is the initial concentration of *p*-cresol, b the initial concentration of formaldehyde, y the amount of formaldehyde reacted at different time intervals, and n the functionality of *p*-cresol, i.e., number of reactive positions = 2.

The overall reaction can be written as

$$C_6H_4(OH)CH_3 + CH_2O \overset{k}{\rightarrow} \text{methylol–}p\text{-cresols} \tag{4}$$
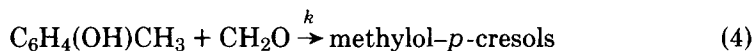
The rate of disappearance of *p*-cresol and formaldehyde can be represented as

$$-\frac{dx}{dt} = nk(a - x)(b - y) \tag{5}$$

$$-\frac{dy}{dt} = k(na - y)(b - y) \tag{6}$$

where k = overall rate constant, and x = amount of *p*-cresol that has disappeared at time t.

Solving the above equations, we get

$$y = na - na^{(n-1)/n}(a - x)^{1/n} \tag{7}$$

The rate equations for the formation of monomethylol–*p*-cresol and dimethy-lol–*p*-cresol can be written as

$$\frac{dx}{dt} = k_1(a - x)(b - y) \tag{8}$$

and

$$\frac{dc}{dt} = k_2(x - c)(b - y) \tag{9}$$

also

$$\frac{dy}{dt} = \frac{dx}{dt} + \frac{dc}{dt} \tag{10}$$

or

$$\frac{dy}{dt} = k_1(a - x)(b - y) + k_2(x - c)(b - y) \tag{11}$$

where c = amount of monomethylol–p-cresol that has disappeared at time t. On solving eqs. (8) and (9) we get

$$c = [a - xu - a^{1-u}(a - x)^u]/(1 - u) \tag{12}$$

where $u = k_2/k_1$. From eqs. (8), (9), and (11) we get

$$y = a + x + \frac{u}{1 - u}(a - x) - \frac{a^{1-u}}{1 - u}(a - x)^u \tag{13}$$

From eqs. (12) and (7) it is possible to calculate the concentrations of all the species present at any stage in the system from the ratio of the reaction rate constants (u) for the formation of methylol derivatives. The concentrations of various methylol–p-cresols are given in Table III. These have been calculated at 65, 70, 75, and 80°C and at pH 10.

By substituting the values of x and y at any time t in eq. (13) and using the method of successive approximations, the value of u has been evaluated to be

$$u = k_2/k_1 = 0.60$$

From eqs. (5) and (8) it has been found that $k_1 = nk$. Thus, k_1 was calculated with the help of the overall rate constant k. Knowing k_1 and u, the values of k_2 were calculated. The values of the stepwise rate constants thus obtained are given in Table IV.

TABLE III
Concentrations of Various Methylol–p-Cresols at Different Temperatures (pH = 10)

Time, sec	Concentration [M]		
	Y	X	c
Temperature 65°C ± 0.05°C			
1800	0.0125	0.0123	0.00015
3600	0.0238	0.0235	0.00167
5400	0.0350	0.0342	0.00212
7200	0.0450	0.0438	0.00265
Temperature 70°C ± 0.05°C			
2700	0.0263	0.0258	0.00050
5700	0.0550	0.0532	0.00210
9300	0.0800	0.0763	0.00437
11100	0.1050	0.0987	0.00752
Temperature 75°C ± 0.05°C			
2400	0.0400	0.0391	0.00110
4800	0.0620	0.0597	0.00260
7500	0.0960	0.0907	0.00617
9600	0.1180	0.1102	0.00932
Temperature 80°C ± 0.05°C			
2400	0.0460	0.0447	0.00165
3900	0.0800	0.0758	0.00485
7500	0.1140	0.1057	0.00985
9300	0.1400	0.1274	0.01477

TABLE IV
Stepwise Rate Constants at Different pH Values and Temperatures

pH	Rate constant, l/mol·sec	
	k_1	k_2
	Temperature 65°C ± 0.05°C	
8.0	3.46×10^{-7}	2.07×10^{-7}
9.0	2.62×10^{-6}	1.57×10^{-6}
9.4	8.82×10^{-6}	5.29×10^{-6}
10.0	3.04×10^{-5}	1.82×10^{-5}
	Temperature 70°C ± 0.05°C	
8.0	13.70×10^{-7}	8.22×10^{-7}
9.0	6.92×10^{-6}	4.15×10^{-6}
9.4	15.10×10^{-6}	9.06×10^{-6}
10.0	4.80×10^{-5}	2.88×10^{-5}
	Temperature 75°C ± 0.05°C	
7.0	3.92×10^{-7}	2.35×10^{-7}
8.0	2.14×10^{-6}	1.28×10^{-6}
9.0	13.64×10^{-6}	8.18×10^{-6}
9.4	1.99×10^{-5}	1.19×10^{-5}
10.0	6.66×10^{-5}	3.99×10^{-5}
	Temperature 80°C ± 0.05°C	
7.0	6.88×10^{-7}	4.12×10^{-7}
8.0	3.74×10^{-6}	2.24×10^{-6}
9.0	2.14×10^{-5}	1.28×10^{-5}
9.4	4.28×10^{-5}	2.56×10^{-5}
10.0	11.44×10^{-5}	6.86×10^{-5}

Using the values of c and those of the stepwise rate constants k_1 and k_2, the overall rate constant k has been calculated at 65, 70, 75, and 80°C at pH 10. These calculated values of k compare well with the experimental values (Table V) at the same temperature and pH.

Mechanism

In a formaldehyde molecule, the electron density is greater around the oxygen atom than around the carbon atom. The carbon atom of the formaldehyde molecule thus acquires a residual positive charge, and the oxygen atom acquires a residual negative charge:

I
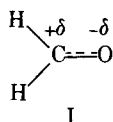
Due to inductive and mesomeric effects, the electron density is greater at the ortho positions in the *p*-cresol nucleus than at the meta position. The formaldehyde molecule I attacks at the ortho position of *p*-cresol, with the carbon atom directed toward the negative end of the cresate ion to form the activated complex II:
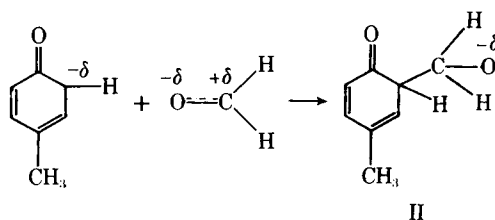

II

Time, sec	k, l/mole·sec	
	Experimental	Calculated
Temperature 65°C ± 0.05°C		
1800	1.590×10^{-5}	1.595×10^{-5}
3600	1.499×10^{-5}	1.504×10^{-5}
5400	1.517×10^{-5}	1.525×10^{-5}
7200	1.481×10^{-5}	1.493×10^{-5}
Temperature 70°C ± 0.05°C		
2700	2.347×10^{-5}	2.361×10^{-5}
5700	2.418×10^{-5}	2.447×10^{-5}
9300	2.257×10^{-5}	2.296×10^{-5}
11100	2.594×10^{-5}	2.650×10^{-5}
Temperature 75°C ± 0.05°C		
2400	3.807×10^{-5}	3.840×10^{-5}
4800	3.061×10^{-5}	2.923×10^{-5}
7500	3.227×10^{-5}	3.291×10^{-5}
9600	3.228×10^{-5}	3.305×10^{-5}
Temperature 80°C ± 0.05°C		
2400	6.092×10^{-5}	6.157×10^{-5}
3900	5.320×10^{-5}	5.420×10^{-5}
7500	5.577×10^{-5}	5.720×10^{-5}
9300	5.879×10^{-5}	6.062×10^{-5}

This is a slow reaction and the rate-determining one. The proton from the nuclear carbon atom then migrates to the oxygen of the
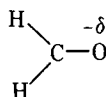
to give a compound which rearranges to give the stable benzenoid structure III:
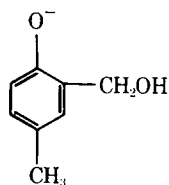
III

This interacts with a neutral water molecule to give a monomethylol–p-cresol, and the regenerated hydroxyl ions continue to catalyze the reaction. The monomethylol–p-cresol reacts with formaldehyde to give dimethylol–p-cresol through a similar mechanism.

According to the suggested mechanism for the formation of monomethylol– and dimethylol–p-cresol, the reaction takes place in two steps: (i) the formation of a cresate ion, and (ii) the formation of the activated complex. The net entropy

of activation will be the sum of entropy involved in the formation of the cresate ion and the entropy required in the formation of the activated complex:

$$\Delta S^*_{obs.} = \Delta S^*_{cresate} + \Delta S^*$$

Since the entropy of protonation is invariably positive, the entropy involved in the process opposite to the protonation will be invariably negative. In the presence of hydroxyl ions, *p*-cresol loses a proton to give cresate ion. Therefore, $\Delta S^*_{cresate}$ would be negative, and its value will become more and more negative with increase in pH. This is because in highly alkaline solutions the *p*-cresol molecule produces a more stable cresate ion.

However, ΔS^*, i.e., the entropy of activation involved in the formation of activated complex, would be positive because of the formation of an unstable and disordered complex. The value of ΔS^* would be assumed to remain constant. Since $\Delta S^*_{cresate}$ is becoming increasingly negative with increase in pH and ΔS^* has large positive values, the net result would be that the entropy of activation would decrease with the increase in pH. This is what is actually observed (Table II).

In the alkali catalyzed *p*-cresol–formaldehyde reaction, the larger values of energies of activation at lower pH values (Table II) indicate that the hydroxyl ions play an important role in the reaction. The rate of reaction increases with increase in pH, the rate constants being significantly lower at pH values of 7.0 than at pH value of 10.0 (Table I).

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