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Kinetics of the Alkali-Catalyzed o-Cresol-Formaldehyde Reaction

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ABSTRACT

A kinetic study of the reaction of o-cresol with formaldehyde was carried out at temperatures of 65 ± 0.05 , 70 ± 0.05 , 75 ± 0.05 , and $80 \pm 0.05^\circ\text{C}$ with NaOH as catalyst. The pH maintained was 7, 8, 9, 9.4, and 10. The reaction follows a second-order rate law. The rate is found to increase with increase of pH. The overall rate constant k was resolved into stepwise rate constants (k_1 and k_2) for the formation of mono-methylol-o-cresols and dimethylol-o-cresol, respectively. The values of Arrhenius parameters and the entropy of activation for the overall reaction were calculated. The experimental and calculated values of k at pH 10 and 65, 70, 75, and 80°C were found to agree well within experimental error.

INTRODUCTION

The kinetics of the alkali-catalyzed reaction of various phenols with formaldehyde has been the subject of several investigations [1-11]. A detailed study of the kinetics of the m-cresol-formaldehyde reaction in relation to the functionality of m-cresol was done by

Malhotra and Gupta [12]. However, no comprehensive study, particularly with regard to the kinetics of the reaction, appears to have been done on the alkali-catalyzed o-cresol-formaldehyde reaction. The present work was carried out to study the kinetics of the o-cresol-formaldehyde reaction in relation to the functionality of o-cresol at pH 7, 8, 9, 9.4, 10 and at temperatures of 65 ± 0.05 , 70 ± 0.05 , 75 ± 0.05 , and $80 \pm 0.05^\circ\text{C}$ with sodium hydroxide as catalyst.

EXPERIMENTAL

Materials

o-Cresol, formalin (37.5%, formaldehyde), iodine, sodium thiosulfate, potassium iodide, sodium bisulfite, and potassium bromate used were B. D. H. products. o-Cresol was distilled twice before use. Sodium hydroxide and methanol were A. R. or C. P. quality.

An oil thermostat having temperature control within $\pm 0.05^\circ\text{C}$ was employed for rate studies.

Procedure

The reaction mixture was placed in a 500 ml round-bottomed flask fitted with a water condenser. The flask was suspended in the thermostat maintained at the desired temperature. After 10 min, when the reaction vessel attained the temperature of the thermostat, an aliquot (10.0 ml) of the reaction mixture was taken and placed in an ice bath to freeze the reaction. Formaldehyde was estimated by the sodium bisulfite method.

RESULTS AND DISCUSSION

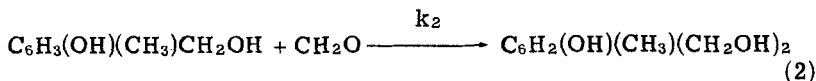
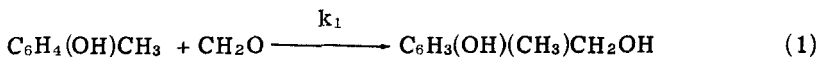
Results of the kinetic studies carried out at different pH values and temperatures are given in Table 1. The overall reaction was found to obey a second-order rate law. The values of the activation energy ΔE and frequency factor A for the overall reaction are given in Table 2. With an increase in pH, the rate of the reaction increases. It is also observed that with an increase in pH, the energy of activation ΔE and entropy of activation ΔS^\ddagger decrease appreciably.

Calculation of the Stepwise Rate Constants

The reaction of o-cresol with formaldehyde in alkaline medium proceeds according to Eqs. (1) and (2):

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

pH	Temperature °C	Initial [HCHO] (mole/liter)	Initial [o-cresol] (mole/liter)	Second-order rate constants k (liter/mole-sec)
8.0	65	0.480	0.4751	$(1.08 \pm 0.10) \times 10^{-7}$
9.0	65	0.496	0.4714	$(1.03 \pm 0.08) \times 10^{-6}$
9.4	65	0.460	0.4515	$(3.09 \pm 0.15) \times 10^{-6}$
10.0	65	0.376	0.4314	$(1.33 \pm 0.07) \times 10^{-5}$
8.0	70	0.451	0.4751	$(4.43 \pm 0.20) \times 10^{-7}$
9.0	70	0.451	0.4714	$(2.56 \pm 0.22) \times 10^{-6}$
9.4	70	0.424	0.4307	$(6.10 \pm 0.23) \times 10^{-6}$
10.0	70	0.368	0.4134	$(1.75 \pm 0.13) \times 10^{-5}$
7.0	75	0.480	0.4789	$(1.20 \pm 0.08) \times 10^{-7}$
8.0	75	0.480	0.4751	$(7.57 \pm 0.25) \times 10^{-7}$
9.0	75	0.424	0.4606	$(5.00 \pm 0.25) \times 10^{-6}$
9.4	75	0.416	0.4307	$(9.76 \pm 0.10) \times 10^{-6}$
10.0	75	0.400	0.4314	$(2.65 \pm 0.20) \times 10^{-5}$
7.0	80	0.484	0.4789	$(2.48 \pm 0.12) \times 10^{-7}$
8.0	80	0.478	0.4751	$(1.31 \pm 0.12) \times 10^{-6}$
9.0	80	0.320	0.4134	$(8.71 \pm 0.27) \times 10^{-6}$
9.4	80	0.370	0.4134	$(1.52 \pm 0.14) \times 10^{-5}$
10.0	80	0.344	0.4134	$(3.99 \pm 0.30) \times 10^{-5}$



where k_1 and k_2 are the stepwise rate constants for the overall formation of monomethylol-*o*-cresols and dimethylol-*o*-cresol, respectively. The overall rate expression for the formation of products is

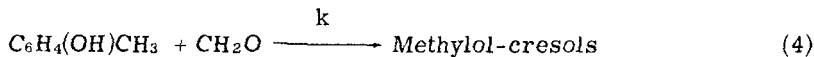
TABLE 2. Various Activation Parameters for the o-Cresol-Formaldehyde Reaction

pH	ΔE (kcal/mole)	log A (liter/mole-sec)	ΔS^\ddagger (cal/deg-mole)
10.0	19.06	7.39	-25.06
9.4	27.59	12.29	- 2,64
9.0	37.80	18.43	+25.46
8.0	44.00	21.52	+39.60

$$kt = \frac{2 \cdot 303}{(na - b)} \log \left(\frac{b}{na} \right) \left[\frac{(na - y)}{(b - y)} \right] \quad (3)$$

where a and b are initial concentrations of o-cresol and of formaldehyde, respectively; y is the amount of formaldehyde reacted at different time intervals; n is the functionality of o-cresol (= 2).

The rate at which o-cresol and formaldehyde disappear can be represented as



$$-dx/dt = nk(a - x)(b - y) \quad (5)$$

$$-dy/dt = k(na - y)(b - y) \quad (6)$$

where k is the overall rate constant and x is the amount of o-cresol having disappeared at time t. Dividing Eq. (6) by Eq. (5) and integrating yields Eq. (7):

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

The rate equations for the formation of monomethylol-o-cresols and dimethylol-o-cresol can be written as

$$dx/dt = k_1(a - x)(b - y) \quad (8)$$

and

$$dc/dt = k_2(x - c)(b - y) \quad (9)$$

also

$$dy/dt = (dx/dt) + (dc/dt) \quad (10)$$

or

$$dy/dt = k_1(a - x)(b - y) + k_2(x - c)(b - y) \quad (11)$$

where c is the amount of monomethylol-*o*-cresols having disappeared at time t . By dividing Eq. (9) by Eq. (8), we get a first-order differential equation Eq. (12):

$$dc/dx + [u/(a - x)] c = [u/(a - x)] x \quad (12)$$

where

$$u = k_2/k_1$$

The integrating factor (I. F.) for this linear differential equation is given by

$$\begin{aligned} \text{I. F.} &= e^{\int [u/(a - x)] dx} \\ &= e^{-u \log(a - x)} \\ &= e^{\log(a - x)^{-u}} \\ &= \frac{1}{(a - x)^u} \end{aligned}$$

On multiplying both sides of Eq. (12) by $1/(a - x)^u$, we get

$$\frac{1}{(a - x)^u} \frac{dc}{dx} + \frac{u}{(a - x)^{1+u}} c = \frac{u}{(a - x)^{1+u}} x \quad (13)$$

or

$$\frac{d\{c[1/(a - x)^u]\}}{dx} = \frac{ux}{(a - x)^{1+u}} \quad (14)$$

TABLE 3. Concentration of Various Methylol-o-cresols at Different Temperatures at pH = 10

Time (sec)	Temperature (°C)	Concentration (mole/liter)		
		y	x	c
4800	65 ± 0.05	0.0200	0.0198	0.0002
10800		0.0400	0.0393	0.0009
13500		0.0520	0.0505	0.0021
18000		0.0620	0.0596	0.0032
4500	70 ± 0.05	0.0220	0.0217	0.0001
7200		0.0420	0.0416	0.0014
12600		0.0660	0.0596	0.0032
18000		0.0760	0.0724	0.0048
1800	75 ± 0.05	0.0200	0.0199	-
3600		0.0400	0.0392	0.0012
9600		0.0600	0.0579	0.0031
10800		0.0740	0.0710	0.0046
2400	80 ± 0.05	0.0280	0.0275	0.0008
4800		0.0480	0.0450	0.0018
7200		0.0720	0.0688	0.0040
9600		0.0800	0.0761	0.0057
12000		0.1040	0.0975	0.0095

On integrating and putting the limits $x = 0$, $c = 0$ at $t = 0$, we get

$$c = [1/(1-u)] [a - xu - a^{1-u}(a-x)^u] \quad (15)$$

Finally, on dividing Eq. (11) by Eq. (8) and using Eq. (12), a differential equation (16) with separate variables is obtained:

$$dy/dx = 1 + [u/(a-x)]x - [u/(a-x)]c \quad (16)$$

or

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

pH	Temperature (°C)	Rate constant (liter/mole-sec)	
		k_1	k_2
8.0	65 ± 0.05	2.16×10^{-7}	1.62×10^{-7}
9.0		2.05×10^{-6}	1.54×10^{-6}
9.4		6.19×10^{-6}	4.64×10^{-6}
10.0		2.66×10^{-5}	1.99×10^{-5}
8.0	70 ± 0.05	8.86×10^{-7}	6.64×10^{-7}
9.0		5.12×10^{-6}	3.84×10^{-6}
9.4		12.19×10^{-6}	9.14×10^{-6}
10.0		3.50×10^{-5}	2.62×10^{-5}
7.0	75 ± 0.05	2.41×10^{-7}	1.81×10^{-7}
8.0		15.14×10^{-7}	11.36×10^{-7}
9.0		10.01×10^{-6}	7.51×10^{-6}
9.4		19.51×10^{-6}	14.64×10^{-6}
10.0		5.30×10^{-5}	3.98×10^{-5}
7.0		80 ± 0.05	4.96×10^{-7}
8.0	2.61×10^{-6}		1.96×10^{-6}
9.0	17.42×10^{-6}		13.06×10^{-6}
9.4	3.04×10^{-5}		2.27×10^{-5}
10.0	7.97×10^{-5}		6.04×10^{-5}

$$y = x + u \int \frac{x}{a-x} dx - u \int \frac{c}{a-x} dx + I_0 \quad (17)$$

we know that

$$\int \frac{x}{a-x} dx = -a \log(a-x) - x$$

$$\int \frac{c}{(a-x)} dx = \frac{1}{1-u} [-a \log(a-x) + ua \log(a-x) + ux + a^{1-u}/u (a-x)^u]$$

TABLE 5. Experimental and Calculated Values of k at Different Temperatures at $\text{pH} = 10$

Time (sec)	Temperature ($^{\circ}\text{C}$)	k (liter/mole-sec)	
		Experimental	Calculated
4800	65 ± 0.05	1.39×10^{-5}	1.45×10^{-5}
10800		1.29×10^{-5}	1.28×10^{-5}
13500		1.38×10^{-5}	1.40×10^{-5}
18000	70 ± 0.05	1.26×10^{-5}	1.30×10^{-5}
4500		1.67×10^{-5}	1.69×10^{-5}
7200		2.68×10^{-5}	2.10×10^{-5}
12600	75 ± 0.05	1.82×10^{-5}	1.89×10^{-5}
18000		1.63×10^{-5}	1.70×10^{-5}
1800		2.79×10^{-5}	2.82×10^{-5}
3600	80 ± 0.05	3.48×10^{-5}	3.56×10^{-5}
9600		2.04×10^{-5}	2.10×10^{-5}
10800		2.30×10^{-5}	2.36×10^{-5}
2400	80 ± 0.05	4.37×10^{-5}	4.44×10^{-5}
4800		3.91×10^{-5}	4.03×10^{-5}
7200		4.14×10^{-5}	4.32×10^{-5}
9600	80 ± 0.05	3.61×10^{-5}	3.78×10^{-5}
12000		3.89×10^{-5}	4.11×10^{-5}

Putting the values of above integrals in Eq. (17) we get

$$y = x + u [-a \log(a - x) - x] - [u/1 - u] [-a \log(a - x) + ua \log(a - x) + ux + (a^{1-u}/u)(a - x^u)] + I_0 \quad (18)$$

The value of I_0 is calculated by putting the limits at $t = 0$, $x = 0$, and $y = 0$; then Eq. (18) reduces to

$$y = a + x + [u/(1 - u)] (a - x) - [a^{1-u}/(1 - u)] (a - x)^u \quad (19)$$

From Eqs. (15) and (19), 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-*o*-cresols are given in Table 3. These have been calculated at 65, 70, 75, and 80°C and at pH = 10.

From Eqs. (17) and (19) we get Eq. (20):

$$na - na^{(n-1)/n} (a - x)^{1/n} = a + x + \frac{u}{1 - u} (a - x) - \frac{a^{1-u}}{1 - u} (a - x)^u \quad (20)$$

By substituting the values of *o*-cresol reacted at any time t , i. e., x in the Eq. (20) and by using the method of successive approximations, the value u is evaluated to be

$$u = k_2/k_1 = 0.75$$

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 . From a knowledge of k_1 and u , the values of k_2 were calculated. The values of the stepwise rate constants thus obtained are given in Table 4.

By use of 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 5) at the same temperature and pH.

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