

Kinetics of Alkali-Catalyzed *m*-Cresol-Formaldehyde Reaction

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Synopsis

The alkali-catalyzed reaction of *m*-cresol with formaldehyde carried out at 65°, 70°, 75° and 80°C and at pH 7, 8, 9, 9.4, and 10 follows second-order kinetics. The rate is found to increase with increase of pH. The overall rate constant (k) has been resolved into stepwise rate constants (k_1 , k_2 , and k_3) for the formation of monomethylol, dimethylol, and trimethylol cresol, respectively. For this purpose, the rate equations for the various possible steps have been given and the concentrations of the various methylol cresols formed determined. The experimental and calculated values of k at pH 10 and temperatures of 65°, 70°, 75°, and 80°C have been found to agree well within the experimental errors. Entropy of activation and the Arrhenius parameters for the overall reaction have also been calculated.

INTRODUCTION

Phenols combine with formaldehyde forming a variety of products. The kinetics of the reaction of various phenols with formaldehyde has been the subject of several investigations.¹⁻¹⁰ A review of the literature reveals that the kinetics of the *m*-cresol-formaldehyde reaction has been a subject of slower growth. Only Sprung¹⁰ studied the kinetics of the various substituted phenols with paraformaldehyde in the absence of water using triethanolamine as catalyst, reporting the overall reaction to be first order. The present work was carried out to study the kinetics of *m*-cresol-formaldehyde reaction in relation to the functionality of *m*-cresol.

EXPERIMENTAL

Materials and Methods

m-Cresol, formaldehyde (37.5% solution in H₂O), iodine, sodium thiosulfate, KI, NaHSO₃, and KBrO₃ used were B.D.H. products. *m*-Cresol was double distilled before use. Other chemicals, sodium hydroxide, and methanol were of A.R. or C.P. quality.

An oil thermostat was employed for rate studies. The reaction was carried out at 65°, 70°, 75°, and 80°C maintained within $\pm 0.05^\circ\text{C}$ and at pH 7, 8, 9, 9.4, and 10 using NaOH as catalyst.

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

pH	Temperature, °C	Initial formaldehyde concn., M	k , l. mole ⁻¹ sec ⁻¹
8.00	65	0.364	8.185×10^{-7}
9.00	65	0.468	5.021×10^{-6}
9.40	65	0.332	2.508×10^{-5}
10.00	65	0.460	6.609×10^{-5}
7.00	70	0.384	4.729×10^{-7}
8.00	70	0.380	3.09×10^{-6}
9.00	70	0.376	1.348×10^{-5}
9.40	70	0.380	3.265×10^{-5}
10.00	70	0.380	8.922×10^{-5}
7.00	75	0.408	1.404×10^{-6}
8.00	75	0.400	5.28×10^{-6}
9.00	75	0.470	3.154×10^{-5}
9.40	75	0.460	3.328×10^{-5}
10.00	75	0.460	1.331×10^{-4}
7.00	80	0.400	6.512×10^{-6}
8.00	80	0.420	1.002×10^{-5}
9.00	80	0.408	4.667×10^{-5}
9.40	80	0.400	7.596×10^{-5}
10.00	80	0.420	1.387×10^{-4}

^a Initial *m*-cresol concn = 0.416*M*.

Procedure

Two hundred thirty milliliters of the reaction mixture, containing 100 ml 0.957*M* *m*-cresol solution in methanol, 100 ml 0.837–1.08*M* formaldehyde solution, and 30 ml NaOH solution of varying concentration to give the reaction mixture the desired pH was added to a 500-ml round-bottom flask fitted with a water condenser and suspended in the thermostat maintained at the desired temperature. After equilibration, an aliquot (2.0 ml) of the reaction mixture was taken and placed in an ice bath to freeze the reaction. Formaldehyde was estimated by the usual sodium bisulfite method.

RESULTS AND DISCUSSION

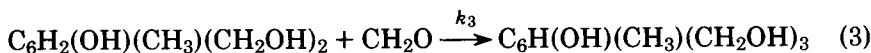
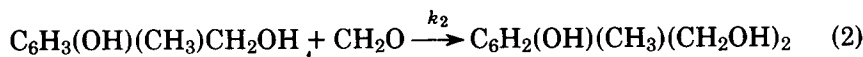
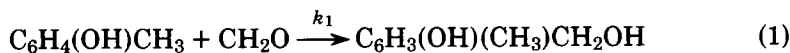
Results of the kinetic studies carried out at different pH values and temperatures are given in Table I. The reaction has been found to obey second-order rate law. A linear plot of $\log (b/na)(na - y)/(b - y)$ versus time also supports this point. Values of the activation energy (ΔE) and frequency factor A calculated from the linear plot of $\log k$ versus $1/T$ for the overall reaction are given in table II. From Table I, it is observed that the rate of the reaction increases with increase in pH. It can be seen from Table II that with increase in pH, the values of activation energy ΔE and activation entropy ΔS^\ddagger decrease appreciably.

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

pH	ΔE , kcal/mole	$\log A$, l. mole ⁻¹ sec ⁻¹	ΔS^\ddagger , cal deg ⁻¹ mole ⁻¹
7.0	60.3	32.6	+86.5
8.0	37.0	17.9	+19.2
9.0	31.5	15.2	+6.7
9.4	17.6	6.4	-32.0
10.0	13.6	4.6	-41.9

Calculation of the Stepwise Rate Constants

The kinetics of formation of the various methylolcresols in alkaline medium may be examined in the light of eqs. (1)–(3):

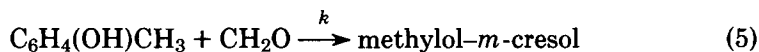


where k_1 , k_2 , and k_3 are the stepwise rate constants for the overall formation of monomethylolcresol, dimethylolcresol, and trimethylolcresol, respectively. The overall rate expression is given by eq. (4):

$$kt = \frac{2.303}{na - b} \log \left[\frac{(b/na)(na - y)}{(b - y)} \right] \quad (4)$$

where a = initial concentration of *m*-cresol, b = initial concentration of formaldehyde, y = amount of formaldehyde reacted at different time intervals, and n = functionality of *m*-cresol.

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



$$\frac{dx}{dt} = nk(a - x)(b - y) \quad (6)$$

$$\frac{dy}{dt} = k(na - y)(b - y) \quad (7)$$

where k is the overall rate constant. Other symbols have the usual significance, and x represents the amount of *m*-cresol disappeared at time t .

Dividing eq. (7) by eq. (6) and integrating, we get eq. (8):

$$y = na - na^{(n-1)/n}(a - x)^{1/n} \quad (8)$$

The rate equations for the formation of monomethylol-*m*-cresol, dimethylol-*m*-cresol, and trimethylol-*m*-cresol can be written as

$$\frac{dx}{dt} = k_1(a-x)(b-y) \quad (9)$$

$$\frac{dc}{dt} = k_2(x-c)(b-y) \quad (10)$$

and

$$\frac{df}{dt} = k_3(c-f)(b-y) \quad (11)$$

also

$$\frac{dy}{dt} = \frac{dx}{dt} + \frac{dc}{dt} + \frac{df}{dt} \quad (12)$$

or

$$\frac{dy}{dt} = k_1(a-x)(b-y) + k_2(x-c)(b-y) + k_3(c-f)(b-y) \quad (13)$$

where c and f are the concentrations of monomethylol- m -cresol and dimethylol- m -cresol, respectively, disappeared at time t .

Dividing eq. (10) by eq. (9), a first-order differential eq. (14) is obtained:

$$\frac{dc}{dx} + \frac{u}{a-x}c = \frac{u}{a-x}x \quad (14)$$

where $u = k_2/k_1$. The integrating factor (*I.F.*) for this linear differential equation is given by

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

Multiplying both sides of eq. (14) by $1/(a-x)^u$, we get

$$\frac{1}{(a-x)^u} \frac{dc}{dx} + \frac{u}{(a-x)^{u+1}}c = \frac{ux}{(a-x)^{u+1}} \quad (15)$$

or

$$\frac{d}{dx} c \frac{1}{(a-x)^u} = \frac{ux}{(a-x)^{u+1}} \quad (16)$$

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

$$c = x + \frac{a-x}{1-u} - \left[\frac{a^{1-u}}{1-u} (a-x)^u \right] \quad (17)$$

or

$$c = \frac{1}{1-u} [a - xu - a^{1-u}(a-x)^u] \quad (18)$$

Similarly, on dividing eq. (11) by eq. (9), we get a differential equation:

$$\frac{df}{dx} + \frac{v}{a-x}f = \frac{v}{a-x}c \quad (19)$$

where $v = k_3/k_1$. The *I.F.* of this linear differential equation is

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

Time, sec	<i>y</i>	<i>x</i>	Concentration, M <i>c</i>	<i>f</i>
Temp. 65° ± 0.05°C				
6900	0.208	0.1754	0.03156	0.0022
7200	0.216	0.1807	0.03375	0.0024
9300	0.228	0.1889	0.03718	0.0026
11700	0.240	0.1969	0.04126	0.0028
14100	0.252	0.2046	0.04469	0.0034
Temp. 70° ± 0.05°C				
6400	0.151	0.1335	0.01688	nil
8400	0.208	0.1754	0.03156	0.002
12000	0.261	0.2103	0.04969	0.051
14400	0.297	0.2319	0.0603	0.0053
Temp. 75° ± 0.05°C				
1200	0.108	0.0989	0.009376	nil
2400	0.152	0.1277	0.01594	nil
3600	0.184	0.1583	0.02563	0.0013
4800	0.222	0.1848	0.03532	0.0020
6180	0.242	0.1982	0.04188	0.0027
Temp. 80° ± 0.05°C				
1200	0.092	0.0853	0.007188	nil
2400	0.168	0.1464	0.02063	0.001
3600	0.212	0.1781	0.03219	0.0019
6000	0.268	0.2146	0.05031	0.0039
7200	0.289	0.2273	0.0575	0.005

$$I.F. = e^{\int v/(a-x)} dx = e^{-v \log(a-x)} = e^{\log(a-x)^{-v}} = \frac{1}{(a-x)^v}$$

Multiplication of eq. (19) by $1/(a-x)^v$ results in

$$\frac{1}{(a-x)^v} \frac{df}{dx} + \frac{v}{(a-x)^{v+1}} f = \frac{vc}{(a-x)^{v+1}} \quad (20)$$

or

$$\frac{d}{dx} \frac{f}{(a-x)^v} = \frac{vc}{(a-x)^{v+1}} \quad (21)$$

Integrating, we get

$$\frac{f}{(a-x)^v} = \lambda + v \int \frac{c}{(a-x)^{v+1}} \quad (22)$$

or

$$\frac{f}{(a-x)^v} = \lambda + v \left(\frac{c}{v(a-x)^v} - \int \frac{dx}{v(a-x)^v} \frac{dc}{dx} \right) \quad (23)$$

Putting the value of *c* from eq. (18) in eq. (23), we get

$$\frac{f}{(a-x)^v} = \lambda + \frac{1}{(a-x)^v} \frac{1}{1-u} [(a-ux-a^{1-u})(a-x)^u] + \frac{u}{1-u} \left[\int \frac{1-a^{1-u}(a-x)^{u-1}}{(a-x)^v} \right] \quad (24)$$

or

$$\frac{f}{(a-x)^v} = \lambda + \frac{1}{(a-x)^v} \frac{1}{1-u} [a-ux-a^{1-u}(a-x)^u] + \frac{u}{1-u} \left[\frac{-(a-x)}{(1-v)(a-x)^v} + \frac{a^{1-u}}{u-v} (a-x)^{u-v} \right] \quad (25)$$

The value of the constant λ is evaluated by making use of the boundary conditions $f = 0$ and $x = 0$ at $t = 0$:

$$\lambda = -\frac{1}{a^v} \frac{1}{1-u} [a-a^{1-u}a^u] - \frac{u}{1-u} \left[-\frac{a}{(1-v)a^v} + \frac{a^{1-u}a^{u-v}}{u-v} \right] = -\frac{ua^{1-v}}{(1-v)(u-v)} \quad (26)$$

On substituting the value of λ in eq. (25), we get

$$f = \frac{1}{1-u} \left[a-ux-a^{1-u}(a-x)^u - \frac{u(a-x)}{1-v} + \frac{u}{u-v} a^{1-u}(a-x)^u \right] - \frac{ua^{1-v}}{(1-v)(u-v)} (a-x)^v \quad (27)$$

To determine the dimethylol- m -cresol concentration at time t , only the ratio of reaction rate constants for the formation of monomethylol- m -cresol, dimethylol- m -cresol, and trimethylol- m -cresol should be known.

Finally, on dividing eq. (13) by eq. (9) and using eqs. (14) and (19), we get a differential eq. (28) with separate variables.

$$\frac{dy}{dx} = 1 = \frac{u}{a-x} x - \frac{u-v}{a-x} c - \frac{v}{a-x} f \quad (28)$$

or

$$y = \lambda + u \int \frac{xdx}{a-x} - (u-v) \int \frac{cdx}{a-x} - v \int \frac{fdx}{a-x} \quad (29)$$

We know that

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

$$\int \frac{cdx}{a-x} = \frac{1}{1-u} \left[-a \log(a-x) + ua \log(a-x) + ux + \frac{a^{1-u}}{u} (a-x)^u \right]$$

$$\int \frac{fdx}{a-x} = \frac{v}{1-u} \left[-\frac{1-u}{v} a \log(a-x) - \frac{u}{1-v} x - \frac{a^{1-u}}{u-v} \frac{(a-x)^u}{u} \right] + \frac{ua^{1-v}}{(1-v)(u-v)} \frac{(a-x)^v}{v}$$

TABLE IV
Stepwise Rate Constants at Different pH Values and Temperatures

pH	Rate constant, l. mole ⁻¹ sec ⁻¹		
	<i>k</i> ₁	<i>k</i> ₂	<i>k</i> ₃
Temp. 65° ± 0.05°C			
8.00	24.555 × 10 ⁻⁷	16.696 × 10 ⁻⁷	7.856 × 10 ⁻⁷
9.00	15.063 × 10 ⁻⁶	10.239 × 10 ⁻⁶	4.819 × 10 ⁻⁶
9.40	7.524 × 10 ⁻⁵	4.866 × 10 ⁻⁵	2.407 × 10 ⁻⁵
10.00	19.827 × 10 ⁻⁵	13.48 × 10 ⁻⁵	6.34 × 10 ⁻⁵
Temp. 70° ± 0.05°C			
7.00	14.187 × 10 ⁻⁷	9.64 × 10 ⁻⁷	4.536 × 10 ⁻⁷
8.00	9.27 × 10 ⁻⁶	6.305 × 10 ⁻⁶	2.965 × 10 ⁻⁶
9.00	4.044 × 10 ⁻⁵	2.723 × 10 ⁻⁵	1.294 × 10 ⁻⁵
9.40	9.795 × 10 ⁻⁵	6.665 × 10 ⁻⁵	3.151 × 10 ⁻⁵
10.00	26.76 × 10 ⁻⁵	18.202 × 10 ⁻⁵	8.564 × 10 ⁻⁵
Temp. 75° ± 0.05°C			
7.00	4.212 × 10 ⁻⁶	2.864 × 10 ⁻⁶	1.348 × 10 ⁻⁶
8.00	15.84 × 10 ⁻⁶	10.77 × 10 ⁻⁶	5.066 × 10 ⁻⁶
9.00	9.462 × 10 ⁻⁵	6.433 × 10 ⁻⁵	3.027 × 10 ⁻⁵
9.40	9.984 × 10 ⁻⁵	6.79 × 10 ⁻⁵	3.195 × 10 ⁻⁵
10.00	3.9948 × 10 ⁻⁴	2.716 × 10 ⁻⁴	1.278 × 10 ⁻⁴
Temp. 80° ± 0.05°C			
7.00	19.536 × 10 ⁻⁶	13.28 × 10 ⁻⁶	6.248 × 10 ⁻⁶
8.00	3.006 × 10 ⁻⁵	2.044 × 10 ⁻⁵	0.9618 × 10 ⁻⁵
9.00	13.001 × 10 ⁻⁵	9.518 × 10 ⁻⁵	4.479 × 10 ⁻⁵
9.40	22.788 × 10 ⁻⁵	15.596 × 10 ⁻⁵	7.29 × 10 ⁻⁵
10.00	4.161 × 10 ⁻⁴	2.843 × 10 ⁻⁴	1.391 × 10 ⁻⁴

Putting the values of above integrals into eq. (29), we get

$$\begin{aligned}
 y = \lambda - u[-a \log(a-x) - x] - \frac{u-v}{1-u} \left[-a \log(a-x) \right. \\
 \left. + ua \log(a-x) + ux + \frac{a^{1-u}}{u} (a-x)^u \right] \\
 - \frac{v^2}{1-u} \left[-\frac{1-u}{v} a \log(a-x) - \frac{u}{1-v} x - \frac{a^{1-u}(a-x)^u}{(u-v)u} \right. \\
 \left. + \frac{uva^{1-v}(a-x)^v}{(1-v)(u-v)v} \right] \quad (30)
 \end{aligned}$$

The value of λ is calculated by putting the limits at $t = 0$, $x = 0$, and $y = 0$, and then eq. (30) is reduced to

$$\begin{aligned}
 y = 2a + x + \frac{u(1-2v)}{(1-u)(1-v)} (a-x) \\
 - \frac{(u-2v)a^{1-u}}{(1-u)(u-v)} (a-x)^u - \frac{ua^{1-v}}{(1-v)(u-v)} (a-x)^v \quad (31)
 \end{aligned}$$

Equations (18), (27), and (31) show that it is possible to calculate the concentrations of all the species present at any stage in the system from the ratio

TABLE V
Experimental and Calculated Values of k at Different Temperatures (pH = 10)

Time, sec	k , l. mole ⁻¹ sec ⁻¹	
	Exptl.	Calcd.
Temp. 65° ± 0.05°C		
6900	7.713 × 10 ⁻⁵	7.735 × 10 ⁻⁵
7200	7.823 × 10 ⁻⁵	7.849 × 10 ⁻⁵
9300	6.585 × 10 ⁻⁵	6.608 × 10 ⁻⁵
Temp. 70° ± 0.05°C		
6400	8.35 × 10 ⁻⁵	8.384 × 10 ⁻⁵
8400	8.40 × 10 ⁻⁵	8.486 × 10 ⁻⁵
12000	8.94 × 10 ⁻⁵	8.944 × 10 ⁻⁵
Temp. 75° ± 0.05°C		
1200	1.692 × 10 ⁻⁴	1.696 × 10 ⁻⁴
2400	1.433 × 10 ⁻⁴	1.457 × 10 ⁻⁴
3600	1.221 × 10 ⁻⁴	1.2588 × 10 ⁻⁴
4800	1.223 × 10 ⁻⁴	1.2288 × 10 ⁻⁴
Temp. 80° ± 0.05°C		
1200	1.428 × 10 ⁻⁴	1.44 × 10 ⁻⁴
2400	1.527 × 10 ⁻⁴	1.542 × 10 ⁻⁴
3600	1.436 × 10 ⁻⁴	1.46 × 10 ⁻⁴

of reaction rate constants (u and v) for the formation of methylol derivatives. The concentrations of various methylol- m -cresols given in Table III were calculated at 65°, 70°, 75°, and 80°C and at pH 10.

From eqs. (8) and (31), we get eq. (32):

$$na - na^{(n-1)/n}(a-x)^{1/n} = 2a + x + \frac{u(1-2v)}{(1-u)(1-v)}(a-x) - \frac{(u-2v)a^{1-u}}{(1-u)(u-v)}(a-x)^u - \frac{ua^{1-v}}{(1-v)(u-v)}(a-x)^v \quad (32)$$

Using this equation, the values of u and v were calculated as given below:

In the initial stages of reaction, the dimethylol- m -cresols would be completely absent and the step reaction (3) does not occur, i.e., k_3 is zero. Therefore, $v = k_3/k_1$ in eq. (32) can be ignored. The values of u can be determined from the calculated values of m -cresol reacted at any time t , i.e., x in the initial stages of the reaction. Thus using the method of successive approximations, the values of u and v were evaluated to be

$$u = k_2/k_1 = 0.68$$

$$v = k_3/k_1 = 0.32$$

From eqs. (6) and (9), it has been found that $k_1 = nk$. Thus, k_1 was calculated with the help of the overall rate constant k . Knowing u , v , and k_1 , the values of k_2 and k_3 were evaluated. The values of the stepwise rate constants thus obtained are given in Table IV.

Utilizing the values of c and f and those of the stepwise rate constants (k_1 , k_2 , and k_3), the overall rate constant k was 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.

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