Kinetics and Mechanism of Acid-Catalyzed 2,5-Xylenol-Formaldehyde Reaction

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ABSTRACT

This paper deals with kinetic studies of the 2,5-xylenol and formaldehyde reaction catalyzed by hydrochloric acid. The catalyst concentrations used were 0.008, 0.012, 0.02, and 0.04 N. The investigations were carried out at 65, 70, 75, and 80°C. It was observed that the reaction follows a second-order rate law. The rate of reaction was found to increase with an increase in acid concentration. The overall rate constant was resolved into stepwise rate constants. It is a two-step reaction, the second step of the reaction being a rapid follow-up of the first step. Activation parameters for the overall reaction have been calculated, and a mechanism conforming to the experimental observations is suggested.

INTRODUCTION

Only a few isolated studies [1-5] involving the different xylenols and formaldehyde reactions catalyzed by acids are available. These studies are mainly concerned with the overall order of the reaction

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and the identification of the products. In the literature, not a single kinetic study on the reaction of 2,5-xylenol and formaldehyde has been reported. For the present paper we have made a detailed kinetic study of this reaction. The reaction was studied at 80, 75, 70, and 65°C using HCl, of varying concentration, as the catalyst. The overall rate constant has been resolved into stepwise rate constants, and their individual values are reported.

EXPERIMENTAL

Materials

2,5-Xylenol, formaldehyde, and hydroxylamine hydrochloride were B.D.H. products. Methanol and sodium nitrite were E. Merck products. All the chemicals used were of AR or C.P. quality. Solvents used for TLC were redistilled and purified by recommended procedures.

An immersion-type thermostat (German, Model E3E) was employed for the kinetic studies.

Measurements

The reactions were carried out in a methanol-water mixture (1:1, v/v). The reactants and the catalyst, preheated to the required temperature, were mixed in a round-bottom flask which was suspended in the thermostatic bath. The flask was fitted with a water condenser. The reaction mixture (25 mL) was withdrawn after definite intervals of time and placed in an ice bath. Formaldehyde was estimated by the hydroxylamine hydrochloride method, and 2,5-xylenol, separated from the reaction mixture by TLC, was estimated spectrophotometrically [6].

RESULTS AND DISCUSSION

Calculation of the Overall Rate Constant

The reaction between 2,5-xylenol and formaldehyde in acid medium is a successive process of formation of monomethylol and methylene derivatives of 2,5-xylenol according to

$$(CH_3)_2.C_6H_3OH + CH_2O \xrightarrow{\ k_1\ } (CH_3)_2C_6H_2(OH)CH_2OH \qquad (A)$$

$$(CH_3)_2.C_6H_2(OH)CH_2OH + (CH_3)_2C_6H_3OH \xrightarrow{\ k_2\ }$$

$$(CH_3)_2.C_6H_2(OH)-CH_2-(CH_3)_2.C_6H_2OH + H_2O \qquad (B)$$
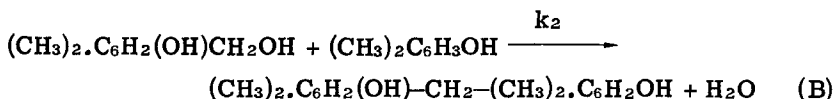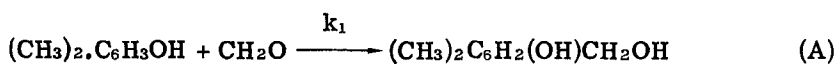
The rate expression for the overall reaction is

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

where a and b are the initial concentrations of 2,5-xylenol and formaldehyde, respectively, and x and y are the amounts of 2,5-xylenol and formaldehyde reacted at time t. The overall rate constant is represented by k.

As is evident from Eqs. (A) and (B), the amounts of 2,5-xylenol consumed will be more than that of formaldehyde at any stage of the reaction. The average proportion of 2,5-xylenol and formaldehyde reacted was found to be nearly x = 1.95y. Substituting this in Eq. (1) and integrating, we get

$$k = \frac{2.303 \times 1.95}{t(1.95b - a)} \log \frac{a}{b} \times \frac{b - y}{a - 1.95y} \qquad (2)$$

Results of the kinetic studies carried out at different temperatures and various acid concentrations are reported in Table 1. The acid-catalyzed reaction between 2,5-xylenol and formaldehyde obeys a second-order rate law. It can also be seen that at any given temperature the rate of reaction increases with an increase in the concentration of the catalyst. The plot of log k versus 1/T for the overall reaction was utilized to obtain the values of the Arrhenius parameters (Table 2).

Determination of the Ratio of the Step Rate Constants and Calculation of the Individual Rate Constants

The ratio of the step rate constants can be determined on the basis of the method suggested by Ryabukhin [5].

x, y, and z are the proportions of reacted 2,5-xylenol, formaldehyde, and methylol derivatives (moles), and n is the functionality of 2,5-xylenol. According to Eqs. (A) and (B), the rate of change of formaldehyde concentration is

$$dy/dt = k_1(b - y)(na - y - z) \qquad (3)$$

Similarly, the change in monomethylol 2,5-xylenol concentration would be given by

TABLE 1. Second-Order Rate Constant for Various Catalyst Concentrations and at Different Temperatures[a]

Temperature ($°C$)	$[HCl] \times 10^3$ (N)	$[HCHO]$, initial (M)	Second-order rate constant (L/mol s)
80	40	0.0504	$(1.66 \pm 0.02) \times 10^{-2}$
	20	0.0510	$(7.38 \pm 0.05) \times 10^{-3}$
	12	0.0514	$(4.22 \pm 0.06) \times 10^{-3}$
	8	0.0498	$(3.34 \pm 0.05) \times 10^{-3}$
75	40	0.0501	$(1.09 \pm 0.01) \times 10^{-2}$
	20	0.0505	$(5.16 \pm 0.09) \times 10^{-3}$
	12	0.0498	$(2.77 \pm 0.01) \times 10^{-3}$
	8	0.0598	$(1.91 \pm 0.03) \times 10^{-3}$
70	40	0.0516	$(7.47 \pm 0.05) \times 10^{-3}$
	20	0.0506	$(3.49 \pm 0.03) \times 10^{-3}$
	12	0.0510	$(1.76 \pm 0.02) \times 10^{-3}$
	8	0.0506	$(1.13 \pm 0.02) \times 10^{-3}$
65	40	0.0496	$(5.26 \pm 0.06) \times 10^{-3}$
	20	0.0502	$(2.37 \pm 0.02) \times 10^{-3}$
	12	0.0508	$(8.95 \pm 0.03) \times 10^{-4}$
	8	0.0496	$(5.60 \pm 0.01) \times 10^{-4}$

[a]Initial $[2,5$-xylenol$] = 0.0500$ M; solvent = methanol-water (1:1, v/v).

$$dz/dt = k_2 (y - z)(na - y - z) \tag{4}$$

where k_1 and k_2 are the step rate constants.
    Adding Eqs. (3) and (4):

$$\frac{d(y + z)}{dt} = k_1 (b - y)(na - y - z) + k_2 (y - z)(na - y - z) \tag{5}$$

Now the rate at which 2,5-xylenol molecules disappear will be proportional to the functionality and instantaneous concentration of 2,5-xylenol

TABLE 2. Activation Parameters at Various Acid Concentrations for Overall Reaction

[Acid] (N)	ΔE (kcal/mol)	log A (L/mol s)	ΔS (eu)
0.008	28.03	14.88	+7.27
0.012	24.02	12.51	-3.56
0.020	20.59	10.65	-12.08
0.040	18.30	9.55	-17.15

and that of HCHO (according to Eq. A) and methylol groups (according to Eq. B). Therefore,

$$dx/dt = nk_1 (a - x)(b - y) + nk_2 (a - x)(y - z) \tag{6}$$

Dividing Eq. (5) by Eq. (6):

$$\frac{d(y + z)}{dx} = \frac{k_1 (b - y)(na - y - z) + k_2 (y - z)(na - y - z)}{nk_1 (a - x)(b - y) + nk_2 (a - x)(y - z)} \tag{7}$$

Rearranging the variables and integrating Eq. (7) and putting the limits at $t = 0$, $y = 0$, and $z = 0$, we get

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

This equation contains the experimental concentration of methylol xylenols which is difficult to determine. Therefore, to establish a relation between the amount of reacted 2,5-xylenol and formaldehyde excluding the concentration of methylol groups, subtract Eq. (4) from Eq. (3):

$$\frac{d(y - z)}{dt} = k_1 (b - y)(na - y - z) - k_2 (y - z)(na - y - z) \tag{9}$$

Dividing Eq. (9) by Eq. (3):

$$\frac{d(y - z)}{dy} = 1 - \frac{k_2 (y - z)}{k_1 (b - y)} = 1 - m\frac{y - z}{b - y} \tag{10}$$

where $k_2 / k_1 = m$.

Integrating Eq. (10) and putting the limits at $t = 0$, $y = 0$, and $z = 0$, we get

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

Adding Eqs. (8) and (11) and rearranging, we get

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

In acid medium, $n = 1$. Knowing the amounts of 2,5-xylenol and formaldehyde reacted at different time intervals, the value of m can be determined by using Eq. (12). The value of k_2/k_1, i.e., m, has been found to be 44 to 46.

To evaluate the individual rate constants, we have from Eqs. (1) and (6),

$$k(a - x)(b - y) = nk_1(a - x)(b - y) + nk_2(a - x)(y - z) \qquad (13)$$

Therefore,

$$k = nk_1 + nk_2 \frac{(y - z)}{(b - y)} \qquad (14)$$

Now, as $n = 1$, Eq. (8) gives

$$z = x - y$$

Putting the value of z in Eq. (14), we get

$$k = k_1 + k_2 \frac{2y - x}{b - y} \qquad (15)$$

By substituting the experimental values of x, y, b, and k in Eq. (15), k_1 and k_2 have been calculated by the method of successive approximations. Table 3 reports the average values of k_1 and k_2 at different temperatures and various concentrations of the catalyst. As is evident from Table 3, the rate of formation of methylene derivatives of 2,5-xylenol is 44 to 46 times more than the rate of formation of monomethylol, 2,5-xylenol.

TABLE 3. Stepwise Rate Constants at Various Concentrations of Acid and Different Temperatures

Temperature ($^\circ$C)	$[HCl] \times 10^3$ (N)	k_1 (L/mol s)	k_2 (L/mol s)
80	40	8.38×10^{-3}	3.83×10^{-1}
	20	3.65×10^{-3}	1.65×10^{-1}
	12	2.09×10^{-3}	9.56×10^{-2}
	8	1.65×10^{-3}	7.73×10^{-2}
75	40	5.37×10^{-3}	2.43×10^{-1}
	20	2.55×10^{-3}	1.16×10^{-1}
	12	1.37×10^{-3}	6.24×10^{-2}
	8	9.45×10^{-4}	4.33×10^{-2}
70	40	3.69×10^{-3}	1.70×10^{-1}
	20	1.73×10^{-3}	7.76×10^{-2}
	12	8.72×10^{-4}	3.97×10^{-2}
	8	5.61×10^{-4}	2.62×10^{-2}
65	40	2.60×10^{-3}	1.16×10^{-1}
	20	1.17×10^{-3}	5.39×10^{-2}
	12	4.42×10^{-4}	2.02×10^{-2}
	8	2.79×10^{-4}	1.28×10^{-2}

As stated earlier, we have made an approximation in calculating the values of the overall rate constant regarding the proportion of 2,5-xylenol and formaldehyde reacted. That this is a good approximation has been confirmed by making a comparison of the values of second-order rate constants obtained by employing Eq. (2) with those of the values of the rate constants as obtained from purely theoretical considerations. The values of the rate constants from theoretical considerations were obtained by substituting the values of (y - z) from Eq. (11) into Eq. (13) and simplifying:

$$k = k_1 + \frac{k_2}{m-1}\left[1 - \left(\frac{b-y}{b}\right)^{m-1}\right] \qquad (16)$$

By making use of the values of k_1 and k_2 (Table 3) and the values of m at different time intervals (Table 4) at 80, 75, 70, and 65°C and at a

TABLE 4. Calculated Values of m at Different Temperatures ([HCl] = 0.040 $\underline{N}$)

Temperature (°C)	Time (s)	[2,5-Xylenol] reacted $\times 10^2$ ($\underline{M}$)	[HCHO] reacted $\times 10^2$ ($\underline{M}$)	m	Average value
80	600	1.75	0.92	46.77	
	840	2.24	1.18	44.37	
					45.72
	1200	2.83	1.45	45.87	
	1680	3.37	1.72	45.86	
75	960	1.87	0.38	45.78	
	1200	2.21	1.17	43.89	
					45.49
	1920	2.92	1.50	44.87	
	2640	3.45	1.76	47.49	
70	1800	2.25	1.15	45.33	
	2700	2.88	1.48	47.00	
					45.97
	3600	3.36	1.72	44.00	
	4500	3.73	1.90	47.97	
65	2400	2.05	1.07	44.22	
	3600	2.70	1.39	45.63	
					44.76
	4800	3.17	1.62	42.75	
	6000	3.49	1.78	46.43	

constant catalyst concentration of 0.04 $\underline{N}$, the values of the overall rate constant k have been calculated (Table 5). These values of k, when compared with the values of k as obtained by Eq. (2), prove that the procedure is satisfactory.

Mechanism

The first step in the acid-catalyzed reaction of 2,5-xylenol and formaldehyde is the addition of protonated formaldehyde to 2,5-xylenol

TABLE 5. Comparison of the Overall Rate Constants ([Acid] = 0.040 $\underline{N}$)

Temperature (°C)	Time (s)	Overall rate constant (L/mol s)	
		From Eq. (2)	From Eq. (16)
80	600	1.63×10^{-2}	1.67×10^{-2}
	840	1.68×10^{-2}	1.72×10^{-2}
	1200	1.67×10^{-2}	1.69×10^{-2}
	1680	1.66×10^{-2}	1.69×10^{-2}
75	960	1.08×10^{-2}	1.08×10^{-2}
	1200	1.10×10^{-2}	1.09×10^{-2}
	1920	1.08×10^{-2}	1.09×10^{-2}
	2640	1.08×10^{-2}	1.06×10^{-2}
70	1800	7.46×10^{-3}	7.52×10^{-3}
	2700	7.42×10^{-3}	7.38×10^{-3}
	3600	7.46×10^{-3}	7.64×10^{-3}
	4500	7.53×10^{-3}	7.34×10^{-3}
65	2400	5.19×10^{-3}	5.28×10^{-3}
	3600	5.25×10^{-3}	5.20×10^{-3}
	4800	5.26×10^{-3}	5.38×10^{-3}
	6000	5.33×10^{-3}	5.15×10^{-3}

to give p- or o-methylol xylenol. The p- or o-methylol derivatives of xylenol produced by acid catalysis cannot be isolated.
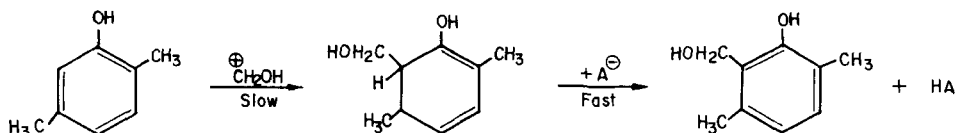
In the presence of H^+ ions, the methylol is present in the form of the carbonium ion:

which then attacks the ortho or para positions of 2,5-xylenol to give the corresponding methylene derivatives.

As is evident from Table 3, in the acid-catalyzed 2,5-xylenol/formaldehyde reaction the rate constants of the addition and condensation reactions are in a ratio of approximately 1:46. Thus the condensation reaction is a rapid follow-up of the addition reaction.

According to suggested mechanism for the formation of monomethylol phenols, the reaction takes place in two steps: (1) the protonation of formaldehyde and (2) the formation of the activated complex. Therefore, the net entropy of activation will be the sum of entropy involved in the protonation and in the formation of the activated complex. The entropy involved in the protonation is always positive. Now, as the activated complex has a more ordered molecular configuration than does the reactant molecules, the entropy involved in the formation of the activated complex will be negative and its value is assumed to remain constant. As is evident from Table 2, the entropy of protonation is numerically less than the entropy for the activated complex up to an acid concentration of 0.012 $\underline{N}$ but becomes more as the catalyst concentration decreases, with the result that the observed entropy of activation becomes positive at 0.008 $\underline{N}$ catalyst concentration.

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