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Kinetics of Alkali-Catalyzed 2,5-Dimethylphenol-Formaldehyde Reaction

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ABSTRACT

A kinetic study of the reaction between 2,5-dimethylphenol (2,5-DMP) and formaldehyde has been carried out at 65, 70, 75, and 80 ± 0.05°C by using sodium hydroxide as the catalyst. The solvent mixture used in the kinetic experiments was 50% (v/v) methanol-water. The various alkali concentrations used were 0.003, 0.006, 0.010, 0.018 and 0.025 N. The reaction was found to obey second-order rate law. The rate of reaction was observed to increase with an increase in the alkali concentration. The effect of changing the reactant concentrations and the nature of the solvent was also studied. The overall rate constant has been resolved into stepwise rate constants. The entropy of activation and Arrhenius parameters for the overall reaction have also been calculated.

INTRODUCTION

Phenols combine with formaldehyde to give both resinous and nonresinous products which are used extensively in the rubber, petroleum, and vegetable oil industries. These products have also been used as intermediates for the manufacture of polyepoxide resins and also in the preparation of emulsifying agents, detergents, and corrosion inhibitors.

Therefore a comprehensive kinetic study of these reactions would no doubt give fuller information regarding the factors controlling the nature and properties of their products.

Extensive studies have been reported [1-17] on the reaction of different phenols with formaldehyde. Most of these studies were concerned mainly with the formation of the final products rather than with the kinetics of the reaction. A thorough review of the literature reveals that not even a single kinetic study has been conducted on the reaction of 2,5-dimethylphenol with formaldehyde.

In this paper we have made a comprehensive kinetic study of the 2,5-dimethylphenol-formaldehyde reaction. The reaction has been studied at 65, 70, 75, and 80 ± 0.05°C and at various sodium hydroxide concentrations. The reactions were studied in 50% (v/v) methanol-water media. The effect of changing molar ratio of the reactants and the nature of the organic solvent has also been studied. The functionality, i. e., the available reactive ortho and para positions of 2,5-dimethylphenol, has been taken into consideration while suggesting the rate equation and interpreting the kinetic data.

EXPERIMENTAL

Materials

2,5-Dimethylphenol used was a BDH (England) product. Formaldehyde, sodium hydroxide, oxalic acid, and isopropanol were BDH products; methanol and dioxane were E. Merck products. Sodium bisulfite was a Thomas Baker product. The chemicals used were either C. P. or A. R. grade.

Measurements

The reactions were carried out in methanol water mixture (1:1, v/v). The flask containing the reaction mixture, fitted with a water condenser, was suspended in a thermostatted bath whose temperature was maintained within ± 0.05°C. Aliquots (20 ml) of the reaction mixture were withdrawn after definite intervals of time and placed in an ice bath to freeze the reaction. Formaldehyde was estimated by the usual sodium bisulfite method.

RESULTS AND DISCUSSION

Effect of Temperature and NaOH Concentration

Results of the kinetic studies carried out at various alkali concentrations and at different temperatures are given in Table 1. The

TABLE 1. Second-Order Rate Constants for Various NaOH Concentrations at Different Temperatures[a]

Temp. (°C)	[NaOH] × 10^4 (N)	Initial [HCHO] (M)	Second-order rate constant (liter/mole-sec)
80	30	0.0550	$5.63(\pm 0.07) \times 10^{-5}$
	60	0.0563	$1.28(\pm 0.01) \times 10^{-4}$
	100	0.0520	$1.85(\pm 0.01) \times 10^{-4}$
	180	0.0622	$3.60(\pm 0.02) \times 10^{-4}$
	250	0.0576	$4.61(\pm 0.01) \times 10^{-4}$
75	30	0.0563	$3.58(\pm 0.01) \times 10^{-5}$
	60	0.0554	$8.61(\pm 0.13) \times 10^{-5}$
	100	0.0532	$1.41(\pm 0.01) \times 10^{-4}$
	180	0.0552	$2.73(\pm 0.01) \times 10^{-4}$
	250	0.0578	$3.63(\pm 0.08) \times 10^{-4}$
70	30	0.0568	$2.75(\pm 0.01) \times 10^{-5}$
	60	0.0558	$6.39(\pm 0.17) \times 10^{-5}$
	100	0.0545	$9.49(\pm 0.22) \times 10^{-5}$
	180	0.0548	$1.97(\pm 0.01) \times 10^{-4}$
	250	0.0585	$2.50(\pm 0.01) \times 10^{-4}$
65	30	0.0550	$1.68(\pm 0.01) \times 10^{-5}$
	60	0.0573	$4.60(\pm 0.02) \times 10^{-5}$
	100	0.0548	$6.80(\pm 0.39) \times 10^{-5}$
	180	0.0548	$1.39(\pm 0.01) \times 10^{-4}$
	250	0.0583	$1.95(\pm 0.02) \times 10^{-4}$

[a] Initial concentration of 2,5-DMP = 0.0500 M; solvent = 50% methanol.

reaction follows a second-order rate law. A linear plot of log $b(na - y)/[na(b - y)]$ versus time [cf. Eq. (3) in the following] supports this view. The plot of log k versus 1/T for the overall reaction was utilized to obtain the values of entropy of activation and Arrhenius parameters (Table 2). It was observed that the rate of reaction increases with an increase in the alkali concentration. This indicates that the phenate ions are the reactive species. It can also be seen from Table 2 that both the energy of activation and entropy of activation decrease with

TABLE 2. Activation Parameters at Various Alkali Concentrations for the Overall Reaction

[NaOH] $\times 10^4$ ($\underline{N}$)	ΔE (kcal/mole)	log A	ΔS (e. u.)
30	18.9	7.44	-26.8
60	16.2	6.15	-32.7
100	15.7	5.97	-33.5
180	14.1	5.19	-36.8
250	13.7	5.16	-37.2

an increase in alkali concentration. The larger values of energy of activation at lower NaOH concentration indicate that the hydroxyl ions play an important role in the reaction.

Effect of Varying Reactant Concentration

The rates of the reactions with the use of NaOH as the catalyst have been measured at different mole ratios of 2,5-dimethylphenol and HCHO. The second-order rate law is observed in the mole ratio range of 0.44:1, 0.94:1, and 1.74:1 (2,5-DMP:formaldehyde) (Table 3). Though the rate of reaction increases with an increase in 2,5-DMP: formaldehyde mole ratio, it did not show a marked variation.

Effect of Solvent

The 2,5-DMP-formaldehyde reaction at 75 ±0.05°C and at a constant NaOH concentration of 0.01 $\underline{N}$ was studied for the solvents methanol, ethanol, isopropanol, and dioxane. An organic solvent-water mixture (1:1, v/v) was used in each case. It was observed that the reaction rate depends much upon the nature of the solvent used. The reactions were found to obey a second-order rate law. Under a given set of conditions the second-order rate constant was maximal when dioxane was used as solvent and minimum in the case of methanol. In fact the rate constant could be arranged in the following order: dioxane > isopropanol > ethanol > methanol (Table 4).

Calculation of Stepwise Rate Constant

In an alkaline medium and at low concentration of substituted phenols and formaldehyde, mono-, di-, and trimethylolphenols are

TABLE 3. Second-Order Rate Constants for Varying Reactant Concentrations[a]

Initial [2,5-DMP] (M)	Initial [HCHO] (M)	Second-order rate constant k × 10^4 (liter/mole-sec)
0.0250	0.0571	1.33(± 0.01)
0.0500	0.0532	1.41(± 0.01)
0.1000	0.0576	1.51(± 0.01)

[a] Temp = 75 ± 0.05°C; [NaOH] × 10^4 N = 100; Solvent = 50% methanol.

TABLE 4. Second-Order Rate Constants for Different Organic Solvent-Water Mixtures (1:1, v/v)[a]

Organic solvent	Initial [2,5-DMP] (M)	Initial [HCHO] (M)	Second-order rate constant k × 10^4 (liter/mole-sec)
Methanol	0.0500	0.0532	1.41(± 0.01)
Ethanol	0.0500	0.0588	4.01(± 0.05)
Isopropanol	0.0500	0.0568	6.70(± 0.13)
Dioxane	0.0500	0.0563	9.30(± 0.07)

[a] Temp = 75 ± 0.05°C; [NaOH] × 10^4 N = 100.

formed. The reaction between 2,5-dimethylphenol and formaldehyde proceeds in alkaline medium as shown in Eqs. (1) and (2),

$$(CH_3)_2C_6H_3OH + CH_2O \xrightarrow{k_1} (CH_3)_2C_6H_2(OH)CH_2OH \tag{1}$$

$$(CH_3)_2C_6H_2(OH){\cdot}CH_2OH + CH_2O \xrightarrow{k_2} (CH_3)_2C_6H(OH)(CH_2OH)_2 \tag{2}$$

where k_1 and k_2 are the stepwise rate constants for the formation of two monomethylol xylenols and dimethylol xylenol. The overal rate expression is given by Eq. (3):

$$k = \frac{2.303}{t(na - b)} \log \frac{b}{na} \frac{(na - y)}{(b - y)} \tag{3}$$

where k is the overall rate constant, a is the initial concentration of 2,5-dimethylphenol, b is the initial concentration of formaldehyde, y is the amount of formaldehyde reacted at different time intervals, and n is the functionality of 2,5-DMP (= 2).

The rate at which 2,5-DMP and formaldehyde disappear is given by Eqs. (4) and (5), respectively,

$$dx/dt = nk(a - x)(b - y) \tag{4}$$

$$dy/dt = k(na - y)(b - y) \tag{5}$$

where k is the overall rate constant and x represents the amount of 2,5-DMP disappeared at time t. Dividing Eq. (5) by Eq. (4) and integrating yields

$$y = na - n\, a^{(n-1)/n}\, (a - x)^{1/n} \tag{6}$$

Also

$$dx/dt = k_1(a - x)(b - y) \tag{7}$$

and

$$dc/dt = k_2(x - c)(b - y) \tag{8}$$

where c is the amount of monomethylolxylenol which has disappeared at time t. Also,

$$dy/dt = (dx/dt) + (dc/dt)$$

or

$$dy/dt = k_1(a - x)(b - y) + k_2(x - c)(b - y) \tag{9}$$

Dividing Eq. (8) by Eq. (7) yields

$$(dc/dx) + [u/(a - x)]c = [u/(a - x)]x \tag{10}$$

where $u = k_2/k_1$. On integrating and putting the limits x = 0, C = 0 at t = 0, we get

$$c = [1/(1 - u)][a - xu - a^{1-u}(a - x)^u] \tag{11}$$

Finally dividing Eq. (9) by Eq. (7) yields

$$dy/dx = 1 + [u/(a - x)]x - [uc/(a-x)] \tag{12}$$

Integrating and putting the limits x = 0, and y = 0 at t = 0 yields

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

From Eqs. (11) and (13) it is possible to calculate the amounts of all the species present at any stage of the reaction. From Eqs. (6) and (13) we get

$$na - na^{(n-1)/n}(a - x)^{1/n} = a + x + \frac{u(a - x)}{1 - u} - \frac{a^{1-u}(a - x)^u}{1 - u} \tag{14}$$

By substituting the various values of 2,5-DMP reacted at different time intervals and using the method of successive approximations, the value of u works out to be 0.35 at each of the four temperatures at which the investigations were conducted; hence it should be valid in the temperature range 65-80° C, i. e.,

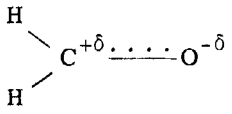
$$u = k_2/k_1 = 0.35$$

From Eqs. (4) and (7), it is found that $k_1 = nk$. Thus by determining the value of overall rate constant and from a knowledge of the functionality of 2,5-dimethylphenol (=2), k_1 can be calculated. The value of k_2 can be calculated from expression $u = k_2/k_1$ (Table 5). By making use of Eqs. (6), (11), and (14) we can calculate the amounts of monomethylol 2,5-xylenols and dimethylol 2,5-xylenol present. Table 6 gives the concentrations of various methylol xylenols at different time intervals and at 65, 70, 75, and 80 ±0.05° C and at a sodium hydroxide concentration of 0.018 N. By using Eq. (9), the different values of x, y, and c at different time intervals and the calculated values of u, k_1, and k_2, the overall rate constant (k) were theoretically calculated. These theoretically calculated values of k at different temperatures and at 0.018 N NaOH concentration are given in Table 6. As is evident, the theoretically calculated values are in good agreement with the experimentally determined values of k.

Due to inductive and mesomeric effects the electron density is greater at the ortho and para positions in the 2,5-DMP nucleus than at the meta position. The molecule

TABLE 5. Stepwise Rate Constants at Various Alkali Concentrations and at Different Temperatures

Temp (°C)	[NaOH] $\times 10^4$ ($\underline{N}$)	Stepwise rate constants (liter/mole-sec) k_1	k_2
80	250	9.22×10^{-4}	3.23×10^{-4}
	180	7.20×10^{-4}	2.52×10^{-4}
	100	3.70×10^{-4}	1.30×10^{-4}
	60	2.56×10^{-4}	8.96×10^{-5}
	30	1.13×10^{-4}	3.94×10^{-5}
75	250	7.26×10^{-4}	2.54×10^{-4}
	180	5.46×10^{-4}	1.91×10^{-4}
	100	2.82×10^{-4}	9.87×10^{-5}
	60	1.72×10^{-4}	6.03×10^{-5}
	30	7.16×10^{-5}	2.51×10^{-5}
70	250	5.00×10^{-4}	1.75×10^{-4}
	180	3.94×10^{-4}	1.38×10^{-4}
	100	1.90×10^{-4}	6.64×10^{-5}
	60	1.28×10^{-4}	4.47×10^{-5}
	30	5.50×10^{-5}	1.92×10^{-5}
65	250	3.90×10^{-4}	1.37×10^{-4}
	180	2.78×10^{-4}	9.73×10^{-5}
	100	1.36×10^{-4}	4.76×10^{-5}
	60	9.20×10^{-5}	3.22×10^{-5}
	30	3.36×10^{-5}	1.18×10^{-5}

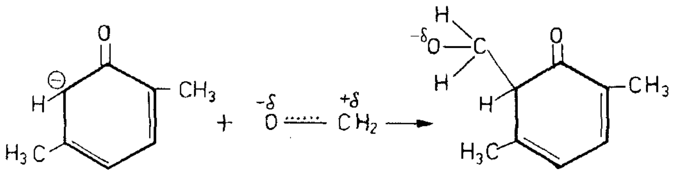


attacks at the ortho or para positions of 2,5-dimethylphenate ion to form activated complexes (I and II) which rearrange to give stable benzenoid structures (III and IV). These then interact with a water molecule to give monomethylol 2,5-dimethylphenols, and the regenerated

TABLE 6. Concentrations of Various Methylol Xylenols at Different Time Intervals and Temperatures[a]

Temp (°C)	Time (sec)	[2,5-DMP] reacted × 10^3 ($\underline{M}$)	[HCHO] reacted × 10^3 ($\underline{M}$)	[Monomethylol 2,5-xylenols] present × 10^3 ($\underline{M}$)	[Dimethylol 2,5-xylenol] present × 10^4 ($\underline{M}$)	k × 10^4 (liter/mole-sec)	
						Exptl	Calcd
80 ±0.05	2100	4.11	4.20	4.04	0.70	3.42	3.38
	3900	7.87	8.20	7.63	2.44	3.78	3.69
	5700	10.39	11.00	9.96	4.33	3.62	3.48
	7500	12.50	13.40	11.86	6.43	3.56	3.40
75 ±0.05	2400	3.33	3.40	3.28	0.48	2.67	2.65
	4200	6.75	7.00	6.57	1.79	2.78	2.72
	6000	7.67	8.00	7.44	2.33	2.74	2.68
	8400	10.21	10.80	9.79	4.19	2.70	2.62
70 ±0.05	2400	2.56	2.60	2.53	0.29	2.06	2.04
	4500	4.50	4.60	4.42	0.80	1.99	1.96
	6300	6.01	6.20	5.87	1.40	1.97	1.94
	8100	7.13	7.40	6.93	2.00	1.86	1.83
65 ±0.05	2400	1.79	1.80	1.77	0.19	1.40	1.39
	4800	3.44	3.50	3.39	0.49	1.40	1.39
	7200	5.07	5.20	4.92	1.46	1.42	1.40
	9600	6.19	6.40	6.04	1.52	1.34	1.32

[a] [NaOH] × 10^4 $\underline{N}$ = 180.



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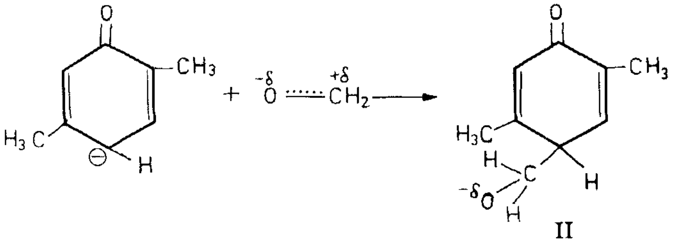

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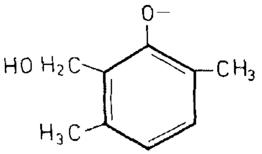

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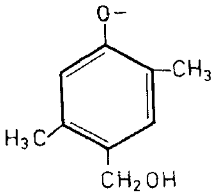

IV

OH^- ions continue to catalyze the reaction. The monomethylol-2,5-dimethylphenols then react with formaldehyde to give dimethylol-2,5-dimethylphenol through a similar mechanism. According to the suggested mechanism for the formation of monomethylols and dimethylol-2,5-dimethylphenol, the reaction takes place in two steps: (1) formation of phenate ion and (2) formation of an activated complex. Therefore, the net entropy of activation will be the sum of the entropy involved in the formation of phenate ion and the entropy involved in the formation of activated complex. The entropy of activation involved in the formation of activated complex would be negative because of the formation of a more ordered complex, and its value is assumed to remain constant. Entropy of protonation is invariably positive, since protonation is required only at the fixed site. As formation of phenate ion is opposite of protonation, the entropy involved in the formation of phenate ion would be negative and would become more and more negative with an increase in pH because in highly alkaline solutions the phenol molecule produces a more stable and ordered phenate ion. Therefore the net result would be that the entropy of activation would decrease with an increase in alkali concentration (cf. Table 2).

It is a well established fact that formation of monomethyl phenols would be the first stage, both in alkaline and acid media. In an alkaline medium, the rate constant of formation of methylol derivatives is much higher than that of methylene derivatives. Therefore, in the alkaline medium, low molecular weight polyfunctional phenolic alcohols would be formed. Xylenols also readily form monoalcohols with formaldehyde, but these are slow to react with full quantity of formaldehyde as determined theoretically by the number of free ortho and para positions available. In the present case, we had observed that the rate constant of formation of dimethylol 2,5-xylenol is 2.85 times lower than the rate of formation of monomethylol 2,5-xylenols. This observation is in conformity with the theoretical aspects, as the introduction of $-CH_2OH$ group in the phenolic nucleus decreases the rate of further uptake of formaldehyde and also, because of steric factors, the rate of formation of dimethylol 2,5-dimethylphenol would be lower than the rate of formation of monomethylol 2,5-dimethylphenol.

As mentioned earlier, the reaction between 2,5-DMP and formaldehyde in this investigation is a bimolecular reaction. Also the rate of reaction depends upon concentration of phenate ion, which ultimately depends upon alkali concentration. It can be seen that at any given temperature the overall rate of reaction increases with increase in concentration of the catalyst. The larger values of energy of activation at lower alkali concentrations indicate that the hydroxyl ions play an important role in this reaction.

Furthermore the experimental concentration of reacted methylol derivatives is difficult to determine, but the functional relations derived from the various rate equations make it possible to have a complete description of our system in terms of the initial concentrations of 2,5-dimethylphenol and formaldehyde and their reacted amounts. The correctness of this procedure for the 2,5-dimethylphenol-formaldehyde system is well established by the agreement of the experimental and calculated results (Table 6).

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