

Chemistry

**ALKALI CATALYSED 2, 3-XYLENOL FORMALDEHYDE REACTION—
ITS KINETICS AND MECHANISM**

H. C. MALHOTRA *and* V. P. TYAGI

Department of Chemistry, University of Delhi, Delhi-110 007

(Received 10 July 1979)

Kinetics of the reaction between 2,3-xyleneol and formaldehyde was studied at 65°, 70°, 75° and 80° ± 0.05 °C. The solvent mixture used in the kinetic experiments was 1 : 1 (v/v) methanol-water mixture. The different NaOH concentrations used as catalyst were 0.006, 0.010, 0.018 and 0.025N. The reaction was found to follow second order rate law. The rate of reaction was found to increase with an increase in catalyst concentration. The effect of changing the molar ratios of the reactants and the nature of the solvent was also studied. The different activation parameters for the overall reaction have also been calculated. The overall rate constant has been resolved into stepwise rate constants.

INTRODUCTION

PHENOLS combine with formaldehyde to give both resinous and non-resinous products which find extensive use in rubber, petroleum and vegetable oil industry. These products have also been used as intermediates in 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 important information regarding the factors controlling the nature and properties of their products.

Though the reactions between different phenols and formaldehyde have been studied extensively (Jones, 1946; Debing *et al.*, 1952; Dejong & Dejong, 1953; Freeman & Lewis, 1954; Toshiro & Tadanao, 1955, 1957; Shoji & Hikuru, 1959; Yeddanapalli & Francis, 1962; Hikuru, 1963; Zavitsas, 1968; Malhotra & Avinash, 1975; Malhotra & Gupta, 1978; Sprung, 1941; von Euler & Dekispectzy, 1941; Finn & Lewis, 1950; Auwers, 1907; Roger Amouroux & Lyon, 1967; Ryabukhin, 1969 and Mirosława Fillipska & Alina Kalinowaka-Kavalis, 1965), a thorough review of the literature reveals that not even a single kinetic study has been done on the reaction of 2, 3-xyleneol with formaldehyde.

In the present paper, the authors have made a comprehensive kinetic study of 2,3-xyleneol formaldehyde reaction. All the reactions were studied in 50 per cent (v/v) methanol-water media. The effect of changing molar ratios 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, 3-xyleneol, has been taken into consideration while suggesting the rate equations and interpreting the kinetic data.

EXPERIMENTAL

Materials and Measurements

(a) *Materials* : 2, 3-xyleneol used was a BDH (England) product. Formaldehyde, sodium hydroxide, isopropanol were BDH products and methanol, dio-

xane were E. Merck products. All the chemicals used were either of C. P. or A. R. grade.

An immersion type thermostat (German, model NBE) was employed for the rate studies.

(b) *Measurements* : The reactions were carried out in methanol-water mixture (1 : 1, v/v). 2, 3-xyleneol, formaldehyde and sodium hydroxide solutions, pre-heated to the desired experimental temperatures, were put in a round bottom flask which was fitted with a water condenser. The flask was suspended in the thermostat bath and aliquots of the reaction mixture were withdrawn after different intervals of time, placed in an ice-bath to freeze the reaction and analysed for the reactant concentrations.

RESULTS AND DISCUSSION

(1) *Effect of Temperature and NaOH Concentration* : Results of the kinetic studies carried out at different temperatures and various alkali concentrations are reported in Table I. The reaction between 2, 3-xyleneol and formaldehyde obeys a second order law. The plot of $\log k$ vs. $1/T$ for the overall reaction was utilised to obtain the values of entropy of activation and Arrhenius parameters (Table II). Both the energy of activation and entropy of activation decrease with 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.

TABLE I

Second order rate constants for various NaOH concentrations at different temperatures

Initial [2,3-xyleneol] = 0.0500M; Solvent = Methanol-Water (1 : 1, v/v)

Temp. °C	[NaOH] × 10 ⁴ N	[HCHO] (M)	Second Order Rate Constant (Litre mole ⁻¹ sec ⁻¹)
80	250	0.0548	$(3.91 \pm 0.02) \times 10^{-4}$
	180	0.0601	$(2.91 \pm 0.01) \times 10^{-4}$
	100	0.0540	$(1.62 \pm 0.01) \times 10^{-4}$
	60	0.0532	$(1.06 \pm 0.01) \times 10^{-4}$
75	250	0.0547	$(3.04 \pm 0.02) \times 10^{-4}$
	180	0.0566	$(2.19 \pm 0.01) \times 10^{-4}$
	100	0.0530	$(1.16 \pm 0.01) \times 10^{-4}$
	60	0.0504	$(6.30 \pm 0.07) \times 10^{-5}$
70	250	0.0547	$(2.05 \pm 0.01) \times 10^{-4}$
	180	0.0556	$(1.48 \pm 0.01) \times 10^{-4}$
	100	0.0528	$(7.55 \pm 0.07) \times 10^{-5}$
	60	0.0507	$(4.15 \pm 0.03) \times 10^{-5}$
65	250	0.0542	$(1.53 \pm 0.01) \times 10^{-4}$
	180	0.0554	$(1.07 \pm 0.01) \times 10^{-4}$
	100	0.0534	$(5.00 \pm 0.02) \times 10^{-5}$
	60	0.0509	$(2.64 \pm 0.01) \times 10^{-5}$

Also the rate of reaction depends upon the concentration of phenate ion which is directly proportional to the alkali concentration. It can be seen that at any given temperature the overall rate of reaction increases with increase in the concentration of NaOH catalyst.

2. *Effect of Variation of the Reactant Concentrations* : The rates of reactions have been measured at different mole ratios of 2,3-xylenol and HCHO using 0.010 N of NaOH and at a temperature of 75 °C. The reaction obeys second order rate law in the mole ratio range of 0.47 : 1, 0.94 : 1 and 1.85 : 1 (2, 3-xylenol : HCHO). Though the rate of reaction increases with an increase in 2,3-xylenol-HCHO ratio, it did not show a marked variation.

3. *Effect of Solvent* : The reaction of 2, 3-xylenol and formaldehyde at 75 °C and with a constant NaOH concentration of 0.010 N was studied for the following solvents : methanol, ethanol, isopropanol and dioxane. An organic solvent-water mixture (1 : 1, v/v) was used in each case. Table IV clearly shows that the rate of reaction depends much upon the nature of the organic solvent used. Under a given set of experimental conditions, the values of the second-order rate constant were found to be maximum when dioxane was used as a solvent. In fact the rate constants could be arranged in the following manner : Dioxane > Isopropanol > Ethanol > Methanol (Table IV).

4. *Calculation of Step Rate Constants* : In alkaline medium and at low concentrations of substituted phenols and formaldehyde, mono, di and trimethylol

TABLE II

Activation parameters at various NaOH concentrations for the overall reaction

[NaOH] × 10 ⁴ N	ΔE (K. cal. mole ⁻¹)	log A	ΔS^\ddagger (e.u.)
250	14.0	5.26	— 36.7
180	14.9	5.66	— 34.9
100	17.4	7.00	— 28.8
60	20.6	8.74	— 20.8

TABLE III

Second order rate constants for varying reactant concentrations

Temp. = 75 ± 0.05 °C; [NaOH] × 10⁴N = 100; Solvent = Methanol-Water (1 : 1, v/v)

Initial [2,3-xylenol] (M)	Initial [HCHO] (M)	Second order rate constant (litre mole ⁻¹ sec ⁻¹)
0.0250	0.0528	(1.05 ± 0.01) × 10 ⁻⁴
0.0500	0.0530	(1.16 ± 0.01) × 10 ⁻⁴
0.1000	0.0540	(1.21 ± 0.01) × 10 ⁻⁴

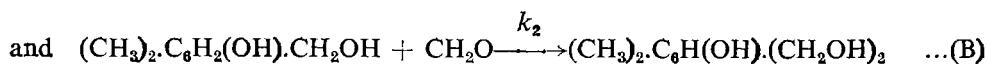
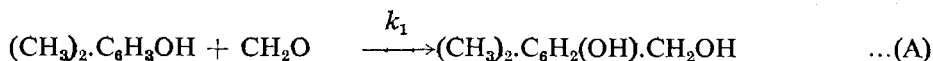
TABLE IV

Second order rate constants for different organic solvent-water mixtures (1 : 1, v/v)

Temp. = 75 ± 0.05 °C; [NaOH] $\times 10^4$ N = 100

Organic Solvent	Initial [2, 3-xylene] (M)	Initial [HCHO] (M)	Second order rate constant (litre mole ⁻¹ sec ⁻¹)
Methanol	0.0500	0.0530	$(1.16 \pm 0.01) \times 10^{-4}$
Ethanol	0.0500	0.0504	$(2.83 \pm 0.01) \times 10^{-4}$
Isopropanol	0.0500	0.0500	$(5.68 \pm 0.02) \times 10^{-4}$
Dioxane	0.0500	0.0507	$(7.83 \pm 0.01) \times 10^{-4}$

phenol are formed. The reaction between 2, 3-xylene and formaldehyde proceeds in alkaline medium as follows:



where k_1 and k_2 are the stepwise rate constants for the formation of two mono-methylol 2,3-xylenols and a dimethylol 2,3-xylene. The overall rate expression is given by eqn. (1)

$$k = \frac{2.303}{t(na-b)} \log \frac{b}{na} \times \frac{(na-y)}{(b-y)}, \quad \dots(1)$$

where k = overall rate constant, a = initial concentration of 2, 3-xylene, b = initial concentration of HCHO, y = amount of formaldehyde reacted at different time intervals and n = functionality of 2,3-xylene (= 2)

The overall rate at which 2,3-xylene and HCHO disappear is given by:

$$+ \frac{dx}{dt} = nk(a-x)(b-y) \quad \dots(2)$$

where x = amount of 2, 3-xylene disappeared at time t .

$$\text{and } + \frac{dy}{dt} = k(na-y)(b-y) \quad \dots(3)$$

where k is the overall rate constant.

Dividing eqn. (3) and eqn. (2) and integrating —

$$y = na - n.a.(n-1)/n. (a-x)^{1/n} \quad \dots(4)$$

The rate equations for the formation of mono- and dimethylol 2, 3-xylenols are—

$$\frac{dx}{dt} = k_1(a-x)(b-y) \quad \dots(5)$$

$$\text{and } \frac{dc}{dt} = k_2(x-c)(b-y) \quad \dots(6)$$

where c = amount of monomethylol 2, 3-xylenols disappeared. Also

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

$$\frac{dy}{dt} = k_1 (a-x) (b-y) + k_2 (x-c) (b-y) \quad \dots(7)$$

From eqn. (6) and (5), we get

$$c = \frac{1}{1-u} [a-xu - a^{1-u} (a-x)^u], \quad \dots(8)$$

where $u = k_2/k_1$

and from eqn. (7) and (5), we get :

$$y = a + x + \frac{u(a-x)}{1-u} - \frac{a^{1-u}}{1-u} (a-x)^u \quad \dots(9)$$

Eqn. (4) and (11) result in :

$$na - n.a^{(n-1)/n} (a-x)^{1/n} = a + x + \frac{u}{1-u} (a-x) - \frac{a^{1-u}}{1-u} (a-x)^u \quad \dots(10)$$

By substituting the values of the different amounts of 2,3-xylenol reacted at different time intervals in eqn. (10) and using the method of successive approximations,

TABLE V

Stepwise rate constants at various NaOH concentrations and at different temperatures

Temp. °C	[NaOH] × 10 ⁴ N	Stepwise rate constants	
		(litre mole ⁻¹ sec ⁻¹)	
		k_1	k_2
80	250	7.82×10^{-4}	2.27×10^{-4}
	180	5.82×10^{-4}	1.69×10^{-4}
	100	3.24×10^{-4}	9.40×10^{-5}
	60	2.12×10^{-4}	6.15×10^{-5}
75	250	6.08×10^{-4}	1.76×10^{-4}
	180	4.38×10^{-4}	1.27×10^{-4}
	100	2.32×10^{-4}	6.73×10^{-5}
	60	1.26×10^{-4}	3.65×10^{-5}
70	250	4.10×10^{-4}	1.19×10^{-4}
	180	2.96×10^{-4}	8.58×10^{-5}
	100	1.51×10^{-4}	4.38×10^{-5}
	60	8.30×10^{-5}	2.41×10^{-5}
65	250	3.06×10^{-4}	8.87×10^{-5}
	180	2.14×10^{-4}	6.21×10^{-5}
	100	1.00×10^{-4}	2.90×10^{-5}
	60	5.28 ± 10^{-5}	1.53×10^{-5}

the value of 'u' works out to be 0.29 at each of the four temperatures at which the kinetic studies were made. Hence this value of 'u' should be valid in the temperature range 65–80 °C.

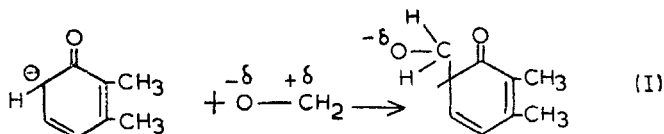
From eqns. (2) and (5) $k_1 = nk$.

Thus determining the value of the overall rate constant and knowing the functionality of 2,3-xylenol, k_1 can be calculated. The expression $u = k_2/k_1$ gives the value of k_2 (Table V). With the help of eqns. (4), (8) and (10), we can calculate the amounts of monomethylol 2,3-xylenols and dimethylol 2,3-xylenol present. Concentrations of various methylol-xylenols at different time intervals and temperatures and at a NaOH concentration of 0.018N are reported in Table VI. By making use of eqns. (3) and (7), the different values of x , y , and c and the calculated values of u , k_1 and k_2 , the overall rate constants 'k' were theoretically calculated (Table VI). As is evident (Table VI), the theoretically calculated values of k are in good agreement with the experimentally determined values. Ryabukhin (1969) used a similar method for studying the phenol-formaldehyde reaction.

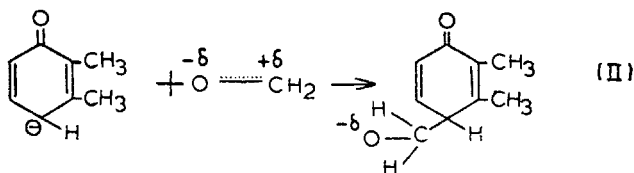
TABLE VI
Concentrations of various methylol xylenols at different time intervals and temperatures
[NaOH] $\times 10^4$ N = 180

Time (Sec)	[2,3-xylenol] reacted (M $\times 10^3$)	[HCHO] reacted (M $\times 10^3$)	[Monomethylol 2,3-xylenol] present (M $\times 10^3$)	[Dimethylol 2,3-xylenol] present (M $\times 10^4$)	$k_{\text{expt.}}$ (litre mole ⁻¹ sec ⁻¹) $\times 10^4$	$k_{\text{calc.}}$
<i>Temp. 65 + 0.05 °C</i>						
3900	2.19	2.20	2.17	0.20	1.11	1.10
7800	4.40	4.50	4.35	0.65	1.11	1.09
11700	5.82	6.00	5.74	0.78	1.01	0.98
15600	7.67	8.00	7.48	1.93	1.04	1.01
<i>Temp. 70 + 0.05 °C</i>						
3300	2.27	2.30	2.25	0.21	1.30	1.29
6570	4.96	5.10	4.88	0.82	1.51	1.48
9900	7.21	7.50	7.04	1.75	1.53	1.48
13200	8.96	9.40	8.69	2.66	1.48	1.42
<i>Temp. 75 + 0.05 °C</i>						
2700	3.24	3.30	3.20	0.37	2.26	2.23
5400	5.82	6.00	5.71	1.10	2.13	2.08
8100	8.41	8.80	8.18	2.32	2.19	2.11
10800	10.57	11.20	10.20	3.75	2.17	2.07
<i>Temp. 80 + 0.05 °C</i>						
2100	3.53	3.60	3.49	0.42	3.02	2.85
4200	6.47	6.70	6.33	1.37	2.94	2.86
6300	8.87	9.30	8.61	2.61	2.80	2.69
8400	11.36	12.10	10.92	4.37	2.86	2.72

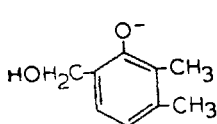
(5) *Mechanism* : Due to inductive and mesomeric effects the electron density is greater at the ortho and para positions in the 2, 3-xyleneol nucleus than at the



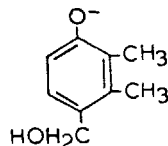
meta position. The $\text{H}_2\text{C}^{+\delta}\dots\text{O}^{-\delta}$ molecule attacks at the ortho or para positions of 2, 3-xyleneolate ion to form activated complex (I) and (II) which rearranges to give



stable benzenoid structures III & IV. These then interact with a water molecule to give monomethylol 2, 3-xyleneols and the regenerated OH^- ions continue to



(III)



(IV)

catalyse the reaction. The monomethylols then react with formaldehyde to give dimethylol 2,3-xyleneol through a similar mechanism.

According to the suggested mechanism for the formation of monomethylols and dimethylol 2, 3-xyleneols, the reaction takes place in two steps—(i) the formation of xyleneolate ion and (ii) the formation of an activated complex. Therefore, net entropy of activation will be the sum of the entropy involved in the formation of xyleneolate ion and the entropy involved in the formation of activated complex. The entropy involved in the formation of xyleneolate ion will always be negative and this would become more and more negative with an increase in alkali concentration because in highly alkaline solutions xyleneol molecule produces a more stable and ordered xyleneolate ion. 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 would be negative, and its value is assumed to remain constant. Therefore, the net result would be that the entropy of activation would decrease with an increase in alkali concentration (Table II).

It is a well-established fact that in phenol-formaldehyde reaction the formation of monomethylol phenols would be the first stage both in alkaline and acid media.

In alkaline medium, the rate constant for the formation of methylol derivative is much higher than that of methylene derivatives. Therefore, in alkaline medium low molecular weight polyfunctional phenolic alcohols would be formed. Xylenols (Bamberger, 1903; and Megson & Drummond, 1930) 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 study, the authors had observed that the rate constant for the formation of dimethylol 2, 3-xylenol is 3.57 times lower than the rate of formation of monomethylol 2, 3-xylenols. This observation is in conformity with the theoretical aspects, as the introduction of $-\text{CH}_2\text{OH}$ 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, 3-xylenol would be much lower as compared to the rate of formation of monomethylol 2, 3-xylenol.

Furthermore, the experimental concentration of reacted methylol derivatives is rather difficult to be estimated but the functional relations derived from the various rate equations make it possible to have a complete analysis of our system in terms of the initial concentrations of 2, 3-xylenol and formaldehyde and their reacted amounts. The correctness of this procedure for 2, 3-xylenol formaldehyde reaction has been corroborated by an excellent agreement of the experimental and calculated results (Table VI).

REFERENCES

- Amouroux, R., and Lyon, F. S. (1967). Comparison of the reactivity of some phenols *vis-a-vis* the formaldehyde in alkaline medium. *C.r. Acad. Sci., Paris*, **265**(6), 396.
- Auwers, K. (1907). Lederer and Manasse's synthesis of phenol alcohols. *Ber.*, **40**, 2524.
- Bamberger, E. (1903). Synthese des 1, 3-Dimethyl-2-oxy-5 Benzyl alcohols. *Ber.*, **36**, 2036.
- Debing, L. M., Murry, G. E. (1952). Kinetics of alkali catalysed phenol-formaldehyde reaction. *Ind. Engng. Chem.*, **44**, 356.
- DeJong, J. I., and De Jong, J. (1953). Kinetics of the hydroxymethylation of phenols in dilute aqueous solution. *Recl. Trav. Chem.*, **72**, 497.
- Euler, H. von, and Dekispectzy, S. V. (1941). Formation of phenol-formaldehyde resins. *Z. physik. Chem.*, A **189**, 109.
- Freeman, J. H., and Lewis, C. W. (1954). Alkaline catalyzed reaction of formaldehyde & methylols of phenol. *J. Am. chem. Soc.*, **76**, 2080.
- Finn, S. R., and Lewis, G. J. (1950). The methylol compounds of 3, 5-dimethylphenol. *J. Soc. Chem. Ind.*, **69**, 129.
- Jones, T. T. (1946). Some preliminary investigations of phenol-formaldehyde reaction. *J. Soc. Chem. Ind.*, **65**, 264.
- Megson, N. J. L., and Drummond, A. A. (1930). Formaldehyde condensations with phenol and its homologs. *J. Soc. Chem. Ind.*, **49**, 251T.
- Malhotra, H. C., and Avinash (1975). Kinetics of alkali catalyzed phenol-formaldehyde reaction. *Indian J. Chem.*, **13**, 1159.
- Malhotra, H. C., and Gupta, V. K. (1978). Kinetics of alkali catalyzed m-cresol formaldehyde reaction. *J. appl. Polym. Sci.*, **22**, 343.
- Miroslawa, F., and Kalinowaka-Kavalis, A. (1965). Polarographic study of the xylenol-formaldehyde condensation. *Chem. Anal.*, **10**(5), 989.
- Ryabukhin, A. G. (1969). Kinetics of reaction of phenol with formaldehyde in difficult media. *Vysokomol. Soedin*, **A11**(11), 2562.
- Sprung, M. M. (1941). Reactivity of phenols towards paraformaldehyde. *J. Am. chem. Soc.*, **63**, 334.

- Shoji, S., and Horiuchi, H. (1959). Reactivity ratio of the ortho positions in the phenolic nucleus under basic catalysis. *Kogyo Kagaku Zasshi*, **62**, 1921.
- Toshiro Manami and Tadanao Ando (1956). Kinetic study of reactions of formaldehyde with phenol and phenol alcohols. *Kogyo Kagaku Zasshi*, **59**, 668.
- Toshiro Minami and Tadanao, A. (1957). Initial reaction of p-substituted phenols with formaldehyde. *Kogyo Kagaku Zasshi*, **62**, 1921.
- Yeddanapalli, L. M., and Josheph, J. Francis (1962). Kinetics and mechanism of alkali catalyzed condensation of o- and p-methylol phenols by themselves and with phenol. *Makromol. Chem.*, **55**, 74.
- Zavitsas, A. A. (1968). Base catalyzed hydroxymethylation of phenol by aqueous formaldehyde. *J. Polym. Sci.*, **6**, 2541.