Alkali Catalyzed Phenol Formaldehyde Reaction — Part I. Formation of Mono-Methylol Phenols

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SUMMARY:

In the sodium hydroxide-catalyzed phenol-formaldehyde reaction, it has now been possible to isolate the first two parallel reactions leading to the formation of o- and pmethylol phenols and to study, by means of quantitative ascending paper chromatography, their kinetics and energetics. The reactions are kinetically of second order, one with respect to phenate ion and one in formaldehyde, but at excess phenol concentration and a given catalyst concentration, they depend only on formaldehyde (concentration). The first order rate constants for production of o- and p-methylol phenols, at 80 °C., are 2.68 and 2.84 $\cdot 10^{-5}$ sec⁻¹ respectively, with about the same energy of activation of 19.77 kcal/mole. Within the $p_{\rm H}$ range of 7–9 studied, the reaction rate is proportional to the alkali concentration, so that the first order rate constants can readily be converted into the true second order constants by means of the relationship, $k_2 = k_1/\text{cat.conc}$. The results indicate that the para position in phenol is twice as reactive in regard to the addition of formaldehyde as the ortho position. A reaction mechanism is suggested to account for the observed results and for the gradual increase of the rate constants with the relative excess concentration of phenol.

ZUSAMMENFASSUNG:

Bei der mit Natriumhydroxyd katalysierten Phenol-Formaldehyd-Reaktion war es möglich, die ersten zwei Parallelreaktionen, die zur Bildung von o- und p-Methylolphenol führen, zu isolieren und mittels quantitativer aufsteigender Papierchromatographie ihre Kinetik und Energetik zu untersuchen. Die Reaktionen sind kinetisch von 2. Ordnung, abhängig von der Phenolat-Ionen- und der Formaldehyd-Konzentration. Bei überschüssigem Phenol und bei gegebener Katalysator-Konzentration sind die Reaktionen nur von der Formaldehyd-Konzentration abhängig. Die Reaktionsgeschwindigkeitskonstanten 1. Ordnung für die Bildung von o- und p-Methylolphenol bei 80°C betragen 2,69 bzw. 2,84 · 10⁻⁵ sec⁻¹ und haben ungefähr die gleiche Aktivierungsenergie von 19,77 kcal/Mol.

Innerhalb des untersuchten Bereichs von p_H 7–9 ist die Reaktionsgeschwindigkeit der Alkali-Konzentration proportional, so daß die Geschwindigkeitskonstanten 1. Ordnung mit Hilfe der Beziehung $k_2 = k_1/K$ atal.konz. in die wahren Konstanten 2. Ordnung überführt werden können. Die Resultate zeigen, daß bezüglich der Anlagerung von Formaldehyd die para-Stellung des Phenols doppelt so reaktionsfähig ist wie die ortho-Stellung.

Es wird ein Reaktionsmechanismus vorgeschlagen, der den gefundenen Ergebnissen und dem allmählichen Anstieg der Geschwindigkeitskonstanten mit dem entsprechenden Phenolüberschuß gerecht wird.

Introduction

The kinetic study of the alkali-catalyzed phenol-formaldehyde reaction had to depend, prior to FREEMAN's¹) paper chromatographic analysis of the reaction products, almost exclusively on the volumetric estimation of formaldehyde and appears to have led to rather divergent results. Thus JONES²) reported the reaction between phenol and formaldehyde, each at 5 M, at a p_{H} 8.5 and 40 °C. to be kinetically of first order up to 45 % consumption of formaldehyde. But GOLDBLUM³) suggested that JONE's results could easily be made to fit into a second order rate expression without any restriction as to the amount of formaldehyde reacted. DEBING et al.^{4, 5}) using technical concentrations of reactants and sodium hydroxide catalyst, found that their results could be expressed only by a modified second order rate equation in which x, the amount of formaldehyde reacted had to be replaced by 2x supposedly to take into account the difference in reactivities of the free positions in the phenol nucleus. The apparent activation energy for the overall reaction was evaluated to be 20,800 cal./mole. MOHAN⁶) working in this laboratory showed that at low equimolar concentrations, about 0.2 M, and with 0.006 M NaOH, the kinetic order in respect of formaldehyde was definitely two, but unity at and beyond a P/F ratio of 2.5. The apparent activation energy for the first order reaction was 20,200 cal./mole. A second order kinetics for this reaction at and above a p_H of 5 was also reported by DE JONG and DE JONGE⁷).

From preliminary experiments designed to check up the above findings, the reaction between phenol, 0.1 M, and formaldehyde, 0.01 M at 0.006 M NaOH and 80 °C., seemed to conform to first order kinetics up to 50% formaldehyde reacted, as shown in Fig. 1, in agreement with Mo-HAN's and JONE's observations. However paper chromatographic analysis revealed the presence, in the reaction products, only of o- and p-methylol phenols. Further it was found that the formation of mono- and di-methylol phenols depended on the relative proportions of phenol and formaldehyde as illustrated by Table 1 from which it is seen that with increasing relative concentration of phenol, the dialcohols appear at later

¹) J. H. FREEMAN, Analytic. Chem. 24 (1952) 955.

²) T. T. JONES, J. Soc. chem. Ind. London 65 (1946) 264.

³) K. B. GOLDBLUM, J. Soc. chem. Ind. London 69 (1950) 102.

⁴⁾ L. M. DEBING, G. E. MURRAY, and R. J. SCHATZ, Ind. Engng. Chem. 44 (1952) 354.

⁵) L. M. DEBING, G. E. MURRAY, and R. J. SCHATZ, Ind. Engng. Chem. 44 (1952) 356.

⁶) G. R. MOHAN, Thesis to Madras University, 1953.

⁷⁾ J. I. DE JONG and J. DE JONGE, Recueil Trav. chim. Pays-Bas 74 (1953) 497.

stages of the reaction. The rate of formation of the dialcohols, as will be shown in the next paper of this series, is slower than that of the monoalcohols, and consequently, the overall kinetic order will be governed by the experimental conditions which control the production of the monoand di-alcohols, and so by itself will lead to little understanding of the mechanism of the reaction.





Initial	Concentration		% CH ₂ O reacted at	
Phenol (mole/l.)	Formaldehyde (mole/l.)	P/F ratio	the appearence of dialcohols	
0.2	0.2	1	2	
0.4	0.2	2	18	
0.6	0.2	3	36	
0.8	0.2	4	45	
1.0	0.2	5	71	

Table I. The nature of the reaction products at different P/F ratiosCatalyst: 0.006 M NaOH; Temp.: 80°C.

Although FREEMAN⁸) was able to estimate quantitatively by paper chromatographic analysis, all the reaction products obtained from the interaction of one mole of phenol with 3 moles of formaldehyde and one of sodium hydroxide at 30 °C., his evaluation of the rate constants of the several reactions involved had to be done by a round-about method which does not seem to have yielded correct values, as will be seen from the results presented here. He did not attempt to isolate the individual steps leading to the formation of the mono-, di- and tri-methylol phenols. This paper deals with the isolation of the two primary steps giving only the o- and p-methylol phenols, their kinetics and energetics and the relative reactivities of the ortho and para positions in phenol, rather different from those reported by FREEMAN.

Experimental

Materials

Phenol of analytical grade was fractionated and the fraction at 180-180.5 °C. was collected for use. Formaldehyde, MERCK formalin, contained less than 2% of methanol which was found not to interfere with the reaction. o-Hydroxybenzyl alcohol was prepared according to the method of LAPWORTH and SHOESMITH⁹) by reduction of salicylaldehyde with sodium amalgam, but at 0 °C. and using conc. HCl for neutralisation in order to obtain better yields (m.p. 86 °C.). p-Hydroxybenzyl alcohol was prepared by reduction of the corresponding aldehyde with sodium amalgam as suggested by BIEDERMANN¹⁰) (m.p. 108 °C.). The indicator for chromatographic analysis, p-nitrobenzene diazonium fluoroborate was prepared according to FREEMAN's¹) method.

Chromatographic Analysis

The ascending chromatographic technique was used and gave, due to slower movement of the solvent, regular spots better adapted for spot-weight analysis. The solvent was butanol-30 % ammonia in the ratio of 4:1 by volume. The solvent front took 19 hours to travel 30 cm whereby phenol alcohols could be separated without overlapping of spots. The optimum concentration of the indicator was found to be 0.1% solution in a cetone, giving coloured spots with colourless or faintly coloured background thus facilitating marking of the spots and sensitive enough to detect amounts less than one micr ogramme, whereas the 1.0% solution used by FREEMAN¹) not only yielded unevenly shaped spots with inconveniently coloured background but could not detect less than 4 or 5 microgrammes.

Results

Formation of o- and p-Methylol Phenols

The analytical data on the products obtained by reacting an excess of phenol, 0.8 M and formaldehyde, 0.2006 M, with 0.006 M NaOH at

⁸⁾ J. H. FREEMAN and C. W. LEWIS, J. Amer. chem. Soc. 76 (1954) 2080.

⁹⁾ A. LAPWORTH and T. B. SHOESMITH, J. chem. Soc. [London] 1922, 1396.

¹⁰) J. BIEDERMANN, Ber. dtsch. chem. Ges. 19 (1886) 2373.

80 °C., are presented in Table II. The last column gives the percentage of formaldehyde reacted, estimated volumetrically, and the preceding column, the corresponding percentage of formaldehyde bound in the two methylol phenols. The satisfactory agreement between the two columns

Time [min.]	o-Methylol phenol [mole/l.·10 ³]	p-Methylol phenol [mole/l.·10 ³]	o-Methylol p-Methylol	% Formalde- hyde bound in products	% Form- aldehyde consumed	k · 10 ⁵ [sec ⁻¹]
20	6.6	7.3	0.89	6.88	6.53	5.62
45	13.8	15.2	0.91	14.62	14.01	5.59
60	17.7	19.2	0.92	18.39	18.25	5.60
90	25.0	26.4	0.95	25.63	25.82	5.55
120	31.7	32.9	0.96	35.21	32.31	5.50
150	37.8	39.2	0.96	38.39	39.18	5.53
180	43.5	44.7	0.97	43.97	45.36	5.58
		А.	$\mathbf{V.}=0.94\pm0.$			

Table II. Chromatographic analysis of the phenol-formaldehyde reaction mixture Phenol: 0.8000 M; Formaldehyde: 0.2006 M; Catalyst: 0.006 M NaOH; Temp.: 80°C.

gives an idea of the accuracy of the quantitative estimation of the two methylol phenols by paper chromatographic spot-weight method. The constancy of the molar ratio of o- and p-methylol isomers, 0.94 ± 0.05 suggests that they are formed by simultaneous parallel reactions.

Kinetic Order with respect to Formaldehyde and the two Methylol Phenols

In the absence of alkali catalyst, the reaction between phenol and formaldehyde, with a P/F ratio varying from 1 to 7.5, at 80 °C. was found to be negligible, about 1 to 2% of formaldehyde being reacted after 8 hours. In the presence of the catalyst the reactive species is the phenate ion. Since the phenate ion concentration, at the low catalyst 0.006 M, and high phenol concentration, 0.8 M, remains practically constant, the reaction rate depends only on formaldehyde (concentration) and hence the kinetic order with respect to formaldehyde, as has already been shown in Fig. 1, is unity. The rates of formation of the two methylol phenols must also depend on the first power of formaldehyde. Hence it is possible to formulate the following rate equations¹¹).

$$-\frac{\mathrm{d}F}{\mathrm{d}t} = \mathbf{k}_1 \mathbf{F} + \mathbf{k}_2 \mathbf{F} = (\mathbf{k}_1 + \mathbf{k}_2) \mathbf{F} = \mathbf{k}\mathbf{F}$$
(1)

¹¹) A. A. FROST and R. C. PEARSON, "Kinetics and Mechanism". John Wiley and Sons, Inc., New York 1953, p. 147.

where k is the rate constant for disappearence of formaldehyde and k_1 and k_2 for its consumption to yield o- and p-methylol phenols respectively. The rates of formation of these two may be expressed by

$$\frac{dM_1}{dt} = k_1 F \text{ and } -\frac{dM_2}{\partial t} = k_2 F \qquad (2)$$

Integration of eq. (1) and (2) leads to

$$\mathbf{F} = \mathbf{F}_0 e^{-\mathbf{k}t}; \quad \mathbf{M}_1 = (\mathbf{k}_1 \mathbf{F}_0 / \mathbf{k})(1 - e^{-\mathbf{k}t}); \quad \mathbf{M}_2 = (\mathbf{k}_2 \mathbf{F}_0 / \mathbf{k})(1 - e^{-\mathbf{k}t})$$

in which F_0 is the initial concentration of formaldehyde. The value of k from Table II is 5.56 $\cdot 10^{-5}$ sec⁻¹. The plot of $(1 - e^{-kt})$ versus M_1 and M_2 is shown in Fig. 2; the slopes of the two straight lines give k_1F_0/k and k_2F_0/k , from which k_1 and k_2 are found to be 2.69 $\cdot 10^{-5}$ and 2.84 $\cdot 10^{-5}$ sec⁻¹



Fig. 2. Plot for parallel first-order reactions Phenol, 0.800 M; Formaldehyde, 0.200 M; NaOH, 0.006 M; Temp. 80°C. (A) p-Methylol phenol, (B) o-Methylol phenol

respectively, the sum of the two being close to the value of k. That the ratio of M_1/M_2 should be equal to k_1/k_2 , a constant, is substantiated by the values in column 4 of Table II, a characteristic of first order parallel reactions.

Phenol: 1.000 M; Formaldenyde: 0.2000 M; Iemp.: 80°C.						
Catalyst conc. [mole/l.·10 ⁸]	k·10 ⁵ [sec ⁻¹]	log k	p _H (calc.)	pk1	p _H (exp.)	
3.0	2.97	5.47	7.40	4.63	7.46	
6.0	5.59	5.75	7.71	4.25	7.78	
12.0	10.79	4.03	8.01	3.97	8.10	
24.0	21.34	4.33	8.32	3.67	8.40	
48.0	41.06	4.60	8.63	3.40	8.70	
100.0	81.45	4.91	8.97	3.09	9.04	

Kinetic order with respect to Phenate Ion

Table III. The effect of catalyst concentration on reaction rate: Phenol: 1.000 M; Formaldehyde: 0.2000 M; Temp.: 80°C.

Table III summarises the results obtained on reacting phenol 1.0 M and formaldehyde 0.2 M at 80 °C. with varying amounts of catalyst, 0.003 to 0.100 M, along with the overall first order constants. The last column lists the $p_{\rm H}$ values measured with a BECKMAN G-Model. At this relatively high P/F ratio of 5, the phenate ion concentration may be taken to be equal to that of the alkali catalyst. The rate of the reaction is then proportional to the first power of formaldehyde and the nth power of the phenate ion:

$$-\frac{\mathrm{d}\mathbf{F}}{\mathrm{d}\mathbf{t}} = \mathbf{k} \cdot \mathbf{F} \cdot (\mathbf{C}_{\mathbf{6}}\mathbf{H}_{\mathbf{5}}\mathbf{O}^{-})^{n} = \mathbf{k}' \cdot \mathbf{F}$$

where k' is equal to k $(C_{6}H_{5}O^{-})^{n}$, or log k' = log k + n log phenate ion. The plot of log k' against log phenate ion, shown in Fig. 3 is a straight line the slope of which gives for n the value of 0.95 or unity, indicating



Fig. 3. Effect of catalyst concentration Phenol, 1.00 M; Formaldehyde, 0.20M; Temp. 80 °C.

that the reaction is of first order in phenate ion also. That the straight line passes through the origin at zero concentration of the catalyst is evidence that the uncatalyzed reaction does not occur between phenol and formaldehyde, as has already been noted earlier. The catalyzed reaction is therefore kinetically of second order, but at constant catalyst concentration, the phenate ion being of constant concentration, it appears to be of first order in formaldehyde. The first order constant k' is related to the second order constant k by the expression $k' = k \cdot$ phenate ion, so that k = k'/cat.conc. From this it follows that pK must vary linearly with $p_{\rm H}$, as illustrated by Fig. 4, over the $p_{\rm H}$ range studied, 7 to 9, or the reaction rate is proportional to the $p_{\rm H}$ of the solution, as observed also by DE JONG and DE JONGE⁷).



Fig. 4. Plot of pK vs. p_H Phenol, 1.00 M; Formaldehyde, 0.200 M; Temp. 80°C. (A) Measured p_H, (B) Calculated p_H

Energy of Activation

The first order rate constants for the reaction at different temperature with 1 M phenol and 0.2 M formaldehyde, and NaOH, 0.006 M, are listed in Table IV, as also the E's evaluated graphically. The close agreement between the activation energies based on formaldehyde consumption and on the production of the two methylol phenols justifies the conclusion that formaldehyde consumed goes exclusively to form the methylol phenols. Identical activation energies are obtained from the second order rate constants calculated according to the method indicated above (cf. supra).

Table IV. Rate of reaction between phenol and formaldehyde at different temperaturesCatalyst: 0.006 M NaOH; Phenol: 1.00 M; Formaldehyde: 0.20 M

Substance	k·10 ⁵ [sec ⁻¹] 60°C.	k · 10 ⁵ [sec ^{−1}] 70 °C.	k·10 ⁵ [sec ⁻¹] 80°C.	k · 10 ⁵ [sec ^{−1}] 90 °C.	E [kcals/mole]
Formaldehyde	0.95	2.26	5.59	11.59	19.94
o-Methylol phenol	0.47	1.16	2.72	5.65	19.77
p-Methylol phenol	0.47	1.21	2.93	5.65	19.77

Temperature dependence of the true second-order rate constant for P-F reaction

Reaction temp. [degrees centigrade]	k · 10 ³ [sec ⁻¹ mole ⁻¹ litre]	E [kcals/mole]
60	1.58	
70	3.77	19.84
80	9.32	
90	19.32	

Effect of Increasing Phenol Concentration

In order to estimate the effect of increasing the relative concentration of phenol on the reaction rate and the methylol phenols, it was varied from 1 to 7.5, formaldehyde being kept at 0.2 M, at a catalyst concentration 0.006 M and 80 °C. The reaction was followed only upto the appearance of the dialcohols. The results are presented in Table V. There is no

Table V. Effect of P/F ratio on rate constants Catalyst: 0.006 M NaOH; Temp.: 80°C.

k₂)·10⁵ c ^{−1}]
.88
.48
.60
.53
.65
.69

significant difference in the relative molar amounts of the two monomethylol phenols, the ortho being always a little less than the para isomer. With increasing P/F ratio, there is a definite increase in all the rate constants, for which explanation is offered in the Discussion Section.

That the relative amount of the p-methylol phenol is greater than that of the ortho isomer under different experimental conditions is again brought out by the results summarised in Table VI. FREEMAN and LE-WIS⁸) reported the ratio of ortho to para methylol phenol to be 1.7, deduced from kinetic analysis of all the reaction products and not from the

Phenol [mole/l.]	Catalyst NaOH [mole/l.•10 ³]	Time [min.]	Temp. [°C.]	o-Methylol phenol [mole/l. · 10 ³]	p-Methylol phenol [mole/l.·10 ³]	o-Methylol p-Methylol
0.2	6.0	15	80	2.10	2.23	0.94
0.4	6.0	60	80	14.28	14.96	0.95
0.6	6.0	150	80	33.60	36.80	0.91
0.8	6.0	120	80	31.70	32.90	0.96
1.0	6.0	40	80	11.74	12.59	0.93
1.5	6.0	60	80	18.79	20.86	0.90
1.0	6.0	120	70	15.75	16.30	0.97
1.0	100.0	25	80	26.66	28.16	0.95
]		A.V	. = 0.94 v 0.03

Table VI. The relative amounts of ortho- and para methylol phenol in the P/F reaction mixture at different experimental conditions

isolated reactions giving only the two mono-methylol phenols, as in the present case. DIJKSTRA and DE JONGE's¹²) observation that 57 to 61 % of o-methylol phenol was obtained from phenol-formaldehyde reaction leading only to mono-methylol phenols, seems also only a closer approximation to the results reported here. It is of interest to note that although there are two reactive ortho positions compared to one para in phenol, the latter seems to be twice as reactive as the former position, whereas according to FREEMAN and LEWIS⁸) it is only 1.2 times as reactive as the ortho position.

Discussion

The reaction between phenol and formaldehyde catalyzed by sodium hydroxide has been shown to be kinetically of the second order one with respect to each of the reactants, formaldehyde and phenate ion, but of

¹²) R. DIJKSTRA and J. DE JONGE, Recueil Trav. chim. Pays-Bas 76 (1957) 92.

first order, independent of phenate ion at a P/F ratio greater than 2.5 and for a given catalyst concentration, as long as only the mono-methylol phenols are the products. Formaldehyde is known to exist in solution at a $p_H 8.7$ and at about 80 °C., from RAMAN spectra ¹³⁻¹⁶) and polarographic studies ^{17, 18}) only in the non-hydrated monomeric form. This must be the reactive species in the present experiments conducted at $p_H 7-9$ and 70-90 °C. In the other reactive species, phenate ion, due to the inductive and mesomeric effects acting in the same direction, the electron density is greater in the ortho and para position in the nucleus. In the presence of this reagent, the inductive effect in the carbonyl group of formaldehyde is reinforced by the electromeric effect with the resulting charge separation, positive on the carbon and negative on the oxygen atoms. The mechanism of the addition of formaldehyde to phenol can therefore be represented as follows:

The rate determining step is the formation of the activated complex (I), followed by the fast migration of the proton from the nuclear carbon atom



to the oxygen of $-CH_2O^-$ to give the compound (II) which rearranges to the stable benzenoid structure (III). This interacts with neutral phenol molecule to give the monomethylol phenol (IV) and regenerate the phenate ion. Since in the rate determining slow step the concentration of phenate ion remains constant, the reaction appears to be of first order.

¹⁸) H. JAHODA, Collect. Czechoslov. chem. Commun. 7 (1935) 415.

¹⁸) P. KRISHNAMURTHI, Indian J. Physics Proc. Indian Assoc. Cultivat. Sci. 6 (1931) 309.

¹⁴) J. H. HIBBEN, J. Amer. chem. Soc. 53 (1931) 2418.

¹⁵) S. A. SCHOU, J. Chim. physique 26 (1929) 72.

¹⁶) N. N. PAL and P. N. SENGUPTA, Indian J. Physics Proc. Indian Assoc. Cultivat. Sci. 5 (1930) 24.

¹⁷) G. A. CROWE and C. C. LYNCH, J. Amer. chem. Soc. 70 (1948) 3795.

The activation energy of about 20 kcal per mole appears to be of the right order of magnitude for a reaction involving an ion and a neutral mole-cule¹⁹).

The same mechanism holds good for the ortho methylol phenol. However, since the para-quinonoidal structure of the activated complex (I) is known to occur more readily than the ortho-form, the para position appears to be twice as reactive as the ortho position, the ultimate reason for this being the steric effect in this latter position and possibility of hydrogen bonding. A similar difference in the reactivities of the two nuclear positions has been observed in the case of the substituted phenols (cf. the subsequent paper of this series). In view of this, FREEMAN and LEWIS's⁸) finding that the para position is only slightly more reactive (viz., 1.2) than the ortho position is difficult to accept.

Finally the definite increase in the rate constant with increasing P/F ratio, for the same formaldehyde and catalyst concentrations, might be attributed to the possible occurrence of proton transfer between the phenate ion and excess phenol,

$$\begin{array}{c} \mathbf{O}^{-} & \mathbf{OH} \\ \mathbf{O}^{+} + \mathbf{OH} \end{array} \rightarrow \mathbf{OH} + \mathbf{OH}$$

so that all the phenol molecules present in the system would acquire partial ionic character and thus influence the effective concentration of the reactive phenolic species. It might also be a neutral molecule effect on this base catalyzed reaction. In view of this fact, comparison of rate constants has been made at the same P/F ratio, for instance, in the evaluation of the positional reactivities of phenol and of activation energies.

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¹⁹) L. P. HAMMETT, "Physical Organic Chemistry", McGraw-Hill Publ. Corp., New York 1940, p. 337.