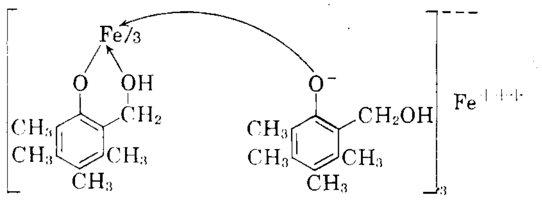
times the molar excess of ferric chloride and the solution was made up to 10 cc. The optical density of the solution was measured against 50% dioxane-water as a blank at various wave lengths (Fig. 1a,b,c). The complex, it is seen, has absorption in the wave length range 5500–6500 Å. with a peak around 6000 Å. The second peak around 4200 Å. is due to ferric chloride (Fig. 1d). The extinction of the ferric chloride in the presence of *o*-monomethylolphenol is found to depend on the *p*H of the solution.[25] The measurements were made at *p*H 4, with reproducibility. Ferric chloride has very little absorption between 5000–7000 Å.

With the three *o*-monomethylol solutions (1×10^{-2} to $3 \times 10^{-4}\ M$) containing ferric chloride, Beer's law is obeyed, deviations occuring for concentrations less than $3 \times 10^{-4}\ M$ of the methylols. Plots of concentration-Klett reading (measurements having been made in a Klett-Summerson colorimeter with a filter for the range 5700–6300 Å.) were calibrated. The Klett readings were found to be depressed when the dioxane content was increased (Fig. 2a,b). The method of Yoe and Jones[28] was employed for establishing the composition of the complexes in the case of the three *o*-monomethylols, the optical density measurements having been made in a Hilger-Watt spectrophotometer at 5500 and 6000 Å. It has been observed that the molecular complex contains three molecules of phenol methylol per one of ferric ion (Fig. 1e in the case of prehentenol methylol). This was found to be true for the complexes formed with the three phenol methylols under study.

Discussion

The insolubility of the complexes in benzene and other organic solvents and the supression of color formation with increase in dioxane content suggested that the complex might be an electrolyte. On electrolysis of a solution containing the complex in Hittorf's apparatus with platinum electrodes it was observed thatt he colored complex migrated to the anode and iron was deposited at the cathode, showing that the complex was an anion. Based on the observations that (1) the complex is present as an anion with iron as the cation, (2) the phenol methylol and ferric ion are present in 3:1 molar ratio in the complex, and (3) the formation of highly colored complexes are observed only with the *o*-hydroxymethylols where formation of chelate rings are possible (the *p*-hydroxy methylols not showing this behavior), the structure suggested for the complex from prehentenolmethylol, taken for illustration is:



In the anion the primary valences and three of the six coordination numbers of ferric iron are satisfied by the formation of a six-membered chelate ring with three moles of *o*-phenol methylol, where as the three remaining coordination numbers of iron are satisfied by formation of a coordinate linkage with three moles of *o*-phenol methylol, thus giving a net negative charge of three to the complex anion.

Acknowledgment.—We wish to thank C.S.I.R., New Delhi, for the grant of Junior Research Fellowship to one of us (H.D.) during the period of this investigation.

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Reactions between Polymethylphenols and Formaldehyde: Kinetic Study. III

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The kinetics of the reactions between formaldehyde and polymethyl phenols like prehentenol, durenol, hemimelletenol, and isopseudocumenol have been studied in 50% dioxane–water. The *ortho-para* relative reactivity and the effect of methyl and methylol groups of the phenols on reaction rates have been discussed.

Reported kinetic studies on the condensation reactions involving methyl substituted phenols and formaldehyde have been few. The products of the reaction in a phenol–formaldehyde system are many. With phenol alone a variety of products are possible, *viz.*, two monomethylols, two dimethylols, and one trimethylol. Further condensation products of the interaction between these phenol methylols among themselves or with excess phenol are possible and these would only emphasize the highly complex nature of the reaction. Monomethylols from phenol have been known for a long time. The formation of dimethylol phenols in the phenol–formaldehyde system has been shown by Sprengling and Freeman,[1] and by Martin[2] who have used different approaches and reported the syntheses of these dimethylols.[3–5] Bruson and Macmullen[6] have indicated the formation of trimethylol

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phenol, which was subsequently isolated by several authors.[7-9] With these model compounds being available, detailed kinetic studies have been made by various workers[10,11] employing paper chromatography, but only with divergent conclusions.

In view of the several advantages, we have used various polymethyl phenols and the corresponding phenol methylols[12a] for rate studies. Fitzgerald and Martin[13] made a similar approach with prehentenol,[14] employing excess sodium hydroxide and 10% dioxane–water as solvent. Excess sodium hydroxide introduced two predominant side reactions, namely loss of formaldehyde by the Cannizzaro reaction and condensation of prehentenol methylol, formed with excess prehentenol, to form a diphenylmethane. There was therefore not a single individual reaction but a summation of three competing reactions, all of which are expected to proceed at a fast rate. In the present investigation, reaction conditions have been chosen with a view of eliminating the side reactions.

Experimental

Materials.—3,4,5- and 2,3,5-trimethylphenol (hemimelletenol and isopseudocumenol) and 2,3,4,5- and 2,3,5,6-tetramethylphenol (prehentenol and durenol) and the corresponding phenol methylols used in this work have been synthesized.[12a] Formaldehyde: Formalin (36%) of B.D.H. A.R. quality containing less than 2% methanol was used, Dioxane was of Merck quality. Impurities such as glycolacetal and acetaldehyde were removed following the procedure giving in Vogel.[15] Sodium hydroxide (used as catalyst) and sodium chloride (used for adjusting ionic strength) were of B.D.H., A.R. grade and carbon dioxide-free distilled water was employed to make up solutions. Ferric chloride used in colorimetry was of B.D.H, A.R. grade.

In view of the insolubility of the experimental phenols in water, it became necessary to use a mixed solvent. Disadvantages of using any alcohol or ketone as solvent are obvious. Dioxane–water (50%) appeared to be ideal as a solvent since the system remained homogeneous to about 50% conversion.

Kinetic Procedure.—The reaction was carried out in a three-necked flask fitted with a mercury-sealed stirrer, reflux condenser, and an automatic sampling device. The flask was immersed in a thermostat at constant temperature, controlled by a hot wire vacuum switch relay and a toluene regulator. The system containing a weighed amount of phenol or phenol methylol in dioxane, catalyst and sodium chloride solution was added to the flask. Formalin solution was then added, the time for the start of the reaction being noted when half the formalin was added. Aliquot portions were taken out at regular intervals and quickly chilled in an ice bath; 5 cc. was used for the estimation of formaldehyde and 2–5 cc. for the colorimetric estimation of *o*-phenol methylols. The rate of disappearance of formaldehyde in the reaction mixture was followed by the hydroxylamine hydrochloride method,[16] dioxane having no interfering effect. *o*-Phenol methylol was estimated by the colorimetric method developed.[12b] Aliquot portions of the reaction mixture were neutralized and excess ferric chloride was added. The whole was made up to a known volume in 50% dioxane–water, and the optical density of the resulting solution was measured against ferric chloride in 50% dioxane–water in a Klett–Summerson colorimeter, using a filter of wave-length range 550–600 mμ, and compared with standard calibrated curve. The rates of formation of prehentenol methylol, followed by the colorimetric method, as well as by the rate of disappearance of formaldehyde, were found to be in good agreement. With durenol the rate of reaction was determined by the estimation of formaldehyde only. With heimimelletenol under certain conditions *o*-monomethylol was formed in the first stage, and later 2,6-dimethylol. Under our experimental conditions only *o*-monomethylol appeared to be formed. The rates of formation of monomethylol by the colorimetric and volumetric methods were in agreement. Further, if dimethylol had formed, the Klett reading for the complex would have been high. Such a phenomenon was not observed. With isopseudocumenol, the rate of formation of its *o*-monomethylol was followed by the colorimetric method, whereas estimation of formaldehyde gave the overall rate of reaction.

Variables in the Reaction.—With all the phenols and phenol methylols under study, side reactions could be minimized by the proper choice of catalyst concentration. With an alkali catalyst (0.006 N to 0.01 N) and phenol (0.05 to 0.1 M) it was observed that the reaction was free from side reactions until after 50% conversion. However, due to solubility difficulties even in 50% dioxane–water, it has not been possible to take higher concentrations of the phenol. This made it difficult for us to study the same reaction over a wider pH range, using higher concentrations of alkali catalyst. The effect of temperature, change of the catalyst concentration and the mole ratios of the reactants has been studied.

Results and Discussion

The reactions between phenols and formaldehyde were found to obey a conventional second-order rate expression. The second-order rate constants (k) at 80° and the activation energies have been evaluated (Table I, Fig. 1 and 2). In the case of isopseudocumenol both *o*- and *p*-monomethylols are formed by two simultaneous reactions. From the over-all rate of reaction of isopseudocumenol (formaldehyde estimation) and estimation of *o*-monomethylol formed at various time intervals (colorimetry), the individual rate constants for the formation of *o*- and *p*-monomethylols have been calculated. From the usual second-order kinetics for the formation of monomethylols from equimolar amounts of isopseudocumenol and formaldehyde, it is obvious that $c = \dfrac{c_0}{1 + c_0Rt}$ where c_0 = initial

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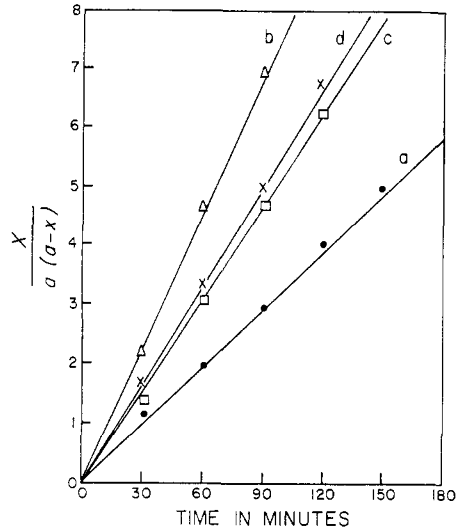

Fig. 1.—II order rate plots with [phenol] = [formaldehyde] = 0.05 mole/l.; NaOH = 0.006 N; temperature = 80°; dioxane = 50%; ionic strength = 0.02

a. Prehentenol
b. Durenol
c. Hemimelletenol
d. Isopseudocumenol

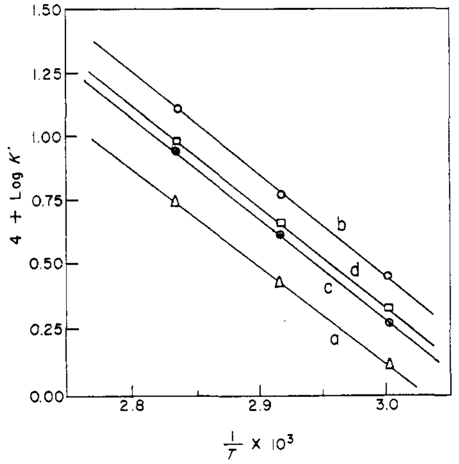

Fig. 2.—Plots of log II order rate constants *vs.* reciprocal of absolute temperatures. [Phenol] = [formaldehyde] = 0.05 mole/l.; NaOH = 0.006 N; ionic strength = 0.02; dioxane = 50%

a. Prehentenol
b. Durenol
c. Hemimelletenol
d. Isopseudocumenol

concentration of isopseudocumenol or formaldehyde, c = concentration at time t, and k = second-order rate constant. Then the rate of formation of o-monomethylol may be given by

$$\frac{dM_1}{dt} = k_1c^2 = k_1\left[\frac{c_0}{1 + c_0kt}\right]^2 \qquad (1)$$

where M_1 = concentration of o-monomethylol formed in time t, c_0 = initial concentration of isopseudocumenol or formaldehyde taken, and k_1 = rate constant for the formation of o-monomethylol. Integration and rearrangement of (1) gives

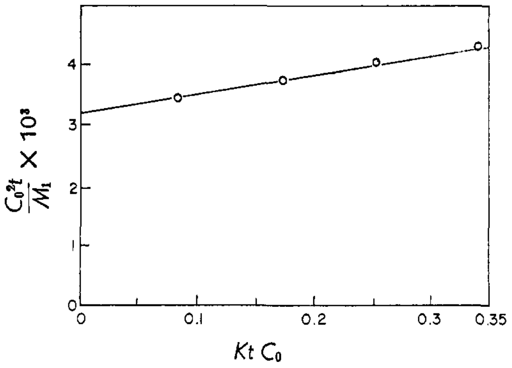

Fig. 3.—*Ortho-para* distribution in isopseudocumenol. [Isopseudocumenol] = [formaldehyde] = 0.05 mole/l.; NaOH = 0.006 N; temperature = 80°; dioxane = 50%; ionic strength = 0.02

$K = 9.25 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$
$K_1 = 3.12 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$
$K_2 = 6.13 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$

$$\frac{c_0^2t}{M_1} = \frac{1}{k_1} + \frac{ktc_0}{k_1} \qquad (2)$$

The value of k obtained from the rate of disappearance of formaldehyde (9.25×10^{-4} l. mole^{-1} sec.$^{-1}$) and 't' are substituted in (2), and a plot of ktc_0 *vs.* $\frac{C_0^2t}{M_1}$ (Fig. 3) was drawn from which k_1 was evaluated (3.12×10^{-4} l. mole^{-1} sec.$^{-1}$). By substracting k_1 from k, the corresponding rate constant k_2 for the formation of p-monomethylol was evaluated (6.13×10^{-4} l. mole^{-1} sec.$^{-1}$). The concept of what may be termed 'positional reactivity' of the individual

TABLE I

RATE CONSTANTS AND ACTIVATION ENERGIES IN THE PHENOLS–FORMALDEHYDE REACTIONS

[Formaldehyde] = 0.05 mole/l. Temp. = 60°, 70°, 80°. [Phenol] or [Phenol methylol] = 0.05 mole/l. NaOH = 0.006 N. Solvent = 50% dioxane–water. Ionic strength = 0.02.

No.	Phenol or Phenol Methylol	$k \times 10^4$ l. mole^{-1} sec.$^{-1}$ at 80°	Activation Energy Kcal./mole
1.	Prehentenol	5.55 (over-all & positional)	17.72
2.	Durenol	12.96 (over-all & positional)	17.00
3a.	Hemimelletenol	8.63 (over-all)	17.61
3b.	Single *ortho* position in hemimelletenol	4.32 (positional)	—
4a.	Isopseudocumenol	9.25 (over-all)	17.33
4b.	*Ortho* position in isopseudocumenol	3.12 (positional)	—
4c.	*Para* position in isopseudocumenol	6.13 (positional)	—
5.	2,3,5-Trimethyl-6-methylolphenol (*para* position)	5.06 (positional)	17.96
6.	2,3,5-Trimethyl-4-methylolphenol (*ortho* position)	2.56 (positional)	18.70
7.	3,4,5-Trimethyl-2-methylolphenol (*ortho* position)	3.24 (positional)	18.47

nuclear positions of the phenol *vs.* the 'over-all reactivity' of the phenol may be introduced. In the case of isopseudocumenol considered above, the over-all rate constant is equal to the sum of the positional rate constants of one *ortho* and one *para* position. Similarly in the case of hemimelletenol the over-all rate constant is a measure of the positional reactivities of two equal *ortho* positions. In the case of durenol and prehentenol the positional and over-all rate constants would be identical. The positional rate constants are also given in Table I. All our phenols with methyl groups in the 3,5- positions were found to be very reactive towards formaldehyde. This observation is similar to that of Sprung,[17] who observed that *m*-cresol and 3,5-xylenol are nearly three and eight times, respectively, more reactive than phenol. The higher reactivity may be explained on the basis of both the inductive and hyperconjugation effect of two methyl groups located *meta* to one another. Further, methyl groups are *ortho-para* directing and when present in the *meta* position they are expected to bring about enhanced reactivity. The rate constants differed widely for the phenols under study emphasizing the effect of methyl groups in the phenolic nucleus. It may be seen that durenol, with the *para* position free, is a little over twice as reactive as prehentenol in which the *ortho* position is free. The positional rate constant of the *para* position in isopseudocumenol is twice that of the corresponding *ortho* position, indicating that the *para-ortho* reactivity ratio is two. It may be seen that durenol has one more methyl group in the *ortho* position, and prehentenol one more in the *para* position than isopseudocumenol. Prehentenol has one more methyl group in the *ortho* position than hemimelletenol. From the values of the positional rate constants (Table I) it is obvious that increased methyl substitution brings about enhanced reactivity, which is in agreement with the theoretical requirements that introduction of an electron repelling methyl group would be expected to increase the reactivity of the *ortho* and *para* positions in the substituted phenol compared to phenol itself.

Addition reactions of the *o*-monomethylols of hemimelletenol and isopseudocumenol with formaldehyde have also been studied (Table I). It is obvious from the results that the introduction of a methylol group in hemimelletenol causes a decrease in the reactivity of its second *ortho* position (compare 3b and 7 of Table I). A similar decrease in the reactivity of the *para* or *ortho* position occurs as a result of the introduction of a methylol group in isopseudocumenol (compare 4c and 5; 4b and 6). These results are in accord with the expectation that the methylol group is electron-attracting and therefore *meta* directing and ring deactivating. Differences between the reactivities of methyl and methylol groups on the nucleus are also obvious from a consideration of 1 and 6; 2 and 7, etc., of Table I.

The following conclusions emerge: (1) The reactivity of the *para* position of the phenolic nucleus is about twice that of the *ortho* position. (2) The introduction of a methyl group in the *ortho* or *para* positions of a phenol brings about enhanced reactivity in the vacant *ortho* or *para* positions, while introduction of a methylol group brings about decreased reactivity. These conclusions are in general agreement with those of Freeman and Lewis[10] and Gopalakrishna and Yeddanapalli,[11] who have used an unsubstituted phenol in an aqueous medium. Freeman[10] has, however observed that a methylol group in the *ortho* position does not bring about the expected deactivating effect. Finn and Lewis[18] have proposed that with phenols having methyl substituents in the *para* or *meta* position, the introduction of a methylol group into one *ortho* position facilitates the entry of a second methylol group into the other *ortho* position. Finn[19] reported that 2,6-dialcohols are obtained in good yield from 3,5-xylenol when one mole of 3,5-xylenol is treated with one mole of paraformaldehyde in absolute alcohol with sodium ethoxide as catalyst at 5°. We have applied the above method to hemimelletenol, isopseudocumenol, durenol, and prehentenol. With hemimelletenol and prehentenol the reaction took place smoothly at 5° in very good yield, resulting in the formation of dialcohol from the former and monoalcohol from the latter. With isopseudocumenol, the product was exclusively the *o*-methylol phenol, no *p*-monomethylol phenol being formed. In the case of durenol no reaction took place. From these observations it is clear that the system paraformaldehyde and sodium ethoxide in ethanol is specific for the introduction of *o*-methylol groups only, a dialcohol being formed exclusively where there were two *ortho* positions available in the phenol nucleus and only monoalcohol being formed whenever a second *ortho* position was not vacant. No proper mechanism could be given to this rather striking phenomenon. That the reaction takes place even at low temperatures as 5° indicates a different type of formaldehyde addition the nature of which is not clear.

Acknowledgment.—We wish to thank C.S.I.R., New Delhi, for the grant of Junior Research Fellowship to one of us (H. D.) during the period of this investigation.

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