Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.49. Found: C, 72.70; H, 8.20.

The compound gave characteristic green color with ferric chloride. The number of hydroxyl groups per mole was found to be 1.93 (theoretical 2). Acetate: m.p. 182°.

Sodium Amalgam Reduction of Hemimelletenol Aldehyde (IV) to Hemimelletenol Monomethylol.—The *o*-hydroxyaldehyde (IV) obtained by the Gattermann reaction on hemimelletenol could be smoothly reduced to hemimelletenolmonomethylol using sodium amalgam and alcohol–water (1:1) between 0 and 5°. The product was recrystallized from alcohol–water, m.p. 203°; a mixed melting point with previous sample was not depressed.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.49. Found: C, 72.53; H, 8.70.

Hemimelletenoldimethylol.—A solution of hemimelletenol (1.36 g.), paraformaldehyde (0.9 g.) and sodium ethoxide (0.68 g.) in absolute ethanol (20 cc.) was left in an ice chest. The separation of crystalline sodium salt was complete within 3 days. This was dissolved in water and acidified with acetic acid. The product was recrystallized from ethyl acetate as white shining flakes, m.p. 150°, yield 85% (lit[14a] m.p. 148°).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.33; H, 8.22. Found: C, 67.00; H, 8.70.

The number of hydroxyl groups per mole was found to be 2.87 (theoretical 3). Triacetate, m.p. 87°. The dimethylol gave an intense blue coloration with ferric chloride, observed to be characteristic of *O*-*O*-dimethylols from 3,5-xylenol, *p*-cresol.

2,3,4,2′,3′,4′-Hexamethyl 6,6′-dihydroxydiphenylmethane was obtained when a mixture of hemimelletenolmonomethylol (1.66 g.), hemimelletenol (2 g.) in dioxane-water (25 cc. of 50%) and hydrochloric acid (10 cc. of 1 *N*) was warmed on a water bath for 1 hr., as shining white flakes, m.p. 275°.

***o*-Monomethylol isopseudocumenol** could not be isolated by a direct reaction between isopseudocumenol and formaldehyde because of side reactions. However, application of Holmes'[18] method on isopseudocumenol resulted in the formation of *o*-methylol only (80% yield), no *p*-methylol or dimethylol being formed. The *o*-monomethylol was recrystallized from petroleum ether, m.p. 120°. It gave a green color with ferric chloride. The compound was considered to be *o*-monomethylol for the following reasons: (1) elemental analysis of the compound was in agreement with requirements for a monomethylol and not for a dimethylol.

Anal. Calcd. for monomethylol, $C_{10}H_{14}O_2$: C, 72.21; H, 8.49. Found: C, 73.10; H, 8.50.

(2) The number of hydroxyl groups per mole was found to be 1.94 (theoretical 2).

(3) The constitution of the *o*-monomethylol was further confirmed by preparation of 2-hydroxy-3,4,6-trimethylbenzaldehyde (IX, m.p. 78°) by a Gattermann reaction on isopseudocumenol and the subsequent reduction of the aldehyde by lithium aluminum hydride to the methylol, m.p. 120°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.21; H, 8.49. Found: C, 72.82; H, 8.61.

***p*-Monomethylolisopseudocumenol** could not be prepared by Holmes[18] method on isopseudocumenol. Its preparation was therefore carried out by the following method not involving formaldehyde addition. 4-Hydroxy-2,3,6-trimethylbenzaldehyde (VIII), m.p. 147°, was obtained by a Gattermann reaction on isopseudocumenol followed by steam distillation to remove the *o*-aldehyde. VIII was subjected to lithium aluminum hydride reduction in dry ether at room temperature. The product was recrystallized from ethyl acetate–petroleum ether, m.p. 169°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.21; H, 8.49. Found: C, 71.60; H, 8.90.

The number of hydroxyl groups per mole was found to be 1.96. Diacetate: m.p. 53°.

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o-Phenol Methylols–Ferric Iron Complex Formation. II.

H. DAKSHINAMURTY AND M. SANTAPPA

Department of Chemistry, University of Madras, Madurai Centre, India

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o-Phenol methylols from certain polymethyl phenols form green colored complexes with ferric chloride. The nature and composition of the complexes were investigated spectrophotometrically.

Lack of adequate analytical tools has been a big handicap for the systematic kinetic study of phenol-formaldehyde reaction. Formaldehyde, even in the presence of phenolic materials, is conveniently estimated[1-5] titrimetrically. A method by Gambier modified by Nordlander[6] involves titration with hydroxylamine hydrochloride. Determination of phenols, phenol methylols, and dihydroxydiphenylmethanes based on infrared absorption has been reported in a few cases.[7-9] Estimation of phenols or phenol methylols by the bromide method has several limitations.[10-12] Our experience has been that with methyl-substituted phenols and dihydroxydiphenylmethanes, overbromination occurs, probably because of substitution in the side chain or at the methylene bridge. Partition paper

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chromatography has been recently applied to the study of the phenol-formaldehyde reaction.[13–17]

We have developed a new colorimetric method for the estimation of *o*-phenol methylols, based on the formation of colored complexes with ferric chloride. Formation of colored complexes between phenol and ferric chloride is well known.[18,19] Ferric salts and boric acid are known to form[20–22] five- or six-membered chelate rings with polyhydroxybenzene compounds, particularly those with hydroxyl groups in the α,β-positions. Formation of complexes between phenol methylols like *o*-saligenin 2,4-dimethylolphenol, and ferric chloride has been noted.[23,24] Dejonge and Dejkstra[25] standardized a colorimetric procedure based on ferric chloride coloration for the estimation of *o*-saligenin in the presence of *p*-saligenin and simple phenol. Kammerer[26a,b] also studied the color reaction given by phenol formaldehyde condensates (particularly compounds with hydroxymethyl groups in the position ortho to the phenolic group) with ferric chloride.

The *o*-phenol methylols reported in Part I of this series[27] and also those prepared from representative phenols like *p*-cresol and 3,5-xylenol are found to form colored complexes with ferric chloride. The complexes are not very soluble in water and are completely insoluble in organic solvents. When an aqueous solution containing the complex is shaken with nonpolar organic solvents, it is not found to be partitioned between the two liquid phases. Dioxane–water was found to be an excellent solvent. In 50% dioxane–water containing ferric chloride the *o*-phenol methylols give a stable green color, whereas the *o*-*o*-dimethylols give a deep blue color. Tri- and tetramethylphenols or the *p*-monomethylols derived from then do not give any color. Based on this a colorimetric method for the estimation of *o*-phenol methylols has been standardized.

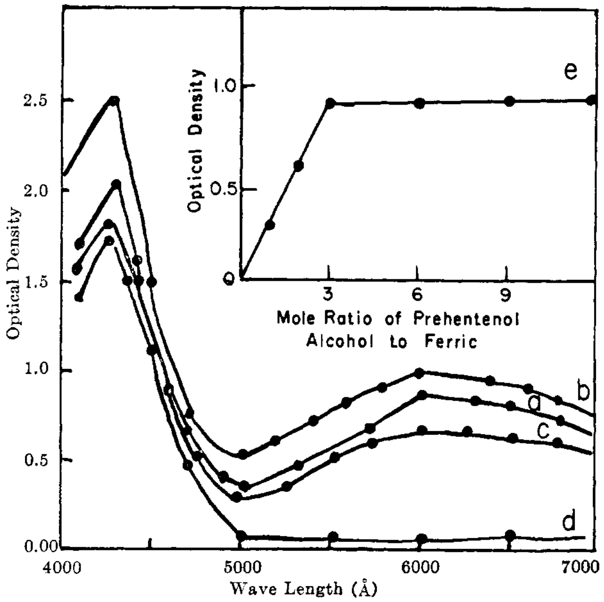

Fig. 1.—Optical density *vs.* wave length of ferric iron complexes with *o*-methylol phenols (0.005 mole/l.) with excess ferric chloride measured against 50% dioxane–water

a. Prehentenol monomethylol
b. Isopseudocumenol monomethylol
c. Hemimelletenol monomethylol
d. Solution of 0.0375 *N* ferric chloride in 50% dioxane-water
e. Optical density (measured at 6000 Å.) *vs.* mole ratio of prehentenol alcohol to ferric chloride (0.005 mole/l.)

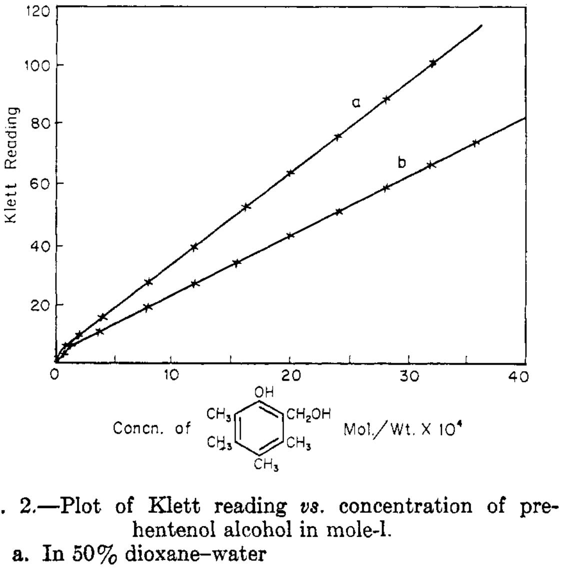

Fig. 2.—Plot of Klett reading *vs.* concentration of prehentenol alcohol in mole-l.

a. In 50% dioxane–water
b. In 60% dioxane–water

Experimental

The *o*-monomethylols studied are from prehentenol, isopseudocumenol, and hemimelletenol.[27] The ferric chloride solution used was prepared by dissolving Analar ferric chloride (B.D.H) in water and standardizing against sodium thiosulfate solution. Absorptiometric measurements were made with a Hilger-Watt spectrophotometer using 1-cm. glass cells. To 5 cc. of dioxane solution containing the *o*-methylol phenol in a 10-cc. standard flask was added ten

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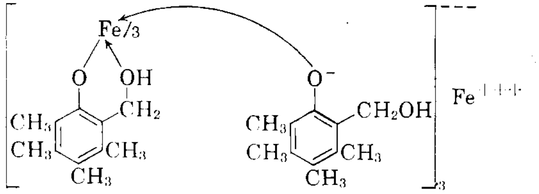
times the molar excess of ferric chloride and the solution was made up to 10 cc. The optical density of the solution was measured against 50% dioxane-water as a blank at various wave lengths (Fig. 1a,b,c). The complex, it is seen, has absorption in the wave length range 5500–6500 Å. with a peak around 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 3×10^{-4} *M*) containing ferric chloride, Beer's law is obeyed, deviations occuring for concentrations less than 3×10^{-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

H. DAKSHINAMURTY AND M. SANTAPPA

Department of Chemistry, University of Madras, Madurai Centre, India

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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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