[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Reactivity of Phenols Toward Paraformaldehyde[1]

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Introduction

In view of the importance of the reaction between phenols and formaldehyde in the manufacture of synthetic resins, surprisingly little has been published concerning the kinetics of such reactions. Various empirical approaches to the problem have been made, of course. For example, Novák and Ĉech[2] attempted to follow the course of phenol–formaldehyde condensations in aqueous media by measuring the decrease in bromine value of that part of the reaction mixture which is insoluble in acetic acid–water mixtures. Somewhat similar measurements were made by Stäger.[3]

Attempts to determine the relative reactivities of phenols and tar acids under various conditions have been made by Megson and collaborators[4] in England, but their interpretations have not been based upon classical kinetic concepts. These authors have introduced two concepts, one of which, RT, the time in minutes for an aqueous phenol–formaldehyde mixture to reach a stage of permanent turbidity, is taken as a measure of intrinsic reactivity; and the second of which, HT, the time in hours for a mixture of a phenol and paraformaldehyde to reach a condition of permanent cloudiness, is taken as a measure of heat hardening capacity. With trimethylamine as the catalyst, the reactivity of phenols toward formalin (1/RT) was observed to fall off in the order: 3,5-xylenol > 180–220° tar > meta-cresol = 2,5-xylenol > 3,4-xylenol > 2,4-xylenol > *o*-cresol > phenol > *p*-cresol. With pyridine as catalyst, the hardening time (HT) of mixtures of phenols and paraformaldehyde increased approximately in the order: 3,5-xylenol < *m*-cresol < phenol < 180–220° tar < *p*-cresol ≪ *o*-cresol.

A different sort of comparison of reaction velocities of phenols has been made by Granger[5] who measured the time required for an equimolar mixture of the phenol, aqueous formaldehyde and sodium hydroxide to yield a "compact granular or powdery form of precipitate on neutralization." The speed with which this condition was realized at 100° was about four minutes for 2,5-xylenol, 3,5-xylenol, thymol, carvacrol and α-naphthol; thirty-five minutes for *m*-cresol; sixty minutes for *o*-cresol and 2,4-xylenol; one hundred twenty minutes for 3,4-xylenol; three hundred sixty minutes for phenol and *p*-cresol.

A more precise study of the reaction between phenol and aqueous formaldehyde was made in this Laboratory by Nordlander[6] who measured the rate of disappearance of formaldehyde and the manner in which the bromine value of the water soluble part of the reaction mixture changed as the reaction proceeded. The rate of disappearance of formaldehyde was found to follow a first order rate law. For the ammonia catalyzed reaction, in which the maximum amount of formaldehyde that reacted was one mole per mole of phenol, this law may be expressed as follows for reactions which are initially equimolar with respect to phenol and formaldehyde

$$K = \frac{1}{c^{1.38}t} \log \frac{a}{a - x}$$

where c is catalyst concentration, a is the initial formaldehyde concentration, and $(a - x)$ is formaldehyde concentration at time t.

There seems to be no information in the literature specifically dealing with the kinetics of the reaction between phenol or its homologs and paraformaldehyde in the absence of water. A study of this sort was therefore undertaken, and the results are described in this paper.

The catalyst used during this work was triethanolamine, chosen because of its non-volatility and ready solubility in the media involved, and because the reactions could easily be controlled in its presence. The following phenols were studied: phenol, *o*-cresol, *m*-cresol, *p*-cresol, saligenin, 3,5-xylenol, 2,6-xylenol, 2,3,5-trimethylphenol, 3,4-xylenol and 2,5-xylenol.

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(1) Presented before the Division of Paint and Varnish Chemistry at the 100th meeting of the American Chemical Society at Detroit, September 10, 1940.

(2) Novák and Ĉech, *Ind. Eng. Chem.*, **20**, 796 (1928); **24**, 1275 (1932).

(3) Stäger, *Helv. Chim. Acta*, **14**, 285 (1931).

(4) (a) Holmes and Megson, *J. Soc. Chem. Ind.*, **52**, 415T (1933); (b) Megson, *Trans. Faraday Soc.*, **32**, 336 (1936); (c) Megson, *J. Soc. Chem. Ind.*, **57**, 189 (1938); (d) Megson, *ibid.*, **58**, 131 (1939); (e) Megson and Paisley, *ibid.*, **58**, 213 (1939); (f) Morgan and Megson, *J. Soc. Chem. Ind.*, **52**, 418T (1933). *Cf.* Tsuruta, *J. Soc. Chem. Ind. Japan*, **40**, 125B (1937).

(5) Granger, *Ind. Eng. Chem.*, **29**, 1305 (1937).

(6) Nordlander, unpublished work; reported at the Pittsburgh meeting of the American Chemical Society, September, 1936; abstracted in *Oil, Paint and Drug Reporter*, September 14, 1936.

Method.—The reactions were carried out in an ordinary 1000-cc. 3-necked flask, fitted with a stirring device, a short air condenser bent downward and terminating in a trap, and a thermometer. The flask was heated by means of a water-bath. Most reactions were carried out at 98°, the temperature which could be most easily maintained in this system. Adjustment of the temperature during the early, exothermic phase of the reaction was accomplished manually.[7] The temperature was maintained constant to within ±1°.

The paraformaldehyde was weighed into the reaction flask and most of the phenol (4 moles) was added. The temperature was then brought to 95°. The catalyst was dissolved in the remainder of the phenol, and this mixture preheated to 95°. The bath was then lowered, the stirrer stopped and the catalyst-phenol solution rapidly added. The stirrer was again started and zero time taken. The temperature usually rose very rapidly to 98°, where it then frequently maintained itself for some time. Occasionally it was necessary to cool the reaction mixture momentarily by means of cold water. As soon as the temperature dropped perceptibly below 98°, the hot water-bath was raised.

Samples of about 2 g. were removed at convenient intervals, and run into tared flasks which were immediately set in the refrigerator to slow down the reaction.

Materials

Paraformaldehyde.—This was a commercial product, obtained from the R. and H. Division of E. I. du Pont de Nemours and Co. It was a white granular powder, which assayed 96% available formaldehyde. The remainder was presumably chemically combined water.

Triethanolamine.—Eimer and Amend C. P. material was used. It was water-white and essentially anhydrous.

Phenol.—U. S. P. water-white crystals were available. They were distilled once before use.

o-Cresol.—This was from the Eastman Kodak Co. Colorless crystals, melting point 30–31°.

p-Cresol.—Barrett *p*-cresol was crystallized twice from a mixture of benzene and petroleum ether; m. p. 35°.

m-Cresol.—A sample obtained from the Eastman Kodak Co. was found, on assay, to be sufficiently pure for our purposes.

3,5-Xylenol.—An Eastman Kodak Co. sample was crystallized once from benzene; m. p., 65°.

2,6-Xylenol.—A pure sample was furnished by the Shell Development Co.; m. p., 44–45°.

2,3,5-Trimethylphenol.—A pure sample was furnished by the Shell Development Co.; m. p., 94°.

Saligenin.—A pure sample was obtained from Hynson, Westcott & Dunning, Inc.; m. p., 86°.

m-p-Cresol.—A sample containing 60% *m*-cresol and 40% *p*-cresol, within about 1%, was furnished by the Reilly Tar and Chemical Corp.

3,4-Xylenol and 2,5-Xylenol.—Samples of these xylenols were furnished by Monsanto Chemicals Limited. They melted at 64–65° and 70–71°, respectively.

Analytical Methods

Determination of Formaldehyde.—The Cambrier method, as modified by Nordlander,[6] was used. The sample, after standing in the refrigerator, was allowed to come to room temperature, and weighed. Sufficient 95% alcohol was added to bring it into solution (usually 25 or 50 cc.). Two drops of brom phenol blue solution were added, and the solution was neutralized exactly with 0.5 N hydrochloric acid. (The amount of acid required served to check the catalyst concentration; this should remain constant throughout the run.) A drop or two of 0.5 N sodium hydroxide was added to bring back a distinct blue color. From five to fifteen cc. of 10% hydroxylamine hydrochloride solution (depending upon the expected formaldehyde content of the solution) was then run in from a buret, and the mixture allowed to stand for ten minutes. A drop or two more of the indicator was added, and the hydrochloric acid liberated was titrated with 0.5 N sodium hydroxide, a distinct blue color again being taken as the end-point.[8] A blank was run on a mixture of alcohol and hydroxylamine hydrochloride.

Determination of Reactive Positions.—A sample of approximately two grams was used for this determination. It was kept in the refrigerator until ready for use. It was then weighed, dissolved in dilute alkali, and brominated according to the procedure outlined in a paper appearing simultaneously with this publication.[9] The significance of the bromination data is discussed there.

Discussion of Results

The Addition Reaction.—Most of the data obtained during this study pertain to the first phase of the reaction, namely, the addition of formaldehyde to the phenol (or possibly to intermediates formed during the course of the reaction, essentially phenolic in nature, and therefore reacting with formaldehyde similarly to the parent substance). The rate of disappearance of formaldehyde is undoubtedly a measure of the velocity of this phase of the reaction.

Because of the impracticability of taking volume samples (the viscosity increases greatly and the density varies appreciably as the reaction proceeds), weight samples were taken and the results expressed on a molar basis, namely, in terms of the number of moles of free formaldehyde per original four moles of phenol. This was the phenol content of the usual batch at the start of the reaction.[10]

When the amount of free formaldehyde, present

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(7) The conventional type of thermostat is not well adapted to this particular problem because of the excessive amounts of heat generated internally at the beginning of the reaction. Under such conditions, a large amount of cooling liquid and very rapid agitation are required to maintain temperature constancy. It is simpler and more convenient to make these adjustments manually, especially during the early, highly exothermic stage of the reaction.

(8) Occasionally the end-point fades somewhat, in which case the solution is brought again to a distinct blue color by the addition of more alkali, and the titer corrected accordingly.

(9) Sprung, *Ind. Eng. Chem. Anal. Ed.*, **13**, 35–38 (1941).

(10) The amount of catalyst used was determined by the *total weight* of the batch.

in the reaction mixture and expressed in this manner, is plotted against time on semi-logarithmic paper, a straight line is obtained in most of the cases studied. This indicates that the addition phase of the reaction follows an apparent first order rate law. The slope of the straight line so obtained is therefore taken as a measure of the reactivity of the phenolic substances under these conditions. It is worthy of note that the general kinetic course of the reaction is similar to that found for the ammonia catalyzed reaction between phenol and formaldehyde in aqueous solution[6] despite the dissimilarity in conditions involved in the two cases.

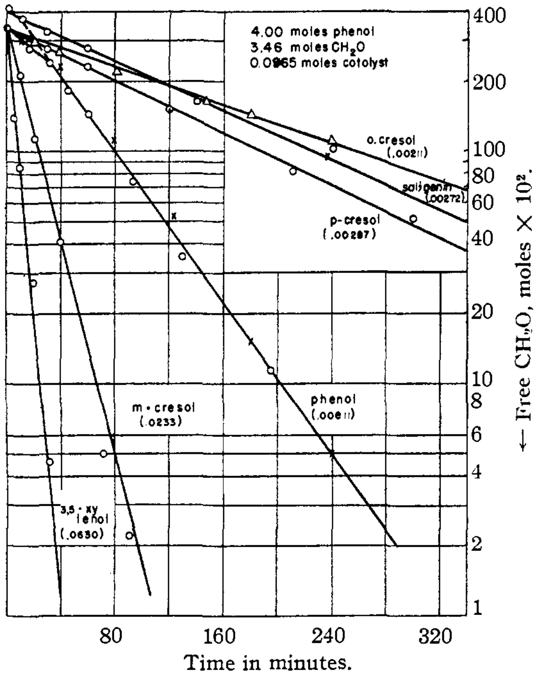


Fig. 1.—Comparison of reactivities of phenols at 98 ± 1°.

Comparative Reactivities at Constant Temperature and Constant Molar Ratios of Phenol to Formaldehyde.—Most of the runs were made at 98°, at a molar ratio of 1 phenol:0.87 available formaldehyde, and with 0.0241 mole of triethanolamine per mole of phenol. The comparative reactivities of various phenols under these conditions are shown in Figs. 1, 2 and 2a. The slopes of the straight lines were determined graphically.

TABLE I

Phenol	Apparent first order rate constant	Comparative rate, phenol taken as unity
3,5-Xylenol	0.0630	7.75
m-Cresol	.0233	2.88
2,3,5-Trimethylphenol	.0121	1.49
Phenol	.00811	1.00
3,4-Xylenol	.00673	0.83
2,5-Xylenol	.00570	.71
p-Cresol	.00287	.35
Saligenin	.00272	.34
o-Cresol	.00211	.26
2,6-Xylenol	.00130	.16

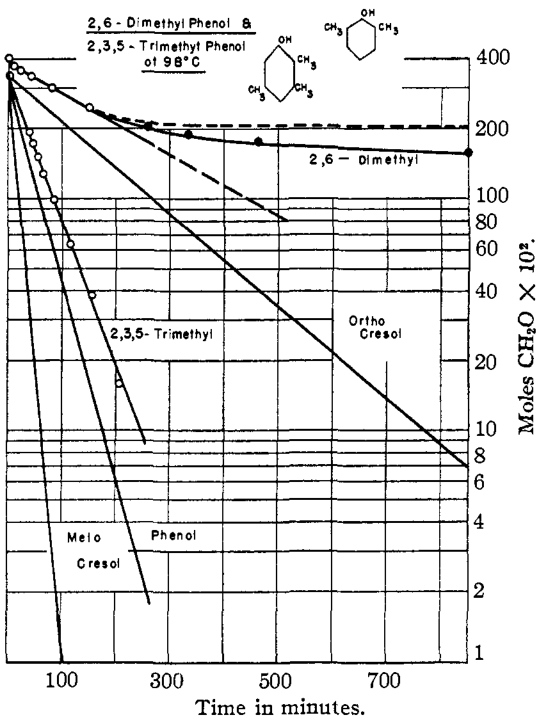


Fig. 2.

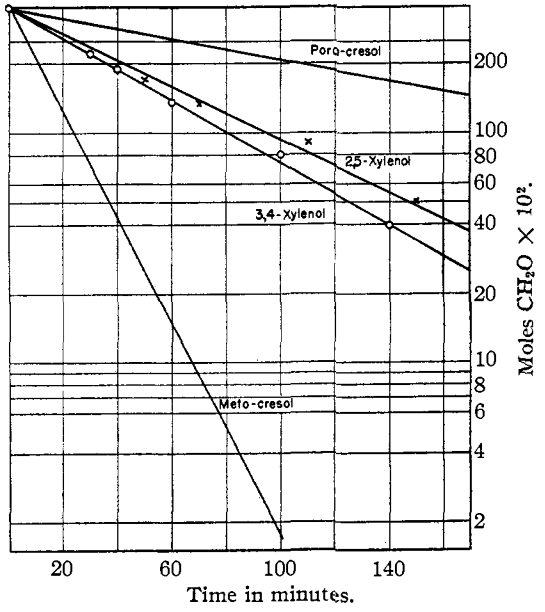
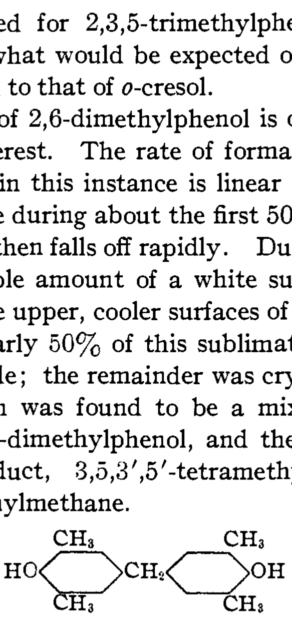


Fig. 2a.—3,4-Dimethylphenol and 2,5-dimethylphenol at 98°.

The rate constants so obtained are summarized in Table I.

The spread of reactivities, from 2,6-xylenol to 3,5-xylenol is thus about 50-fold. The ratio of the reactivities of *m*-cresol and phenol is 2.88, that of 3,5-xylenol and *m*-cresol is 2.70. Thus the introduction of a methyl group in the meta position increases the reaction rate under these conditions about 2.8 times. This is borne out approximately, also, by two of the less reactive xylenols. The rate for 3,4-xylenol is 2.5 times that found for *p*-cresol; and that for 2,5-xylenol is 2.7 times that found for *o*-cresol. However, the rate observed for 2,3,5-trimethylphenol is only about half what would be expected on this basis, as compared to that of *o*-cresol.

The case of 2,6-dimethylphenol is of somewhat peculiar interest. The rate of formaldehyde disappearance in this instance is linear on the logarithmic scale during about the first 50% of the reaction, and then falls off rapidly. During this run a considerable amount of a white sublimate collected on the upper, cooler surfaces of the reaction vessel. Nearly 50% of this sublimate was paraformaldehyde; the remainder was crystalline material, which was found to be a mixture of unchanged 2,6-dimethylphenol, and the *dimeric* reaction product, 3,5,3′,5′-tetramethyl-4,4′-dihydroxydiphenylmethane.



This was isolated in the following manner. The unchanged 2,6-dimethylphenol was separated by extraction with hot benzine and the paraformaldehyde by extraction with boiling dilute sulfuric acid. The residue, the crystalline dimer, was washed with water, dried and crystallized twice from aqueous methanol. It melted at 173°, whereas Auwers,[11] who prepared it from 2,6-dimethylphenol and aqueous formaldehyde in the presence of strong sodium hydroxide, gave 175°. The main part of the reaction product also crystallized on standing, and was found to consist largely of the above dimer.

The total amount of paraformaldehyde which sublimed (on the basis of a 4 mole run) was found to be 0.77 mole. The actual amount of unreacted paraformaldehyde at the end of the run was therefore 2.11 moles, and since 4.22 moles was taken in this case, it is apparent that *almost exactly 50%* of the paraformaldehyde was used up to form the crystalline dimer, after which the reaction came to a virtual stop, as shown by the dotted line in Fig. 2.[12] Thus, it appears that in a non-aqueous medium, the sole reaction product formed from 2,6-dimethylphenol and paraformaldehyde is the crystalline dimer, which is, of course, incapable of reacting further with formaldehyde under ordinary conditions. This is in accord with the observation of Auwers[11] that the dimer is the sole reaction product formed at 100° in aqueous alkaline solution, although Bamberger[13] showed earlier that the monomeric methylol derivative (2,6-dimethyl-4-hydroxymethylphenol) can be isolated at low temperatures. Obviously, this latter substance must be an intermediate in the reaction at higher temperatures, as well. Granger[14] has also referred to this behavior of 2,6-dimethylphenol in aqueous alkaline solution. However, his observation that the second half of the formaldehyde is consumed by the Cannizzaro reaction is at variance with the results found during the present investigation, carried out, to be sure, under quite different experimental conditions. The observations described above lend support to the view, now generally accepted, that dihydroxydiphenylmethane derivatives are intermediates in the formation of phenolic resins, in alkaline as well as in acid solution.[4,15]

The behavior of saligenin is also of special interest in connection with theories of reactivity of phenols toward formaldehyde. The rate of reaction of saligenin with formaldehyde is about the same as that of *p*-cresol, and similar to that of *o*-cresol. Thus, a methylol group in the ortho position depresses the reactivity of phenol about to the same extent as a methyl group similarly placed. From another point of view, it may be said that the second mole of formaldehyde is introduced into phenol at about one-third the rate at which the first mole of formaldehyde enters. If this is true, then the rate law observed to hold for a given di- or tri-functional phenol expresses, apparently, a summation of the rates at which the first, the second and presumably also the third molecule of formaldehyde react.

(11) Auwers, *Ber.*, **40**, 2528 (1907).

(12) The apparent falling off in free formaldehyde concentration from this point on is entirely accounted for, within experimental error, by the physical process of sublimation.

(13) Bamberger, *Ber.*, **36**, 2036 (1903).

(14) Granger, *Ind. Eng. Chem.*, **24**, 442 (1932).

(15) (a) Seebach, *Fette u. Seifen*, Sept., 509–511 (1938); (b) Stäger and Biert, *Helv. Chim. Acta*, **21**, 642 (1938); (c) Zincke, Hanus and Ziegler, *J. prakt. Chem.*, **152**, 128 (1939). These papers may be consulted for references to much of the previous literature in the field.

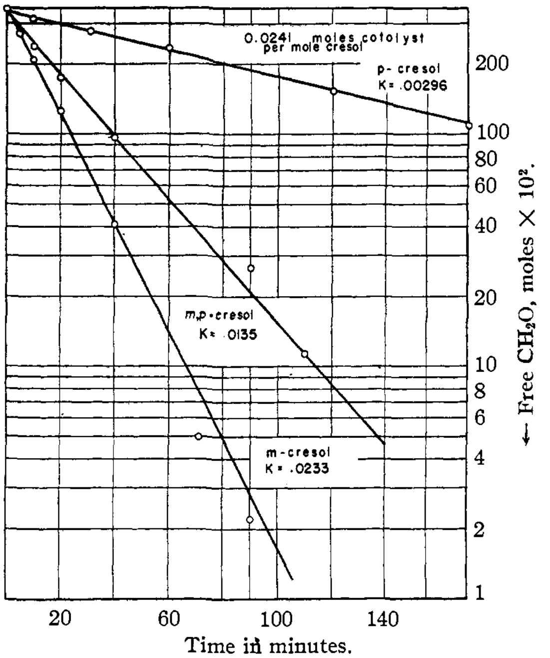


Fig. 3.—Comparison of the reactivities of *p*-cresol, *m*-cresol and *m,p*-cresol at 98 ± 1°.

More light is thrown on this particular question by the behavior of a mixture of 40% *m*- and 60% *p*-cresol, shown in Fig. 3. This mixture apparently reacts with formaldehyde in accordance with a first order law, during at least 95% of the reaction. The rate for *m-p*-cresol (0.0135) is much closer to that of *m*- than to that of *p*-cresol. The observed rate is about 10% lower than that which would be calculated on the assumption that the rate should be given by the expression:

$$K_{\text{meta-para}} = 0.6\,K_{\text{meta}} + 0.4\,K_{\text{para}}$$

Variations of Phenol-Formaldehyde Ratio.—The effect of increasing the ratio of paraformaldehyde to phenol is to decrease the speed of the reaction. This is shown in Figs. 4 and 5. In the case of phenol at 98 ± 1°, with 0.0241 mole of triethanolamine per mole of phenol the rate of the reaction is given by

$$K = 0.0069\,C$$

where K is the rate of disappearance of formaldehyde, and C is the molar ratio of phenol to formaldehyde.

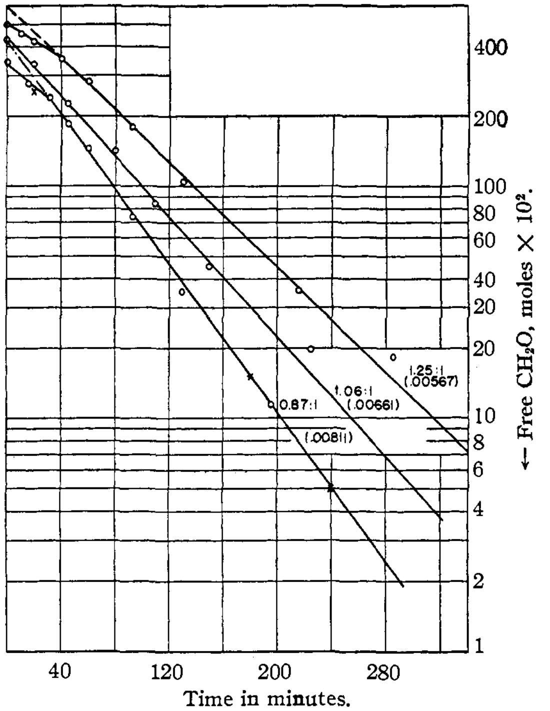


Fig. 4.—Dependence of rate on initial formaldehyde concentration, phenol at 98°.

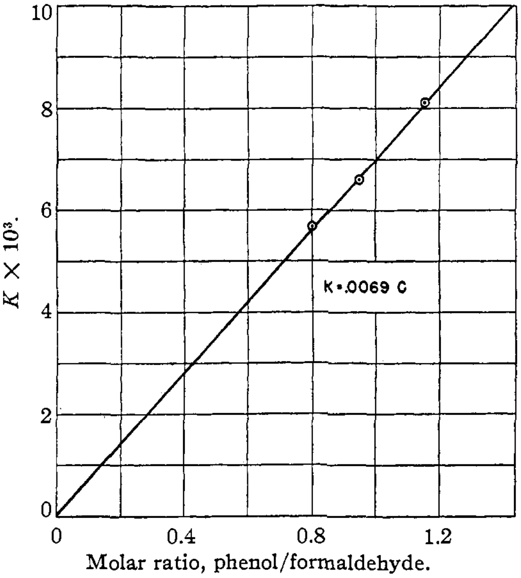


Fig. 5.—Variation of rate with formaldehyde concentration, phenol at 98°.

The straight lines in graph 4 do not go through the points representing initial formaldehyde concentrations. The reaction rates during the first twenty to forty minutes, in other words, are abnormally slow. This phenomenon was observed only in the case of phenol (and during two runs with *m*-cresol, as shown in Fig. 6), and although it is apparently real, there seems to be no obvious explanation for it. These reactions appear to follow, approximately, a bimolecular rate law during this period, an observation that may have some significance for the question of the reaction mechanism involved. This question cannot be treated more fully at this time.

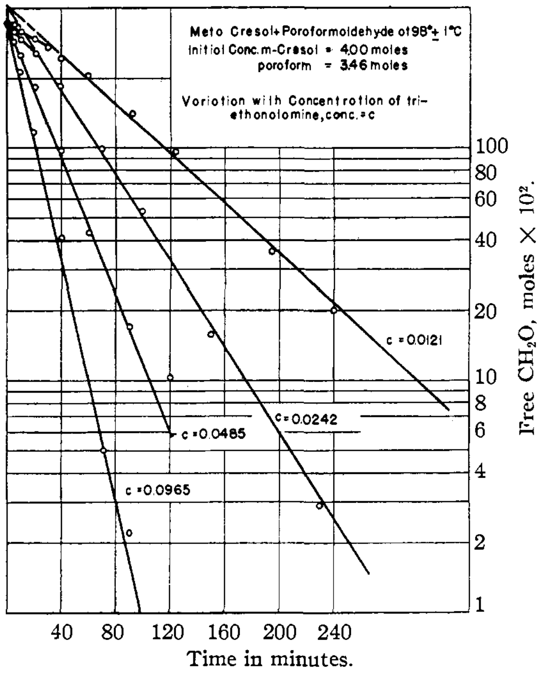


Fig. 6.

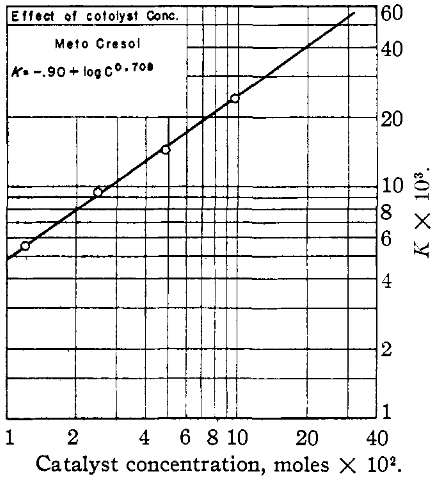


Fig. 7.—Effect of catalyst concentration.

Effect of Catalyst Concentration.—The effect of the catalyst concentration was determined at 98°, using *m*-cresol, and the results are shown in Figs. 6 and 7. The catalyst concentration was varied from 0.0241 mole to 0.00302 mole per mole of *m*-cresol. The catalyst function is shown by the log–log plot of Fig. 7 to be defined by the equation

$$\log K = -0.90 + \log C^{0.708}$$

where C is catalyst concentration in moles per 4 moles of *m*-cresol.[16]

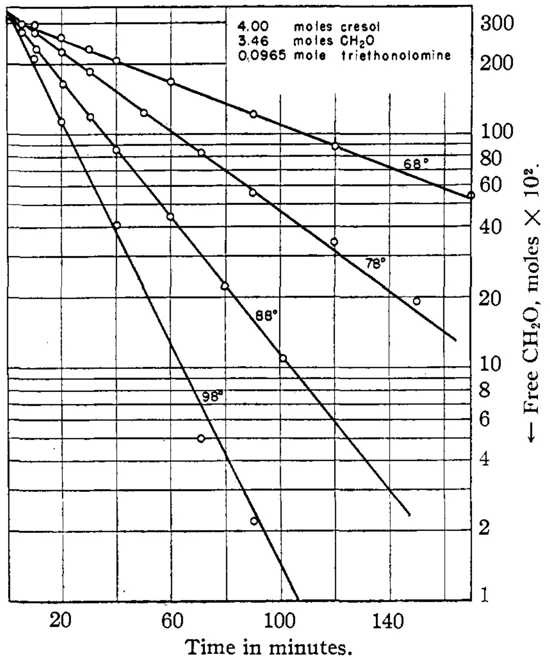


Fig. 8.—*m*-Cresol + paraformaldehyde, variation of rate with temperature.

Effect of Temperature.—Using *m*-cresol, again, and 0.0241 mole of triethanolamine per mole of cresol, the temperature was varied from 98 ± 1° to 68 ± 1°. These data are reproduced in Fig. 8. In Fig. 9 the graphically determined

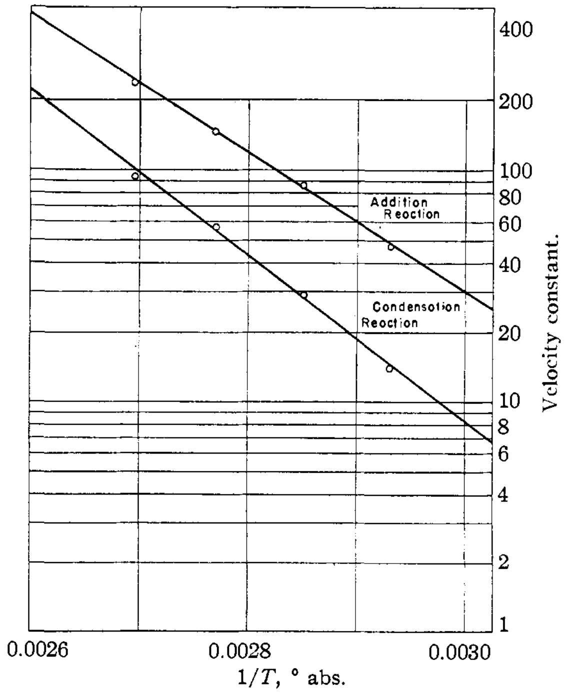


Fig. 9.—Variation of velocity constant with temperature; *m*-cresol + paraform in presence of triethanolamine.

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(16) If the catalyst concentration is expressed in moles per mole of *m*-cresol, this equation becomes $\log K = -1.20 + \log C^{0.708}$.

values of the rate constant, K, are plotted against the reciprocal of the absolute temperature. From the slope of the straight line obtained, the heat of activation may be calculated from the Arrhenius equation

$$\frac{\log K_2 - \log K_1}{1/T_2 - 1/T_1} = -\frac{E}{4.57}$$

from which E = 13,800 cal. per mole, for the addition reaction. This rather low value is understandable when one considers that the addition of formaldehyde to most phenols in the presence of alkaline catalysts occurs readily at room temperature, and very readily at 100°. The average temperature coefficient over the range studied is 1.71 per 10°.

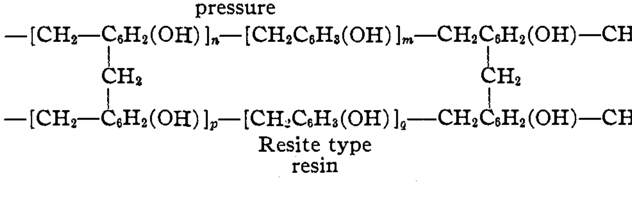
The Condensation Reaction

General Considerations.—Evidence accumulated during the past twenty years indicates that when phenol and formaldehyde are caused to react together in the presence of an alkaline catalyst, the following equations fundamentally describe the processes which occur

$$\text{(1)}\quad C_6H_5OH + CH_2O \xrightarrow[\text{low temp.}]{OH^-} \begin{array}{c} C_6H_4(OH)(CH_2OH) \\ o\text{-hydroxybenzyl alcohol (saligenin)} \\ p\text{-hydroxybenzyl alcohol} \\ \downarrow \\ \underset{\text{dimethylol phenols}}{C_6H_3(OH)(CH_2OH)_2} + \underset{\text{trimethylol phenol}}{C_6H_2(OH)(CH_2OH)_3} \end{array}$$

$$\text{(2)}\quad n\text{-}C_6H_4(OH)(CH_2OH) \xrightarrow[H^+ \text{ or } OH^-]{\text{heat}}$$

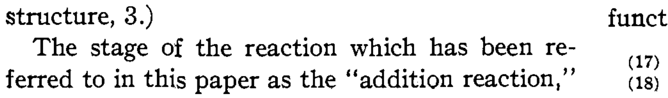
$$HOC_6H_4[CH_2C_6H_3(OH)]_{n-1}—CH_2OH + (n - 1)H_2O$$



$$\text{(1a)}\quad C_6H_5OH + 1.1\text{-}1.5\ CH_2O \xrightarrow{OH^-}$$

$$—CH_2\underset{\substack{|\\ CH_2\\ |\\ C_6H_4OH}}{C_6H_2(OH)}—[CH_2C_6H_3(OH)]_m—CH_2\underset{\substack{|\\ CH_2\\ |\\ C_6H_3(OH)(CH_2OH)}}{C_6H_2(OH)}—CH_2OH$$

Resole type resin



$$\text{(3)}\quad \text{Resole resin} \xrightarrow[\text{pressure}]{\text{heat}}$$

$$\begin{array}{l} —[CH_2—C_6H_2(OH)]_n—[CH_2C_6H_3(OH)]_m—CH_2C_6H_2(OH)—CH_2— \\ \qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\quad CH_2 \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2 \\ \qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ —[CH_2—C_6H_2(OH)]_p—[CH_2C_6H_3(OH)]_q—CH_2C_6H_2(OH)—CH_2— \end{array}$$

Resite type resin

(Potential cross-linking is indicated in the resole structure, 1a; actual cross-linking in the resite structure, 3.)

The stage of the reaction which has been referred to in this paper as the "addition reaction," consisting in the addition of one or more molecules of formaldehyde to the phenol (and possibly to more complex phenolic substances, once these have been formed), is represented by process 1; and also as a step, or steps, is implicit in process 1a. The condensation stage of the reaction is implicit in processes 1a, 2 and 3.

The discussion which is to follow will be predicated on the assumption that we are dealing with these reactions in the systems now under consideration.

Results of Bromination Studies.—The bromination procedure, which is described in detail elsewhere,[9] has been used previously, particularly in relation to the specific questions now under consideration by Nordlander,[6] and by Koebner.[17] It was applied to the present problem in an attempt to learn something about the speeds of the condensation reactions. The assumption that bromine reacts quantitatively at unsubstituted ortho and para positions, and at no other positions in the molecule, was found earlier not to be justified.[9] However, a partial analysis of the condensation reactions can be made, if one makes the proper allowance for certain observed abnormalities.

First, however, it is of interest to present, purely empirically, the results obtained from the bromination studies. The decrease in reactive positions, (that is, positions in an aromatic nucleus which are capable of reaction with formaldehyde) measured by the decrease in bromine value, occurs at a very slow rate, compared to the decrease in free formaldehyde concentration. These data are shown in Figs. 10 and 10a. This decrease in potential reactive positions appears, within the limits of experimental error, to be approximately a linear function of time; in other words, the condensation reactions seem, at first glance, to be governed by a zero order rate law, or at least to proceed at a very slow tempo compared to the addition reactions. Somewhat similar observations have been made previously by Granger[18] and by Holmes and Megson.[4a] The phenols studied are divided sharply into two groups. The first group, consisting of the trifunctional phenols and saligenin, is characterized

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[17] Koebner, *Z. angew. Chem.*, **46**, 253 (1933).

[18] Granger, *Ind. Eng. Chem.*, **29**, 860, 1125 (1937).

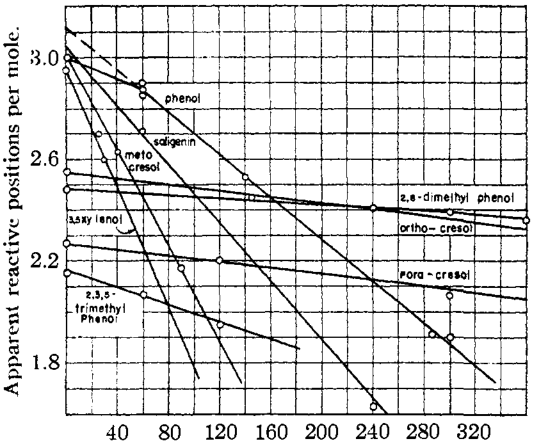


Fig. 10.—Apparent decrease in reactive positions with time for various phenols during reaction with paraform at 98 ± 1°.

by a much faster speed of condensation than the second group, consisting of the bi-functional phenols and a single mono-functional phenol. In both groups, the rate at which condensation occurs parallels, roughly, the rate at which addition of paraformaldehyde occurs under the same conditions; *i. e.*, 3,5-xylenol > *m*-cresol > phenol; and 2,3,5-trimethylphenol > 3,4-xylenol and 2,5-xylenol > *o*- and *p*-cresol > 2,6-xylenol. Saligenin occupies a unique position: whereas its rate of addition of formaldehyde is about equal to that of *o*- and *p*-cresol, its rate of condensation under these same conditions (as measured by the change in bromine value) is about equal to that of phenol.

The rate of condensation of phenol itself seems to be abnormally slow during the first forty to sixty minutes of reaction at 98°. There is no obvious explanation of this peculiarity; it seems to parallel the similar abnormality in speed of addition of formaldehyde during this interval.

Under the conditions used in this study,[9] saligenin reacts with exactly three moles of bromine, rather than with two, as anticipated from its structure. By analogy, it seems reasonable to assume that any methylol group in the ortho or para position to a phenolic hydroxyl will behave as though it were free, rather than combined, formaldehyde. This implies that when one measures the decrease in bromine value of a system in which the composite reaction

$$nC_6H_5OH + nCH_2O \longrightarrow C_6H_4(OH)—[CH_2C_6H_3(OH)]_{n-1}—CH_2OH + (n - 1)H_2O$$

or its equivalent, is occurring, this analysis con-

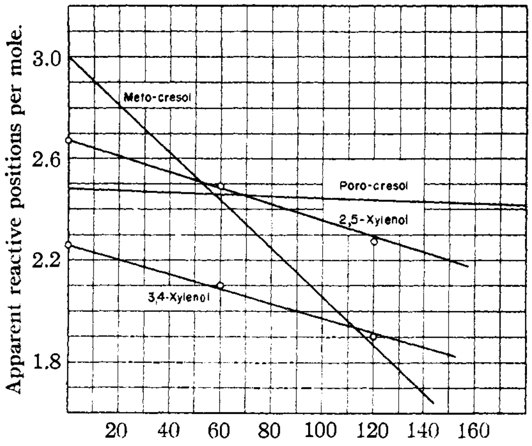


Fig. 10a.—Apparent decrease in reactive positions for 3,4-dimethylphenol and 2,5-dimethylphenol at 98°.

stitutes a measure of the extent of condensation. This is apparent if one considers that the addition of a methylol group causes no change in bromine value, but its loss by condensation eliminates *two* apparent reactive positions. One complication must be taken into consideration in the interpretation of such data, namely, that a *methylene group* in the ortho or para position to a hydroxyl group reacts with bromine under the conditions involved in these measurements. Certain compounds having structures closely resembling those of the condensation products formed from phenols and formaldehyde were studied,[9] including dihydroxydiphenylmethane, which is of particular interest in the present connection. In this case, the methylene group caused the absorption of 0.15 mole of bromine in excess of that calculated. Taking this into account, a calculation of the amount of condensation can be made from the disappearance of formaldehyde and the decrease in bromine value.

Let a = initial amount of phenol, in moles
b = initial amount of paraformaldehyde, in moles
c = amount of formaldehyde at time t
n = average chain length of phenols present *including unchanged monomer*
r_0 = initial reactive positions per mole of phenol
r_t = final reactive positions (apparent) per mole of phenolic nucleus.

Assuming that comparatively little cross-linking occurs at low initial ratios of formaldehyde to phenol, the decrease in formaldehyde then determines the decrease in free phenol concentration. Then, at time t, the number of moles of polymer formed is equal to $(b - c)/n$. The total number

TABLE II

AVERAGE CHAIN LENGTH OF PHENOL–PARAFORMALDEHYDE REACTION PRODUCTS

Phenol	Moles of CH_2O per mole phenol Taken	Reacted	Reaction time, at 98°, min.	Apparent reactive positions Initial	Final	n (av.)	Remarks
Phenol	0.87	0.85	291	3.00	2.03	2.6	
Phenol	1.05	1.04	300	3.00	1.90	2 .3	
Phenol	1.25	1.20	285	3.00	1.89	2.0	
o-Cresol[a]	0.87	0.78	545	2.57[a]	2.13	1.4	
p-Cresol	.87	.81	420	2.27	1.96	1.3	
m-Cresol	.87	.86	90	2.98	1.71	2.1	98°
m-Cresol	.87	.84	101	2.98	2.43	1.6	88°
m-Cresol	.87	.83	150	2.98	2.57	1.4	78°
m-Cresol	.87	.83	300	2.98	2.68	1.3	68°
3,5-Xylenol	.87	.85	30	2.95	1.91	1.3	
2,6-Xylenol	1.05	.53	855	2.56	2.58	2.0	Dimer formed
2,3,5-Trimethylphenol	0.87	.77	155	2.15	1.94	1.2	
3,4-Xylenol	.87	.77	120	2.26	1.90	1.3	
2,5-Xylenol[a]	.87	.74	120	2.67[a]	2.14	1.6	

[a] *o*-Cresol and 2,5-xylenol, structurally related to *o*-cresol, show an appreciably higher absorption of bromine in the presence of formaldehyde than in its absence. Slightly high initial bromine values were shown by other phenols in the presence of formaldehyde, but in general the discrepancies were within the experimental error. The peculiarity of these two phenol–paraform systems in this regard is not at present understood.

of apparent reactive positions is given by the expression

$$r_t a = r_0 a - (b - c) + [(n - 1)(r_0 - 1.85) + r_0](b - c)/n$$

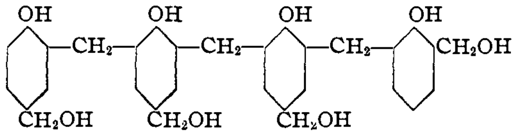
from which

$$\frac{n - 1}{n} = \frac{a(r_0 - r_t)}{1.85(b - c)}$$

The chain length of the resin at any given time can be estimated *approximately* by means of this relationship. Approximate values of n at fairly advanced stages of the "addition" reaction, for various phenol–formaldehyde reaction products, are given in Table II.

It appears, from Table II, that resins of very low average chain length are formed under the conditions described in this paper. In so far as comparisons are possible, resins of greatest complexity are obtained from phenol. The introduction of methyl groups, the use of increased amounts of paraformaldehyde, or a decrease in the temperature at which the resinification is carried out leads to a decrease in the average chain length.

Saligenin Condensation.—Since the case of saligenin involves the introduction of considerably more than one mole of formaldehyde per phenolic nucleus, the chain length cannot be estimated in the above manner. But on the preliminary assumption that all methylol groups in the resin behave toward bromine as does the single one in saligenin itself, an approximate estimate of the average molecular weight can be obtained. The final bromine value indicated 1.62 apparent reactive positions per mole, and at this time 0.77 mole of formaldehyde had combined per mole of saligenin (or 1.77 mole per mole of phenol). Using these results, equating the values for combined formaldehyde and for apparent reactive positions per mole according to the relationships previously elucidated, and solving the simultaneous equations set up, it may be estimated that the reaction product[19] consists essentially of "methylene-saligenin" tetramers, of which one possible isomeric modification is shown below.



	Calcd.	Found
Methylene and methylol groups per phenolic nucleus	1.75	1.77
Apparent reactive positions per phenolic nucleus	1.61	1.62

Effect of Temperature on the Condensation Reaction.—The apparent rate of decrease in reactive positions for *m*-cresol at 68, 78, 88 and 98° is shown in Fig. 11. Taking the slopes of the approximately straight lines obtained, and plotting these values against the reciprocal of the absolute temperature, an estimate of the heat of activation of the condensation reaction can be

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[19] This product was a very slow "curing" resin, a fact which is understandable when it is considered that such molecules have relatively few unoccupied positions available for further condensation. The above molecule, for example, has only 0.25 position per nucleus available for condensation, whereas saligenin itself has 2.00 available positions and phenol has 3.00.

obtained (Fig. 9), namely, 15,800 cal. per mole, or about the same as that calculated for the addition reaction.

Summary

The reaction between phenols and paraformaldehyde in the presence of a weak alkaline catalyst has been studied with ordinary phenol, eight alkylated phenols and saligenin.

The addition of formaldehyde apparently follows a first order rate law. The rate constants decrease in the following order: 3,5-xylenol > *m*-cresol > 2,3,5-trimethylphenol > phenol > 3,4-xylenol > 2,5-xylenol > *p*-cresol > saligenin > *o*-cresol > 2,6-xylenol.

2,6-Xylenol reacts with exactly one-half mole of formaldehyde under these conditions, and the chief reaction product is the diphenylmethane derivative.

The observed velocity constants are composites of the rates of addition of the first, second and third moles of formaldehyde. The behavior of saligenin indicates that the second mole of formaldehyde is added at about one-third the rate of the first.

The effects of variation in phenol–formaldehyde ratio, catalyst concentration and temperature are discussed and illustrated graphically.

A bromination procedure has been used to gain an insight into the condensation processes, which involve the conversion of methylol to methylene groups. These reactions are very slow compared to the addition reactions.

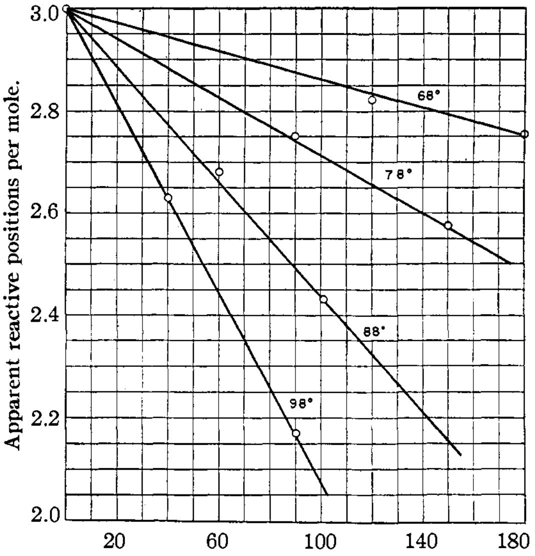

Fig. 11.—The condensation reaction: variation with temperature for *m*-cresol + paraformaldehyde.

The condensation rates for the phenolic systems studied are in the same relative order as the addition rates, except that a saligenin–formaldehyde mixture condenses at a rate about equal to that of a phenol–formaldehyde mixture.

A method is given for estimating the average chain length from the formaldehyde addition and bromination data.

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[CONTRIBUTION NO. 89 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Nature of Oils Obtained from the Hydrogenation of a Few Typical Bituminous Coals[1]

BY CLAIRE D. LECLAIRE

From a study of the oils resulting from the high pressure hydrogenation of the extract and residue from the benzene extraction of Pittsburgh coal, Biggs and Biggs and Weiler[2] concluded that the benzene soluble and insoluble parts of this coal are similar in their essential chemical structure and that the oils formed by their hydrogenation are chiefly polycyclic hydroaromatic hydrocarbons. This conclusion is supported by further data described in the present paper, which summarizes hydrogenation studies not only of Pittsburgh coal, but also of Pocahontas no. 3, High Splint, and Illinois no. 6 coals.[3] These latter three coals were selected to determine the dependence of the nature of the hydrogenation products on the rank and type of certain bituminous coals. The hydrogenations were carried out in the presence of Adkins catalyst at 350°, a temperature that gave good yields of petroleum ether soluble products and avoided extensive degradation of the hydrocarbon structures.

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(1) Original manuscript received March 16, 1940.

(2) (a) B. S. Biggs, THIS JOURNAL, **58**, 1020 (1936); (b) B. S. Biggs and J. F. Weiler, *ibid.*, **59**, 369 (1937).

(3) Wm. B. Warren, *Ind. Eng. Chem.*, **30**, 136 (1938).