93. Y. Iwakura, Y. Imai, S. Inone, and K. Uno, *Makromol. Chem.*, **95**, 236 (1966).
94. W. Wrasidlo and H. H. Levine, *J. Polymer Sci.*, *A*, **2**, 4795 (1964).
95. D. N. Gray, G. P. Shulman, and R. T. Conley, *J. Macromol. Sci.*, *Chem.*, A-**1**(3), 395 (1967).
96. R. Gosnell, Whittaker Research and Development, San Diego, Cal., private communications.
97. H. H. Levine, in *Encyclopedia of Polymer Science and Technology* (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Vol. 11, Wiley-Interscience, New York, 1969, p. 188.
98. M. Saga, M. Hachihama, and T. Shono, *J. Polymer Sci.*, *A1*, **8**, 2265 (1970).
99. B. L. Loudas, Minnesota Mining and Manufacturing Co., U.S. Patent 3,503,929 (1970).
100. W. Fitzgerald and H. H. Levine, Whittaker Research and Development, San Diego, Cal., private communications.
101. W. R. Sorenson, *Am. Chem. Soc., Div. Polymer Chem., Preprints*, **2**(2), 226 (1961).
102. G. P. deGaudemaris and B. J. Sillion, *J. Polymer Sci.*, *B*, **2**, 203 (1964).
103. G. P. deGaudemaris, B. J. Sillion, and J. Prévé, *Bull. Soc. Chim. France*, **1964**, 1763.
104. J. K. Stille and J. R. Williamson, *J. Polymer Sci.*, *A*, **2**, 3867 (1964); *ibid.*, *B*, **2**, 209 (1964).
105. J. K. Stille, J. R. Williamson, and F. E. Arnold, *J. Polymer Sci.*, *A*, **3**, 1013 (1965).
106. P. M. Hergenrother and H. H. Levine, *J. Appl. Polymer Sci.*, **14**, 1037 (1970).
107. P. M. Hergenrother, *J. Polymer Sci.*, *A1*, **6**, 3170 (1968).
108. W. Wrasidlo and J. M. Augl, *J. Polymer Sci.*, *A1*, 7, 3393 (1969).
109. W. Wrasidlo and J. M. Augl, *Am. Chem. Soc., Div. Polymer Chem., Preprints*, **10**(2), 1353 (1969).
110. P. M. Hergenrother, *J. Macromol. Sci., Rev. Macromol. Chem.*, *C*, 6(1), 1 (1971).
111. P. M. Hergenrother and W. Wrasidlo, unpublished work.
112. P. W. Morgan, *Condensation Polymers*, Wiley-Interscience, New York, 1965, p. 125.
113. W. Wrasidlo, *J. Polymer Sci.*, *A1*, **8**, 1107 (1970).
114. W. Wrasidlo, Gulf Energy & Environment Systems, San Diego, Calif., private communication.
115. W. Wrasidlo, *Am. Chem. Soc., Div. Polymer Chem., Preprints*, **11**(2), 1159 (1970).
116. W. Wrasidlo, *J. Polymer Sci.*, *A-2*, **9**, 1603 (1971).
117. J. K. Stille, in *Encyclopedia of Polymer Science and Technology* (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Vol. 11, Wiley-Interscience, New York, 1969, p. 389.
118. V. L. Bell and G. F. Pezdirtz, *J. Polymer Sci.*, *B*, **3**, 977 (1965).
119. F. Dawans and C. S. Marvel, *J. Polymer Sci.*, *A1*, **3**, 3549 (1965).
120. J. G. Colson, R. H. Michel, and R. M. Paufler, *J. Polymer Sci.*, *A1*, **4**, 2349 (1966).
121. V. L. Bell and R. A. Jewell, *J. Polymer Sci.*, *A1*, **5**, 3043 (1967).
122. V. L. Bell, *J. Polymer Sci.*, *B*, **5**, 941 (1967).
123. R. M. Paufler, E. I. du Pont de Nemours & Co., U.S. Patent 3,414,543 (1968).
124. V. L. Bell, in *Encyclopedia of Science and Technology* (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Vol. 11, Wiley-Interscience, New York, 1969, p. 240.
125. R. L. Van Deusen, *J. Polymer Sci.*, *B*, **4**, 211 (1966).
126. R. L. Van Deusen, O. K. Goins and A. J. Sicree, *J. Polymer Sci.*, *A1*, **6**, 1777 (1968).
127. F. E. Arnold and R. L. Van Deusen, *Macromolecules*, **2**, 497 (1969).
128. J. K. Stille and E. Mainen, *J. Polymer Sci.*, *B*, **4**, 39 (1966); *Ibid.*, *B*, **4**, 665 (1966).
129. H. Jadamus, F. DeSchryver, W. DeWinter, and C. S. Marvel, *J. Polymer Sci.*, *A1*, **4**, 2831 (1966).
130. F. DeSchryver and C. S. Marvel, *J. Polymer Sci.*, *A1*, **5**, 545 (1967).
131. M. Okada and C. S. Marvel, *J. Polymer Sci.*, *A1*, **6**, 1259 (1968).
132. M. Okada and C. S. Marvel, *J. Polymer Sci.*, *A1*, **6**, 1774 (1968).
133. R. Wolf, M. Okada, and C. S. Marvel, *J. Polymer Sci.*, *A1*, **6**, 1503 (1968).
134. J. K. Stille and M. E. Freeburger, *J. Polymer Sci.*, *A1*, **6**, 161 (1968).

Chapter 5

THE REACTIONS OF FORMALDEHYDE WITH PHENOLS, MELAMINE, ANILINE, AND UREA

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I. Introduction

The original intent of this chapter was to discuss the chemistry of the reaction of formaldehyde with compounds containing active hydrogens, to form polymers or products capable of polymerization. Partly because this scope was much too broad, but mostly for personal preference, this work will be limited to materials and systems of commercial significance. We are convinced that resinous materials of commerce offer great scientific challenge. They are seldom exposed to ideal conditions, they require convenient process manipulation, and synthesis procedures are dictated by economics and performance. The result is a "controlled" randomness. Mechanisms involve simultaneous, competitive, and consecutive reactions which result in a large number of isomeric structures and, more likely than not, these can react intermolecularly to form high molecular weight products leading to three-dimensional networks.

The progress in the field of kinetics and mechanisms is largely dependent on the analytical tools available for quantitative description of the systems. Periodically, new techniques become available and a resurgence of research occurs to refine old results, generate new information, and open new areas of interest. In the present case, early work followed classical synthetic organic chemical approaches. Without the necessary analytical tools, studies were restricted to artificial conditions bearing little relation to practical synthetic approaches. Painstakingly, however, a reasonable understanding of the fundamentals of condensation was acquired.

In the early 1950's, paper chromatographic analysis was adapted for the separation of some phenol–formaldehyde condensates and is still used in studies of these systems. More recently, proton magnetic resonance, gas–liquid chromatography, and gel permeation chromatography have added new dimensions to our analytical capabilities. These techniques have yet to be extended significantly to amino systems where detailed knowledge of structure is still lacking.

It was felt appropriate at this time to update the records of kinetics and mechanisms of formaldehyde reactions with compounds containing active hydrogens. To cover the field in its entirety would be a prohibitive task. We have, therefore, chosen to limit our discussions to reactions of formaldehyde with phenol, melamine, aniline, and urea. Emphasis will be placed on systems which are closely akin to commercial practice when possible, closely relatable where not, or a bit removed where little information exists but is relevant. Many favorite subjects of past years will be omitted. Not that they are unimportant, but we choose to emphasize results of the past decade, with reference to earlier work where necessary.

It seems most appropriate to begin our discussion with a review of the one common denominator, formaldehyde. Its properties and behavior relative to the conditions under which most reactions are performed are of greatest interest. Reactions with active hydrogens will emphasize unsubstituted monomers and other conditions most typical of commercial practice. Thus aqueous systems will predominate in the discussion. Likewise, discussion of variables such as molarity of reactants, mole ratios, pH, temperatures, etc., will emphasize those of commercial importance where possible. Exceptions will be numerous, owing to lack of other data, and these must be considered as illustrative. With all due respect to workers of earlier years, we may be more partial to those using recent concepts and newer analytical techniques. Where literature is reviewed elsewhere, it will not be repeated here unless the specific work is essential to our presentation.

Although we may disagree with the conclusions of some reported research we freely acknowledge the experimental results and often find that our reluctance to accept conclusions is based on the need for more detail. Finally, we may disagree on occasion, reinterpret on others, and offer suggestions freely. If we accomplish no more than encourage more research to satisfy controversy, we will have achieved our goal.

II. Formaldehyde

For all practical purposes, commercial products synthesized by the reaction of formaldehyde with compounds containing active hydrogens (1) use a source of formaldehyde containing little monomer, as CH_2O, (2) are manufactured in aqueous media, with or without the presence of low molecular weight alcohols, (3) are catalyzed over a pH range of 1–12, and (4) may be subjected to temperatures of 50°–105°C during the initial reaction. Formaldehyde is present in a reactive form owing to a series of equilibria affected by the preceding conditions. The nature of these equilibria and of the reactive form of the coreactant in the reaction environment govern the kinetics and mechanisms of the reactions.

Although the chemical nature of formaldehyde itself has been studied in depth under controlled conditions, little has been done to describe the effects of specific reaction media on the equilibria which provide the reactive form and on the rate at which they are established. This is unfortunate because one cannot quantify kinetics without this knowledge. It becomes particularly important as the reactions proceed toward completion. We feel that future research in this direction will explain anomalies and uncertainties which now exist.

Reference to the reactive form of formaldehyde and equilibria in specific environments will be made throughout this chapter. Some of the more significant properties of formaldehyde, important to the context of our subsequent discussions, will be reviewed here.

The most complete reference on formaldehyde is by Walker (*1*), which is current through 1963. Reactions with active hydrogens are reviewed; however, emphasis is placed on the coreacting species and the treatment is incomplete. On the other hand, the chemistry of formaldehyde is discussed most thoroughly and this reference will be used extensively in this chapter.

Formaldehyde in pure form is not readily available and is often impractical to use in the chemistry discussed in this chapter. As a gas, formaldehyde (CH_2O) polymerizes slowly at room temperature, but is reported to be stable between 80° and 100°C and to obey the laws of an ideal gas (*2*). Liquid monomer polymerizes slowly at −80°C, even in the purest form. Slight traces of impurities promote rapid polymerization; rates can be explosive. Water, acids, and alcohols are catalytic.

The most important commercial sources of formaldehyde are aqueous solutions, usually containing small amounts of formic acid and in some cases up to 15% methanol, and solid polymeric hydrates (paraformaldehyde). For reasons to be explained later, water (and methanol) are added to some extent when paraformaldehyde is used in some reactions. In the presence of water, paraformaldehyde dissolves with hydrolysis and depolymerizes, resulting in solutions identical to those obtained by dissolving formaldehyde (*3*). Thus it is subject to the same equilibria as the aqueous formaldehyde solutions of commerce.

A special source of methylene groups, hexamethylenetetramine, will be dealt with in the text where appropriate. The reactions of this distinct entity do not fall within the field of typical formaldehyde chemistry.

In aqueous media, formaldehyde is present in such small amounts (<0.1%) that it is usually neglected in considerations of equilibria and often in reactions with active hydrogens. This is not totally justified as will be seen later. These solutions are composed of the monomeric hydrate, presumably as methylene glycol ($HOCH_2OH$), and low molecular weight polymeric hydrates $HO(CH_2O)_nH$ in equilibrium, which may be represented by

$$CH_2O + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCH_2OH \qquad K_1 = \frac{k_1}{k_{-1}} \tag{1}$$

$$nHOCH_2OH \overset{K_2}{\rightleftharpoons} HO(CH_2O)_nH + nH_2O \tag{2}$$

$$HOCH_2OH + HO(CH_2O)_nH \overset{K_3}{\rightleftharpoons} HO(CH_2O)_{n+1}H + H_2O \tag{3}$$

etc.

The K represents an equilibrium constant and k a velocity or rate constant. Low degrees of condensation are favored by dilution, higher temperatures, and the presence of alcohols (methanol). These equilibria are only slowly established, particularly when solid polymer is present.

Kinetics of condensation reactions are obviously influenced by the conditions that promote the presence of a reactive species. It is becoming more generally accepted that, in many reactions, the reactive form of formaldehyde in aqueous medium is a monohydrate, $CH_2O{\cdot}H_2O$. The structure of this hydrate is unknown but it is usually assumed to be $HOCH_2OH$, or methylene glycol.

Although the concepts using this form have been commonly accepted, proof is not rigorous or exclusive. Formaldehyde is present in such small concentrations that it has been concluded to be a less influential form than the hydrate. Yet mechanisms can be rationalized using either species. Kinetics are less defined since formaldehyde equilibria are not adequately quantified.

At this time we are in no position to defend or accept either form as exclusive. It will be seen that both forms are used in our discussion. We are not pleased with this limitation.

Iliceto, Auerbach, Bell, and their co-workers have provided much of the extensive background on aqueous formaldehyde systems. Their research will be cited where appropriate. Working with solutions of relatively pure formaldehyde, they have, in extensive analytical work, described these aqueous systems in detail, recognizing, however, that such complex equilibria are seldom completely defined. Such solutions differ from commercial formaldehyde solutions which contain methanol and formic acid in various amounts. This does not detract seriously from the significance of this work, but the presence of methanol will be shown to be important in the study of reactions with active hydrogens.

Equilibria represented by Eqs. (1)–(3) have been described kinetically. In general, studies have neglected equilibria between solution and vapor and between solution and solid polymer. These equilibria are not quickly attained (*4*).

Equation (1) illustrates solvation of formaldehyde by water. Methylene glycol has never been isolated, but its existence is reasonably substantiated. With dilute formaldehyde solutions, 2% for example, ultraviolet absorption and Raman spectra show that the carbonyl group is virtually absent, while in hexane the spectrum for formaldehyde ($H_2C{:}O$) is characteristic (*5*). Nielson and Ebers (*6*) review the subject of monomeric formaldehyde and emphasize the absence of Raman spectra corresponding to CH_2O in aqueous solution. The formaldehyde content has been measured at solution concentrations from 2 to 28.4% and at 30° and 60°C (*1*, p. 61). It varies from 0.001

to 0.026 wt% which is very small indeed. Formaldehyde is generally neglected in considerations of equilibria concerning polyoxymethylene glycols in water. Some mechanisms of reactions with active hydrogens are difficult to explain when using methylene glycol; most may be explained when using formaldehyde. If the latter is the important species in aqueous systems, much more refined analytical techniques are needed to avoid reliance on the hydrated form in studies of reactions.

The hydration of formaldehyde is rapid. It has been concluded (*7*) that the lowest velocity constant (k_1) for this reaction is about 10 sec^{-1} at ordinary temperatures. The direct measurement of this constant has not been studied. The rate of dehydration has been studied most recently by Bell and Evans (*7*) and by Hénaff (*8*), the former being much more thorough. These workers show an order of magnitude of $k_{\text{dehyd}} = k_{-1} = 5.1 \times 10^{-3}\ \text{sec}^{-1}$ at pH 7 and 25°C. The rate is increased at higher and lower pH values and account must be taken of the catalytic effect of the reagent used to measure the concentration of dehydrated monomer.

Using a scavenger for formaldehyde, Bell and Evans (*7*) determined the rate constants of dehydration of methylene glycol at pH < 7 where many reactions with active hydrogens are performed. The difference in calculated and measured values at pH 1 is attributed to conversion of the scavenger (semicarbazide) to an inactive form at this low pH. Values above pH 8.5 (another condition for many reactions) could not be measured since dehydration of methylene glycol was too fast for the method of measurement used.

	k_{-1}, sec^{-1}	
pH	Observed	Calculated
2	2.5×10^{-2}	3.4×10^{-2}
1	9×10^{-3}	2.9×10^{-1}

A situation exists, therefore, which may justify questions regarding the active form of formaldehyde at pH less than 3 and greater than 8; these are conditions for most reactions of formaldehyde of the type discussed in this chapter. Since so few quantitative data exist on the equilibrium in Eq. (1), we have chosen to consider $HOCH_2OH$ as the active form, particularly in aqueous systems at low pH, with recognition that formaldehyde must be reconsidered in this light as more quantitative data become available. Formaldehyde and its monohydrate are in proportion to one another, thus kinetic equations can be adapted to the concentration of either so long as it is consistent that the reactive forms are monomeric structures, not formaldehyde polymers.

The equilibrium constant for the dehydration of methylene glycol [Eq. (1)] varies from $K_1 = 1 \times 10^{-4}$ to 30.1×10^{-4} over a temperature range of 0° to 64°C (*1*, p. 62) at the "equilibrium" pH ≅ 3:

$$K_1 = \frac{(CH_2O_{aq})(H_2O_{liq})}{CH_2(OH)_{2aq}} \tag{4}$$

Obviously K_1 is temperature dependent. Using the data summarized by Walker (*1*, p. 62), mathematical extrapolation of a plot of $\log_{10}K_1$ vs 1/°K results in a straight line represented in Fig. 1. Statistical confidence in this extrapolation is 95% and the plot includes the upper and lower confidence limits of the best least-squares line. The equation for the line is given by

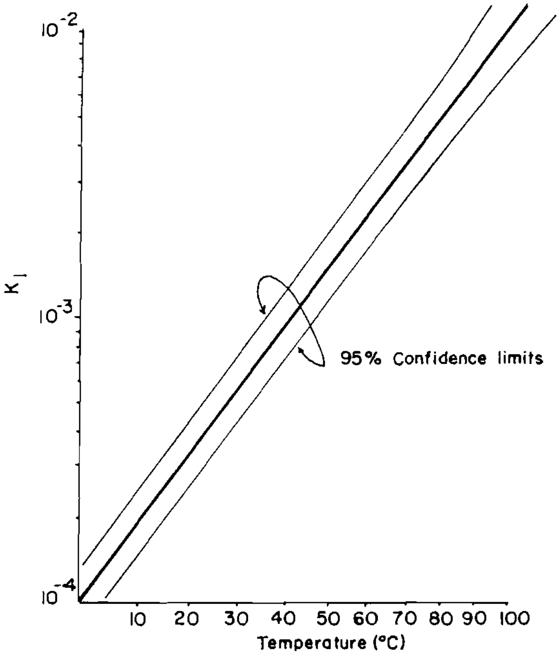


Fig. 1. Equilibrium constant for the dehydration of methylene glycol as a function of temperature: $K_1 = [CH_2O_{aq.}][H_2O]/[CH_2(OH)_{2\,aq.}]$; $\log_{10} K_1 = 7.61 - 2080\ (1/°K)$, Eq. (5).

$$\log_{10} K_1 = 7.609943 - \frac{2079.23}{T + 273.16} \tag{5}$$

Extrapolation to 25°C results in $K_1 = 4.2 \times 10^{-4}$. Bell (*9*) recently concluded, based on the information available, that $K_1 = 5(\pm 0.5) \times 10^{-4}$. The accuracy of extrapolation to elevated temperatures has not been tested. Recognizing the limits of accuracy and the dangers in such extrapolations, this treatment indicates that K_1 varies from 1.5×10^{-3} to 5.3×10^{-3} at 50°–80°C, and at 100°C is 10.9×10^{-3}. These are the most commonly used temperatures for reactions that are of interest in this discussion.

In aqueous solution, methylene glycol dissociates as a weak acid according to

$$\mathrm{HOCH_2OH} \rightleftharpoons \mathrm{HOCH_2O^-} + \mathrm{H^+}. \tag{6}$$

The first dissociation constant has been shown to vary from 1.0×10^{-14} g-mole/liter at 0°C to 33×10^{-14} g-mole/liter at 50°C (*1*, p. 107). A value of 5.62×10^{-14} at 25°C is reported by Bell (*9*). Aqueous solutions of formaldehyde generally have a pH range of 2.5–3.5. The dissociation constant for methylene glycol is too small to give this pH. The second dissociation constant for methylene glycol, Eq. (7), is yet to be determined:

$$\mathrm{HOCH_2O^-} \rightleftharpoons \mathrm{{}^-OCH_2O^-} + \mathrm{H^+}. \tag{7}$$

It is known that traces of formic acid exist in these solutions; this accounts for the acid character of aqueous formaldehyde. The presence of formic acid is attributed to the Cannizzaro reaction, Eq. (8), and to oxidation of formaldehyde during its manufacture:

$$\mathrm{2CH_2O} + \mathrm{H_2O} \rightarrow \mathrm{HCOOH} + \mathrm{CH_3OH}. \tag{8}$$

The Cannizzaro reaction is favored as the explanation for the acidic character of formaldehyde solutions. Neutral solutions become acid on standing and reach an "equilibrium pH" range of 2.5 to 3.5. Shifts in the equilibria of hydration and polymerization in aqueous systems are minimal under these conditions. They are accelerated at lower and higher pH.

Reactions or equilibria which have an influence on the concentration of the reactive species in solutions of formaldehyde would be expected to affect the measurement of kinetics. For example a pH greater than 10 gives an abrupt change in the kinetics of the reaction between formaldehyde and phenol. The Cannizzaro reaction is one which may become significant at this pH and is a recognized influence on the reaction. The general equation for this reaction is Eq. (8). Walker (*1*, p. 214) discusses this briefly and points out that it is favored in a temperature range of 40°–60°C, typical of many alkali-catalyzed reactions of aqueous formaldehyde. Martin (*10*) suggests that the reaction is between third and fourth order. The proposed mechanism and kinetics depend upon the presence of $^+\mathrm{CH_2OH}$ in alkaline aqueous solution, for which Martin gives some theoretical evidence. He also takes into account the equilibria shown in Eqs. (6) and (8) and considers the hydrolysis constant of methylene glycol. A least-squares fitting of data over a broad range of pH and formaldehyde concentrations of a plot of rate/$(\mathrm{HOCH_2OH})^2$ vs $(\mathrm{OH^-})$ resulted in a rate equation, rate $= a(\mathrm{HOCH_2OH})^2 \times$

$(OH^-) + b(HOCH_2OH)^2(OH^-)^2$ in which a is a third-order velocity constant equal to 3.35×10^{-4} liter^2/mole^2 sec and b is a fourth-order velocity constant equal to 9.02×10^{-4} liter^3/mole^3 sec. In this case K_h is the hydrolysis constant of methylene glycol which is $(CH_2(OH)_2)(OH^-)/(HOCH_2O^-)$ equal to 0.30 g-mole/liter. The constant a represents reactions (a) and b reaction (b).

$$\begin{array}{ll} (a) & \left\{ \begin{array}{l} {}^+CH_2OH + {}^-OCH_2O^- \rightarrow HCOO^- + CH_3OH \\ CH_2O + HOCH_2O^- \rightarrow HCOOH + CH_3O^- \end{array} \right. \\ (b) & \quad CH_2O + {}^-OCH_2O^- \rightarrow HCOO^- + CH_3O^- \end{array}$$

In reaction (a), the concentration of ${}^+CH_2OH$ is very small, ($< 10^{-18}$ mole/liter). Owing to the complexity of the kinetic equation and the desire to avoid assumptions and the inclusion of all terms, it is often preferred to express the rate as a third-order constant but include the concentrations of ingredients which apply. For example, at 40°C and $[F]/[OH^-] \cong 2$, the third-order velocity constant is 2×10^{-4} liter^2/mole^2 sec while at $[F]/[OH^-] = 1$, the constant is 5×10^{-4} liter^2/mole^2 sec. The [F] represents the measured concentration of formaldehyde and it must be recognized that present analytical methods rely on complete depolymerization of formaldehyde solutions. These are ratios which approximate some used in studying kinetics of phenol–formaldehyde reactions.

Cupit (*11*) offers a slightly different approach. He emphasizes that the reaction follows third-order kinetics but the rate is concentration dependent. A fourth-order equation does not satisfy the kinetics, nor does one of intermediate order. He agrees generally with Martin (*10*), but suggests a mechanism involving an intermolecular hydrogen ion transfer which involves singly and doubly ionized methylene glycol entities. Cupit gives considerable attention to equilibria which influence this reaction.

Equations (1)–(3) illustrate the equilibria present in aqueous solutions of formaldehyde. Some description of those solutions has been possible. The mole fraction of methylene glycol in aqueous solution is influenced by the concentration of dissolved formaldehyde and by the temperature. Comparing the analytical data of Iliceto and Bezzi (*12*) and partial pressure data of Piret and Hall (*13*), Walker (*1*, p. 71) rationalizes the differences in their results and proposes that the quantity of methylene glycol in solution is somewhere between his calculated values and those of Iliceto and Bezzi (*12*). The reasonable assumptions used were that at the elevated temperature for vapor pressure measurements, analytical procedures used by Iliceto and Bezzi would result in low values, and that at 5 wt % concentration, all of the dissolved formaldehyde is present as hydrated monomer. Table 1 summarizes these data.

Table 1

FRACTION OF DISSOLVED CH_2O AS METHYLENE GLYCOL AT 100°C (*1*, pp. 67, 71)

CH_2O (wt %)	Bisulfite analysis	Partial pressure data
5	0.78	1.00
10	0.63	0.93
15	0.55	0.87
20	0.48	0.80
25	0.43	0.75
30	0.40	0.69
35	0.36	0.62
40	0.33	0.56
45	0.29	0.49
50	0.25	0.43

Equations (2) and (3) represent equilibria of the polymerization of methylene glycol. Polyoxymethylene glycols are formed by the progressive condensation of methylene glycol. There is no evidence to indicate that the polymers undergo condensation to form higher molecular weight products. Equilibrium constants for the formation of polyoxymethylene glycols [Eqs. (2) and (3)] have been determined experimentally (*12*):

$$K_2 = \frac{[\mathrm{HOCH_2OH}]^2}{[\mathrm{H_2O}][\mathrm{HO(CH_2O)_2H}]} = 0.33 \tag{9}$$

$$K_3 = \frac{[\mathrm{HOCH_2OH}][\mathrm{HO(CH_2O)}_n\mathrm{H}]}{[\mathrm{H_2O}][\mathrm{HO(CH_2O)}_{n+1}\mathrm{H}]} = 0.205 \qquad n > 2. \tag{10}$$

Iliceto et al. (*14*) used these equilibrium constants to mathematically predict the concentration distribution of methylene glycol and polymers ($n = 2$–10) at 35°C over a dissolved formaldehyde concentration of 5–50 wt %. The data are presented in total by Walker (*1*, p. 64). This work presumes that only linear molecules exist. Moedritzer and Van Wazer (*15*) considered the presence of trioxane, $(CH_2O)_3$, and made calculations similar to those of Iliceto et al. (*14*). To arrive at the distribution of polymers at equilibrium, three equilibrium constants were determined by nuclear magnetic resonance on solutions of trioxane and deuterated water:

Hydrolysis of chain molecules to $DOCH_2OD$	$K = 1.0$
Equilibrium involving trioxane	$K = 1.3$
Equilibrium between formaldehyde and polyoxymethylenes	$K = 4.0 \times 10^{-3}$.

The results from both sources are given in Table 2, those in parentheses and the added line for $(CH_2O)_3$ being from Moedritzer and Van Wazer (*15*). The data are in fair agreement and represent formaldehyde concentrations of commercial importance with the numbers rounded to ±0.1 for illustrative purposes.

Table 2

DISTRIBUTION OF FORMALDEHYDE AS METHYLENE GLYCOL AND POLYMER IN AQUEOUS SOLUTION AT 35°C AND (30°C)[a]

	$HO(CH_2O)_nH$ wt % for CH_2O wt % =		
n	35	40	50
1	31.2 (27)	26.8 (30.0)	19.0 (16.3)
[$(CH_2O)_3$	(1.1)	(1.2)	(1.4)][b]
2	21.0 (25.8)	19.4 (33.8)	15.5 (19.3)
3	15.6 (18.5)	16.4 (18.5)	14.8 (17.2)
4	11.6 (11.7)	12.3 (12.8)	12.7 (13.6)
5	7.6 (7.0)	8.7 (8.3)	10.1 (10.1)
6	4.8 (4.0)	5.9 (5.1)	7.8 (7.2)
7	3.0 (2.2)	3.9 (3.1)	5.8 (5.0)
8	1.8 (1.2)	2.5 (1.8)	4.2 (3.4)
9	1.0 (0.7)	1.6 (1.1)	3.0 (2.2)
10	0.6 (0.4)	1.0 (0.6)	2.2 (1.5)
> 10	0.8 (0.4)	1.6 (0.8)	4.9 (2.7)

[a] Values in parentheses taken from ref. (*15*); others from ref. (*14*).

[b] Single-line entry showing concentration of trioxane (*15*).

Solvents which lower the ion product of H_2O (e.g., CH_3OH) decrease the rate constant of dilution (depolymerization). As little as 4% methanol cuts the rate constant in half (*1*, p. 73). The methylene glycol and formaldehyde are in equilibrium with hemiformals:

$$HOCH_2OH + CH_3OH \rightleftharpoons HOCH_2{-}O{-}CH_3 + H_2O \tag{11}$$

$$HO(CH_2O)_nH + CH_3OH \rightleftharpoons HO(CH_2O)_nCH_3 + H_2O. \tag{12}$$

Although ample evidence exists to suggest the presence of hemiformals under conditions typical for reactions of formaldehyde with active hydrogens, little has been done to determine their equilibria in such aqueous solutions. This is unfortunate since alcohols are used in many commercial condensation reactions and their effect on reaction kinetics must be significant.

Typical analyses of commercial aqueous formaldehyde solutions are shown in Table 3. The significance of methanol content becomes apparent when

Table 3

TYPICAL AQUEOUS FORMALDEHYDES OF COMMERCE

	A	B	C
Formaldehyde as CH_2O[a]	37.0–37.3%	37.0–37.3%	49.75–50.25%
Methanol	3.0% max	1.0% max	1.5% max
Formic acid	0.02% max	0.02% max	0.05% max

[a] By analytical methods which do not distinguish hydrolyzable derivatives of CH_2O.

sensitive reactions are attempted using these three solutions. Solutions B and C have almost equal mole ratios of methanol/formaldehyde and can be used interchangeably with due allowance for the higher formaldehyde concentrations (and lower condensables). On the other hand, shifts between B or C and A require more abrupt changes in catalysis, temperatures of reaction, and, in some cases, formaldehyde ratios in some reactions. The additional methanol is significant in changing the methylene glycol or formaldehyde availability owing to hemiformal formation. It has a retarding effect on reactions with reactive hydrogens.

*Paraformaldehyde is a commercially important source of formaldehyde. It is solid and is a mixture of low molecular weight polyoxymethylene glycols analyzing at 91–98% CH_2O. Paraformaldehyde is formed according to

$$n\mathrm{HOCH_2OH} \rightleftharpoons \mathrm{HO(CH_2O)_nH} + (n-1)\mathrm{H_2O}. \tag{13}$$

Estimates for n have varied, but it is certain that the molecular weight distribution is broad. It has not been possible to isolate and identify the individual polymers. Although it has been proposed that $n_{\mathrm{ave}} = 8$, it has also been concluded that the largest number of molecules are $n > 12$ (*1*, p. 147).

Paraformaldehyde depolymerizes in the presence of water to form lower molecular weight polyoxymethylene glycols and under identical conditions will establish the same equilibria as formaldehyde with its polymers. With the use of solid paraformaldehyde, the commercial significance is obvious; reaction of paraformaldehyde with an active hydrogen to generate a methylol group (hydroxy methyl; $-CH_2OH$) is anhydrous. No water results other than that in the raw materials. However, formaldehyde is apparently not active when present in the form of polymers, thus paraformaldehyde must be depolymerized with some water or alcohol, using a catalyst if necessary. In the case of alcohols, hemiformals are formed. It is generally necessary to proceed with these reactions with extreme caution when using paraformaldehyde. The exotherm of these reactions is difficult to control when the concentration of reactants is high and condensables low. Removal of heat must be achieved. These reactions are further complicated by the fact that a finite time is required for depolymerization of paraformaldehyde to a reactive form. Under catalytic conditions used for many reactions, this can be abrupt once the solid paraformaldehyde goes into solution. There have been many instances in commercial use where reactions have been initiated too fast to control the heat output resulting from the exotherm. Otherwise, paraformaldehyde results in reactions with active hydrogens much the same as formaldehyde under identical conditions. Although more expensive than aqueous formaldehyde, it does offer some advantages in special cases where water is not desired in the reaction medium and it results in better resin yields from a reaction vessel.

Hexamethylenetetramine (hexa) reacts as formaldehyde only in the presence of catalysts, at elevated temperatures, or in the presence of an active formaldehyde acceptor. In water, hydrolysis to ammonia and formaldehyde is slight:

$$(CH_2)_6N_4 + 10H_2O \rightleftharpoons 6CH_2O + 4NH_4^+ + 4OH^-. \tag{14}$$

In aqueous solution, the pH is 8–8.5 showing mildly basic character. Under these conditions the dissociation constant of 1.4×10^{-9} has been reported (*16*). Hydrolysis is accelerated by acid and by heat. At pH 6, the hydrolysis constant is reported as 1×10^{-4} and at pH 2 as 2×10^{-3} (*17*). The temperature effect is less dramatic, showing small shifts in equilibria and in pH. After heat is removed, recombination takes place.

Hexa is used in reactions with reactive hydrogens as a source of methylene groups only in special cases and then usually in small amounts. In aqueous solution, dissociation results in the formation of aqueous formaldehyde. It is much more practical and economical to use aqueous formaldehyde and provide the ammonium ion, the other product of hydrolysis, with ammonium hydroxide. Hexa can be used in nonaqueous systems where methylene linkages are desired; however, the decomposition of hexa under these conditions is complex and results in amines and imines which often enter the reaction with active hydrogens. The primary use for hexa in relation to our subject is as a crosslinking agent for hydroxyphenylmethane polymers (novolacs).

In summary, any consideration of the kinetics and mechanisms of the reactions of formaldehyde in solutions with materials containing active hydrogens must take into account the state of formaldehyde during reaction. Too often these reactions are viewed strictly on the basis of the coreactant, treating the reactive species in formaldehyde solutions as CH_2O. This will often prove adequate in idealized situations under the conditions adopted for much of the research to date. As commercial conditions are approached and as reactions go to completion, many anomalies and unexplained phenomena occur; these have yet to be satisfactorily explained in most cases. We have pointed out that the complex equilibria in more concentrated commerical solutions of formaldehyde in water and/or alcohol must have a bearing on the chemistry of reactions. The most significant characteristics of these solutions as related to the reactions within the scope of this chapter are outlined as follows:

1. Commercial sources of formaldehyde, utilized in reactions with reactive hydrogens, are available as aqueous solutions, water–alcohol solutions, and solid polymer (paraformaldehyde). Most reactions are conducted in solution; generally water is present if only in small amounts.
2. Solutions of formaldehyde or paraformaldehyde in water and/or alcohol can assume the same equilibria under favorable conditions. Attainment of equilibrium is generally quite slow.
3. In water formaldehyde is hydrated to form methylene glycol which is in equilibrium with polymer hydrates. Formaldehyde, CH_2O, is present in such small amounts that it is often neglected in chemistry in aqueous systems, although studies at extremes in pH may change this conclusion as data become available.
4. In aqueous media, shifts in equilibria favoring the presence of methylene glycol are caused by dilution, heat, and shifts in pH from the range pH 2.5–3.5.
5. The presence of alcohols favors the formation of hemiformals and related equilibria. These are less reactive species than methylene glycol or formaldehyde. Also, alcohols decrease the rate of dissociation of polymethylene glycols.
6. Methylene glycol dissociates as a very weak acid, but the acid character of aqueous formaldehyde is mainly owing to the presence of formic acid. An alkaline pH favors formation of formic acid by the Cannizzaro reaction.
7. In contrast to the conditions under which many of the equilibrium data have been determined, commercial use of formaldehyde involves relatively concentrated solutions. As the reactive form may be used up quickly in reactions, and equilibria are slow to shift and be reestablished, the complexity of formaldehyde chemistry increases, particularly as the reactions proceed toward completion. Yet, description of the effects of these equilibria must be accomplished if one is to understand these reactions.

The reactions of formaldehyde with the reactive hydrogens of phenol, melamine, etc., are often referred to as condensation reactions and the products are often termed condensation resins, polymers, or products. These labels lead to confusion for those not associated with this field.

In all cases, the initial reaction of formaldehyde in aqueous solution with the materials included in our discussion results in the formation of methylol groups ($—CH_2OH$). In every case, these can react further to form multinuclear products. The first reaction is an addition reaction if formaldehyde is the reactive species. If methylene glycol is the reactive form, this initial reaction may be considered a condensation. The reactions of the methylol group are the condensation type.

The problems in interpretation arise when the reactive species is in question, thus the terms "addition" and/or "condensation" may be found in reference to the initial reaction. Also it is common to use the description "condensation chemistry" to denote the field covered in our presentation. We have attempted to minimize this confusion, but are undoubtedly influenced by familiarity.

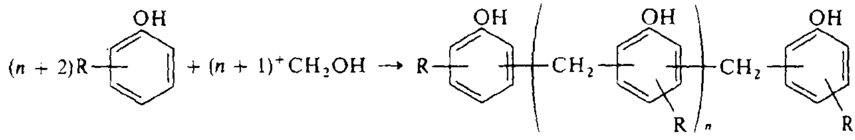
III. The Acid-Catalyzed Reactions of Formaldehyde with Phenols

A. GENERAL CONCEPTS

Chain molecules in which phenol (P) nuclei are joined by a methylene linkage constitute the class of compounds termed "novolacs." Reaction of formaldehyde with ring positions on phenol can give polymers that are permanently fusible if the conditions are used which are mild enough to prevent rearrangement, oxidation, or other inter- or intramolecular changes that cause the formation of three-dimensional networks. The reaction is not limited to phenol (P) and formaldehyde (F). It is required, however, that formaldehyde have a functionality (f) of 2 toward the phenol and that the phenol likewise have a functionality of at least 2. If either or both reactants have functionality < 2 or if other reactants are incorporated with functionality < 2, chain termination results. This is a means of controlling the molecular weight. If either has functionality > 2, branching can occur and the likelihood of gelation is increased. However, in the novolac structure it is usual to have reactive sites which are capable of entering into combination with other difunctional reactants under controlled conditions. Thus a crosslinked matrix can be generated to provide the useful properties of this resin family. One can readily appreciate the scope of chemistry which is characteristic of the field of novolacs.

Our purpose to discuss the kinetics and mechanisms of novolac formation can be met only by being restrictive in the chemical constitution of these systems. Previous workers such as Hultzsch, Zinke, and von Euler dealt mainly with phenols of limited functionality, $f = 1$ or 2, and with formaldehyde. They used the classical organic chemical approach which emphasized materials that favored the reaction desired. Their work forms the basis for knowledge up to 10–15 years ago. This work is most thoroughly reviewed by Megson (*18*). These workers used the only practical approach possible at the time. Analytical techniques were not utilized extensively to determine the molecular species present in phenol–formaldehyde resins until Freeman (*19*) published chromatographic methods for the analysis of phenol–formaldehyde resin mixtures synthesized under alkaline conditions. In a later section, it will be shown that these resin systems are much more thoroughly understood than the novolacs due to convenient analytic tools. Extension of chromatographic techniques (paper, gas–liquid, gel permeation) and the adaptation of nuclear magnetic resonance to phenol–formaldehyde systems have occurred in the last decade. Thus novolacs are beginning to yield their secrets of molecular structure.

Restrictions were implied. The present discussion will be restricted in a sense opposite to the early research. We will deal principally with phenol (P) with functionality = 3, to a lesser extent with monosubstituted phenols, functionality = 2, and almost exclusively with formaldehyde (F), functionality = 2. Aqueous systems will be emphasized although nonaqueous reaction media will be discussed where pertinent. Thus the reaction under consideration is illustrated by Eq. (15). This is greatly oversimplified.



$+ (n + 1)H_3O^+$ R = H, alkyl or halogen. (15)

Phenol is represented when R = H, and this case will receive the most attention. Other phenol derivatives will be discussed where the information adds to the knowledge of more common novolacs or where it can be applied to phenol/formaldehyde chemistry. In aqueous systems, methylene glycol ($HOCH_2OH$) has often been considered the reactive component of formaldehyde (F) and we will here be bearing in mind the reservations stated in Section II. Phenol has a functionality = 3 toward formaldehyde, all reactive hydrogens at *ortho* and *para* ring positions. The phenolic hydroxyl is not a functional group in this sense and the meta positions do not enter the reactions under usual conditions; this requires specific catalysis and selectively substituted phenols.

Before becoming specific, the general nature of novolac chemistry will be examined. Well-accepted concepts will not be documented since the credits are so numerous and represent work thoroughly reviewed (*18*, *20–22b*).

The generalized novolac structure shown in Eq. (15) requires chain termination by phenol to meet the accepted definition which implies lack of inter- or intramolecular reactivity. Obviously, termination with the methylol ($-CH_2OH$) group or a branch unit of this structure would not meet this convenient concept. Methylol-terminated structures are of some importance, but will not be included in the initial discussion except where they serve as intermediates or as derivatives in novolac chemistry.

Termination with a phenol unit requires that reactions be performed under conditions where the total phenol functionality $N_P f_P$ is greater than that of formaldehyde $N_F f_F$, N and f represent the number of molecules and the functionality, respectively. The final structure will contain $N_P > N_F$ where $N_P = N_F + 1$.

Novolacs may be synthesized in acidic or basic media and by stepwise procedures using acidic and basic media. Mole ratios of formaldehyde/phenol can be adjusted to meet the requirements of the desired result. The mechanisms and kinetics of novolac formation under acidic and basic conditions are very different. Without elaboration at this point, suffice it to say that the alkaline-catalyzed reactions used in novolac synthesis add complexity to the course of novolac formation and tend to favor branching and gelation. Thus novolac synthesis is usually performed under conditions where acid catalysis is the governing and regulating influence. Base-catalyzed reactions of formaldehyde with phenol will be discussed in a later section.

Even under acid conditions, novolac formation is a complex process and total definition is far from complete. A general summary will first be given. What is known will be outlined; what is not known will be indicated; what is reasonable to be assumed will be included.

Most phenol–formaldehyde reactions are performed in aqueous media. This is not a requirement, however, since paraformaldehyde or trioxane is often used in systems with a low water content and provides products not significantly different from those obtained from aqueous formaldehyde solutions. Ideally, phenol has a functionality of three ($f_P = 3$) and formaldehyde has a functionality of two towards phenol ($f_F = 2$). Stoichiometry requires 3F/2P or a mole ratio of $N_F/N_P = 1.5$. Under these conditions, a fully crosslinked structure is possible. For a chain molecule (linear or branched) of high molecular weight $N_F/N_P = 1.0$. In theory, a phenol–formaldehyde novolac is such a molecule, or could be. Acid catalysis is generally carried out at $\text{pH} < 5$ for kinetic and mechanistic reasons; generally $\text{pH} < 3$. Under these conditions, it is required that $N_F/N_P < 0.85$ or even < 0.8 to avoid gelation. This has not been explained adequately, but has been observed repeatedly.

Since chains do exist, and branching and gelation can occur, one might expect that the general equations for the most probable molecular weight distribution and branching coefficient as provided by Flory (*23*) would apply. They do not in the generalized form since the phenol–formaldehyde reaction system does not meet the requirement of equal reactivity of like functional groups. Adequate kinetic data to modify these equations have been lacking. Although several equations which are amenable to generalization have been suggested for P–F systems, they are of very limited utility. This will be considered in more detail later.

It is well accepted that the reaction of formaldehyde with phenol, under acid conditions, to form novolacs proceeds according to Fig. 2. This is greatly simplified. Formaldehyde reacts with phenol to form a methylol phenol

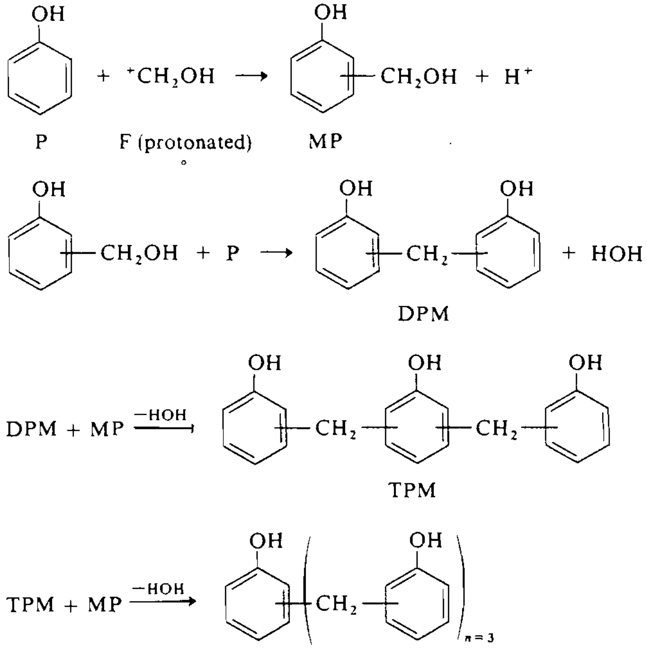


Fig. 2. Acid-catalyzed reaction of formaldehyde with phenol. MP: methylol phenol. DPM: Eq. (15), R = H, $n = 0$; dihydroxydiphenylmethanes. TPM: Eq. (15), R = H, $n = 1$; hydroxybis(hydroxybenzyl)benzene.

(MP) which is the reactive species in polymer growth during early stages of the reaction. It becomes immediately obvious that chain termination with phenol is structurally consistent. This is possible only because condensation of methylolphenol with phenol or chain units is faster than reaction of formaldehyde with either species. The relative rates are such that some formaldehyde condenses with methylol phenol or phenol and consequently a ratio of $N_F/N_P < 0.85$ should be used to avoid gelation. The ratio $N_F/N_P \approx 0.85$, pH < 3, and the use of strong mineral acids all increase the possibility of gelation. Under the normal conditions of reaction no evidence exists for methylol groups on molecules other than phenol. However, it must be emphasized that complete analyses are available only at low degrees of reaction. At high degrees of polymerization in novolacs (unpublished work from this laboratory), methylol groups (CH_2OH) have been found. These generally result from a combination of the conditions just discussed.

It can be seen that a novolac is formed by initial reaction of a methylol phenol (two are possible) with phenol, to form dinuclear products (three are possible), followed by continued condensation to the trinuclear materials (seven are possible). At this point, branching can occur although there is little evidence that it does; in fact there is little experimental evidence of branching in novolac systems at all, though the probability becomes greater as the molecular weight increases. As the condensation proceeds to the tetramer, pentamer, etc., analysis for the complete molecular constitution becomes extremely difficult because of the number of isomers. Even without branching, complexity is great. The complexity of novolac structure is obvious if one recognizes that the molecular size distribution of most novolacs includes the basic unit phenol and may contain polymers with more than 20 units. Nonequivalence of functional reactivity and the use of nonstoichiometric quantities of reactants favor a broader molecular weight distribution and a lower average molecular weight than is suggested by probability equations. The complexity (theoretical) of novolacs is dramatically pointed out by Megson (*24*) and Hollingsdale and Megson (*25*). Table 4 summarizes their conclusions.

Table 4

STRUCTURAL ISOMERS IN PHENOL–FORMALDEHYDE NOVOLACS (*25*)

Number of units	Number of unbranched isomers	Total including branched isomers	Molecular weight
4	21	27	428
5	57	99	535
6	171	439	642
9	4,401	8,500 (extrapolated)	963
10	13,203		1,070

Fortunately, the complexity of a novolac structure as predicted by theory is not found in practice. As will be seen, there is selectivity in the reactions of formation as a result of differences in reaction of functional groups, and the number of isomers formed is far less than is predicted by theory. Nevertheless, the systems are by no means simple and have yet to be explained satisfactorily beyond the dinuclear stage. Available structural data deal only with early stages of the reaction, and even this comes from studies in which dilute solutions of reactants were used.

Evidence will be presented to substantiate the course of the phenol–formaldehyde reaction in aqueous/acid media. In general, this has been qualitatively defined through the formation of trinuclear components, but for the larger components experimental data are fragmentary although many of the possible structures have been synthesized. Evidence on the higher condensation products is essential for the ultimate characterization of the molecular species present in the resin.

It is well accepted that the first step in the phenol–formaldehyde reaction is the formation of monomethylol phenols and that this is slow by comparison to subsequent reactions. The methylol phenols, in turn, quickly react with phenol (in preference to the formaldehyde reaction with phenol) to form dinuclear materials. Little or no self condensation occurs at $pH < 3$ and no reaction of F with polynuclear structures is observed, at least until molecular weights become large or the reaction proceeds until polynuclear materials predominate. Methylol phenols continue to react with phenol, the dinuclear molecules, and polynuclear compounds. There is selectivity in each reaction and some quantification will be possible.

Formaldehyde reacts faster with phenol in the *para* (*p*) position, although the presence of two *ortho* (*o*) positions results in almost equal amounts of *p*-methylolphenol (*p*-MP) and *o*-methylolphenol (*o*-MP). Monosubstitution is heavily favored. Methylol phenols are more reactive toward phenol nuclei than formaldehyde and react preferrentially in the *p* position. As the concentrations of formaldehyde and phenol decrease, those of dinuclear and trinuclear products increase. This stage is followed by formation of polynuclear materials. These reactions occur stepwise but steady state conditions have yet to be defined and there is some doubt that any steady state is reached. Since an excess of phenol is present, termination would be expected to limit molecular size and to give a broad molecular weight distribution. This is found to be true.

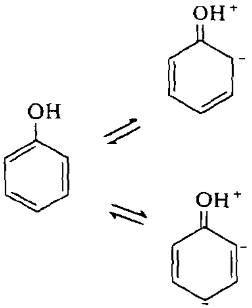
Branching can first occur in the tetranuclear structures, although convincing evidence of their presence is lacking. Gardikes and Konrad (*35*) indicated as much as 25% branched or trisubstituted phenol molecules in a novolac with a number average molecular weight ($\overline{M}_n$) = 670 by fractionation and vapor pressure osmometry procedures. No details, however, were given but this value at a $\overline{M}_n = 670$ is not unreasonable, as will be seen later.

B. THE INITIAL REACTION—FORMATION OF METHYLOL PHENOLS

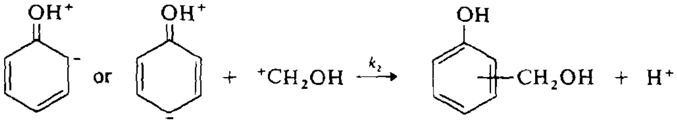
In discussing supporting evidence for the kinetics and mechanisms of novolac formation from phenol and formaldehyde, each phase of the reaction will be considered separately. They will be summarized finally into one reaction scheme which reflects the latest information. First, phenol and formaldehyde will be considered in the environment of the reaction system. Methylene glycol is discussed glibly as contributing the reactive species of formaldehyde in aqueous media. Our personal reservations on this point have been discussed. In the presence of acid, it exists in a protonated form [(Wadano, see Ref. (*1*, p. 73)]:

$$\mathrm{HOCH_2OH + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^+CH_2OH + HOH} \qquad \mathrm{pH} < 2.6. \tag{16}$$

Phenol is considered to exist as shown in Eq. (17). These structures result from electron shifts and are generally accepted. The net result is an increase in electron density at the *ortho* (*o*) and *para* (*p*) positions of phenol, thus favoring cationic (electrophilic) attack by the $^+CH_2OH$ ion. The reaction of formaldehyde with phenol is usually as illustrated by Eq. (18). The inductive effect on the *p* position is considered strongest owing to the relatively more stable quinoid structure; this has been the rationalization of the greater reactivity of the *p* position.



(17)



(18)

This difference in reactivity cannot be generalized. Even though there are two *o* positions and one *p* position, we find that *p* substitution is favored, because the rate of reaction at the *p* position is greater than twice the average rate for the two *o* positions. The rates for successive reaction of each *o* position have not been determined. One cannot deny that *p* substitution is favored, but inductive effects alone are insufficient grounds for this conclusion. For example, one might add that the induced positive charge on the phenolic hydroxyl would render at least one of the *o* positions less liable for attack by the cation $^+CH_2OH$, particularly since quinoid formation would restrict rotation and fix the hydroxyl hydrogen in an unfavorable steric position relative to one *o* position. Difficulties in making kinetic measurements to quantify positional reactivities limit the understanding of detailed mechanisms. This will be apparent in discussions which follow.

Jones (*27*) and de Jong and de Jonge (*28*) examined the kinetics of the reaction in Eq. (18) under conditions where second-order kinetics are obeyed. The mole ratios used, N_F/N_P, approached those commonly used in practice. However, de Jong worked in very dilute solutions. Yeddanapalli and Kuriakose (*29*) studied these kinetics under conditions favoring pseudo-first-order kinetics (tenfold excess of phenol), also in very dilute solution. Each study was performed under different combinations of temperature and pH so that comparison is difficult. However, some assumptions based on the experimental evidence make possible approximate comparisons. The works of Jones and of de Jong and de Jonge will be dealt with together. That of Yeddanapalli and Kuriakose must be considered separately. A summary of data from these references is given in Table 5.

The information which will be of particular interest is that obtained at 100°C and pH ≤ 2. These are very common conditions for the practical synthesis of novolacs. For the initial reaction rate, the data of Jones gives a value of $k_2 = 2.12 \times 10^{-5}$ liter/mole-sec at 100°C, a pH = 1.92, and molarity of reactants 5.5 in both phenol and formaldehyde ($N_F/N_P = 1$). The concentration of reactants is similar to practice, but the mole ratio is higher than practical and side reactions occur easily. We took the liberty of converting the initial rate of reaction given by Jones (*27*) (38.5×10^{-6} moles/gram-min of formaldehyde reacted) to a rate constant at time zero and made a conversion in units. Use of Jones' data in this discussion is thus qualified. Working at 110°C at a molarity of 0.2 for formaldehyde and phenol ($N_F/N_P = 1$) and pH = 2.1, de Jong and de Jonge (*28*) obtains $k_2 = 3.0 \times 10^{-5}$ liter/mole-sec. Both references show that second-order kinetics are followed under these conditions. Jones points out that a sixfold increase in k_2 occurs by increasing the temperature from 80° to 100°C. If the value of de Jong and de Jonge is thus decreased threefold by a 10°C reduction in temperature, the values will compare as follows: k_2 (*27*) 2.12×10^{-5} liter/mole-sec and k_2 (*28*) 1×10^{-5} liter/mole-sec.

Jones used solutions of high molarity of reactants and de Jong and de Jonge used dilute solutions and consequently further adjustments might be considered. Concentrated reaction media have a much lower dielectric constant than solutions dilute with water. Zavitsas (*30*) shows that the preceding difference as represented, changes the rate constant of methylolation under alkaline conditions by a factor of two. The medium with lower

Table 5

SUMMARY OF KINETIC DATA FOR ACID-CATALYZED REACTION OF FORMALDEHYDE WITH PHENOL

Jones (*27*):	$N_F/N_P = 1/1$	Molarity = 5.5 (calculated by estimate—authors)						
T°C	80°	80°	80°	80°	80°	100°	100°	100°
Catalyst	H_2SO_4 or HCl	Oxalic acid	p-Toluene sulfonic	HCl	HCl	HCl	HCl	HCl
pH	1.18	1.18	1.18	2.57	0.87	2.78	1.92	1.19
k_2 liter/mole-sec × 10^5	2.12	1.07	1.93	0.701	5.79	0.271	2.12	13.5
de Jong and de Jonge (*28*):	$T = 100°C$	pH = 2.1		Catalyst HCl				
N_F/N_P	1/1			1/2				
Molarity	0.2F–0.2P			0.2F–0.4P				
k_2 liter/mole-sec × 10^5	3.0			3.5				
Yeddanapalli and Kuriakose (*29*):	$N_F/N_P = 1/10$		$T = 80°C$	Molarity = 0.07F–0.7P	Catalyst H_2SO_4		pH < 3	
k'_2 (1/sec) × 10^5				3.3 (pseudo first-order)				
k'_o for formation of o-methylol phenol				1.5				
k'_p for formation of p-methylol phenol				1.8				

dielectric constant has the greater rate constant. Assuming that the same is true in acid media, the value of k_2 (*27*) would require adjustment upward.

A further consideration complicates this comparison. Zavitsas (*30*) shows that, in alkaline media, it is necessary to consider the formaldehyde equilibria in aqueous solution if rate constants are to fit experimental data. There is no reason to suppose that this should not be the case in acid-catalyzed reactions. In aqueous solutions formaldehyde exists in equilibrium with its hydrate(s) and its polymers and has the facility to form formals with methylol phenols. The latter can be ignored in very acid systems. Since the reactive species in aqueous formaldehyde is expected to be ionized methylene glycol (protonated formaldehyde) and since both sources (*27*, *28*) determined rate constants by measuring the total unreacted formaldehyde as methylene glycol and formaldehyde polymers, a true measure of the methylene glycol concentration was not obtained.

To expand this concept, it is necessary to recall Eqs. (2), (3), and (16) and to add Eq. 20 (*28*). Equation (19) combines Eqs. (2) and (3):

$$(n+1)\mathrm{HOCH_2OH} \overset{K}{\rightleftharpoons} \mathrm{HOCH_2O(CH_2O)_nH} + n\mathrm{HOH} \tag{19}$$

$$\mathrm{HOCH_2OH} + \mathrm{H^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^{+}\mathrm{CH_2OH} + \mathrm{HOH} \tag{16}$$

$$v = k_2(k_1/k_{-1})[\mathrm{H^+}][\mathrm{P}][\mathrm{F}] \tag{20}$$

where v is the velocity constant for acid-catalyzed phenol–formaldehyde reaction (*28*), k_2 the rate constant for reaction in Eq. (18), and [ ] = concentration in moles/liter. Equation (20) was offered (*28*) to represent the reaction velocity of formaldehyde with phenol in acid environment. The term [F] represents the concentration of unreacted F determined analytically. The analytical techniques used by researchers (*27*, *28*) determine all of the F available in monomeric, hydrated, and polymeric form. Actually, the term [F] must be replaced by [methylene glycol] if this is chosen as the reactive species or is proportional to it. The [methylene glycol] is dependent upon the equilibrium represented by Eq. (19). It has been pointed out that the equilibrium constant K is not influenced greatly by temperature, only the rate at which equilibrium is established (*1*, p. 67), and this is still relatively slow at 100°C. At a pH < 3 one would expect depolymerization to be fast. No analytical measurements have been made. However, it has been shown, that in water the fraction of formaldehyde existing as methylene glycol varies with the concentration of formaldehyde (see Table 1). At the beginning of reaction, Jones (*27*) used a 5.5 molar solution in both formaldehyde and phenol and this represents a formaldehyde concentration of 39.5%. Others (*28*) used 0.006% F. Table 1 shows that the fractions of formaldehyde as methylene glycol at these concentrations under equilibrium conditions in water are

0.33 and $\gg 0.78$, respectively. Thus, if equilibrium were attained at the beginning of the reaction in both cases, [F] of Eq. (20), would require adjustment. If this is done, one value (*27*) for k_2 increases and another (*28*) remains the same since [F] $\approx$ [methylene glycol] in very dilute solutions. Upon examination of the experimental procedures in both cases, it might be questioned whether equilibrium was established in the second work; concentrated formaldehyde was added to a very dilute solution of phenol. Jones added concentrated formaldehyde to a high concentration of phenol. For a relative comparison, it would be necessary in de Jong and de Jonge to adjust the value for k_2 upward.

Adjustments of the type suggested above have not been justified experimentally for these reaction media. The considerations of environmental effects on kinetics are valid, however, and surely suggest further research in acid systems.

It is necessary to treat the work of Yeddanapalli and Kuriakose (*29*) separately from that of the other two (*27*, *28*). This work (*29*) was performed under conditions favoring first-order kinetics ($N_F/N_P = 0.1$) and was done for reasons other than to arrive at an accurate rate constant for accepted procedures of novolac synthesis. The intent was to perform synthesis under conditions which would allow formation of intermediate products, with minimum side reactions, so that they could be isolated and identified. It was suitable to have relative rate constants for the definition of the novolac system. This work will be used as the basis for discussion of the kinetics and mechanisms of resin formation. At this point, only the reaction in Eq. (18) will be treated.

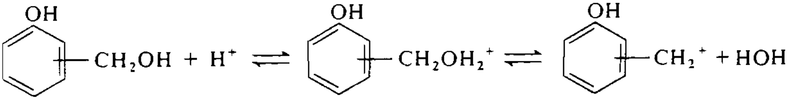
The researchers (*29*) worked with molarities of 0.7 in phenol and 0.07 in formaldehyde. The catalyst was sulfuric acid and the reaction temperature 80°C. Comments on dielectric constant and formaldehyde equilibria would apply here just as for Jones and de Jong and de Jonge, but discussion about these factors would serve little purpose since it is the relative rate constants which will ultimately be of interest. The rate constants determined for the reaction in Eq. (18) (*27*, *28*) represent the over-all rate of methylolation which does not distinguish between *o*- and *p*-methylolation. Yeddanapalli and Kuriakose showed that the "first-order" rate constants for this reaction were $k_2' = 3.3 \times 10^{-5}$/sec., while $k_o' = 1.5 \times 10^{-5}$/sec and $k_p' = 1.8 \times 10^{-5}$/sec. This is a reactivity ratio of $p/o = 2.4$, since there are two *o* positions. In the initial stages of the phenol–formaldehyde reaction, the proportions are *o*-methylol phenol/*p*-methylol phenol = 1.7. The activation energies were given as $E_o = 22.35$ kcal/mole and $E_p = 19.08$ kcal/mole for reaction to *o*-methylol phenol and *p*-methylol phenol, respectively, adding more reason why *p*-methylol phenol is favored. The individual rate constants, k_o' and k_p' were calculated by determining the amounts and ratios of the dinuclear products which can result from the reactions of *o*- and *p*-methylol phenol with phenol. Knowing the amount of formaldehyde reacted will give the initial ratio of *o*- and *p*-methylol phenol. Individual rate constants can then be calculated. The sum of these rate constants is compared to the measured value of the over-all rate constant and found to be in good agreement: $k'_o + k'_p = 3.3 \times 10^{-5}$/sec $= k'_2$ (calc) and k'_2 (measured) $= 3.5 \times 10^{-5}$/sec.

C. THE SECOND REACTION—FORMATION OF DINUCLEAR COMPOUNDS

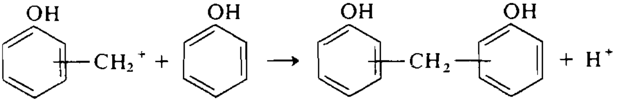
The next step in the formation of novolacs is the reaction of MP's with phenol to form dinuclear compounds (DPM). This is followed by further reaction to form trinuclear (TPM) and higher molecular weight materials. Lilley (*31*) pointed out that early work on phenol–formaldehyde reactions, in which monoreactive phenols were used, led to results of doubtful validity where the formation of DPM's was concerned. The general feeling at the time was that this synthesis proceeded primarily through the formation, and subsequent decomposition, of the dibenzylether. In most cases studied, no other course for the reaction was obvious. In systems where multiple reactions can occur, and where there are many unreacted phenol positions, this generalized mechanism is not satisfactory. Lilley suggested that an ionic mechanism exists in aqueous systems where protons are available. His mechanisms are very similar to those given by Rodia and Freeman (*32*). Lilley points out that phenol has an available proton and selectively substituted phenols ionize to an appreciable extent and can contribute to an ionic mechanism. It is also pointed out that in media of a narrow but specific pH range a nonionic mechanism may occur. Lilley suggests that hydrogen bonding in the *o*-methylol phenol would favor formation of ether links by reaction of *p*-methylol groups. (This selectivity is found to be true as will be seen later.)

"Hydrogen bonding" is recognized as one property exhibited by phenol–formaldehyde compounds which has an effect on the rates and the site of reaction. It will be shown that phenol–formaldehyde materials show both intra- and inter-molecular H bonds and these do in fact explain some facets of chemical and physical behavior. For the present, we will accept this phenomenon and use it freely in the text. The H bonding will be treated in a subsequent section where it will be discussed as it relates to phenol–formaldehyde chemistry and will be examined in terms of experimental evidence.

Rodia and Freeman (*32*) provided indirect evidence that methylol phenol reacts with a phenolic ring position as the benzyl cation. Although the reactions in Eqs. (21) and (22) had been suggested previously, there was little evidence to support them. Working under conditions favoring formation of benzyl carbonium ions and using selectively substituted phenols and benzyl compounds it was shown in (*32*) that catalysts which produce the benzyl cation were necessary for reaction of the benzyl group with a ring position on the phenol. Although the proof is not rigorous or direct, it is very suggestive. We are inclined to accept this suggestion as an explanation of the relative rates of reaction in phenol–formaldehyde chemistry. Thus it is rationalized why the reaction in Eq. (22) is faster than that of formaldehyde with phenol or with a polymer and that of the condensation of methylol phenol in alkaline media. Ether formation was rationalized also through the benzyl cation, Eq. (23), although this does not normally occur at pH < 3. These mechanisms are quite similar to those suggested by Lilley (*31*).



(21)



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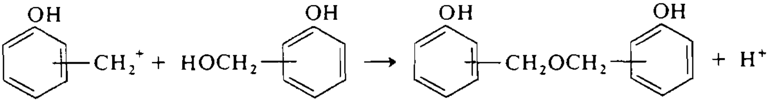


(23)

In the discussion of kinetics, the first-order rate constants of Yeddanapalli and Kuriakose (*29*) will be used, unmodified. They will be designated as k_3, k_4, etc., and must not be confused with those of Jones (*27*) or de Jong and de Jonge (*28*). This is for convenience since relative rates of reaction form the basis for the molecular constitution of the polymer. Also Ref. (*29*) is the most complete in this respect. To follow the discussion, Fig. 3 which is a refinement of Fig. 2 will be referred to frequently. The first thing to note is the change in nomenclature of the rate constants and that they all represent first-order kinetics; $k'_o = k_3 = 1.5 \times 10^{-5}$/sec and $k'_p = k_4 = 1.8 \times 10^{-5}$/sec.

Several investigators have examined the kinetics involving reactions to form (**1**), (**2**), and (**3**), and three studies were in sufficient detail to invite comparison of results. All used paper chromatographic methods for separation of isomers. Finn and James (*33*) studied phenol–formaldehyde reactions in a range of $N_F/N_P = 1/5$ to $5/1$, at pH $= 0$ to 10.95 and at a temperature of 90°C. For the moment, only the results from $N_F/N_P \leq 1$ and pH < 3 will be discussed. Molarities were changed depending on the reaction being studied.

In examining acid-catalyzed reactions Peer (*26*) varied the molarities of P and F as well as N_F/N_P to facilitate selective reactivity and analysis,

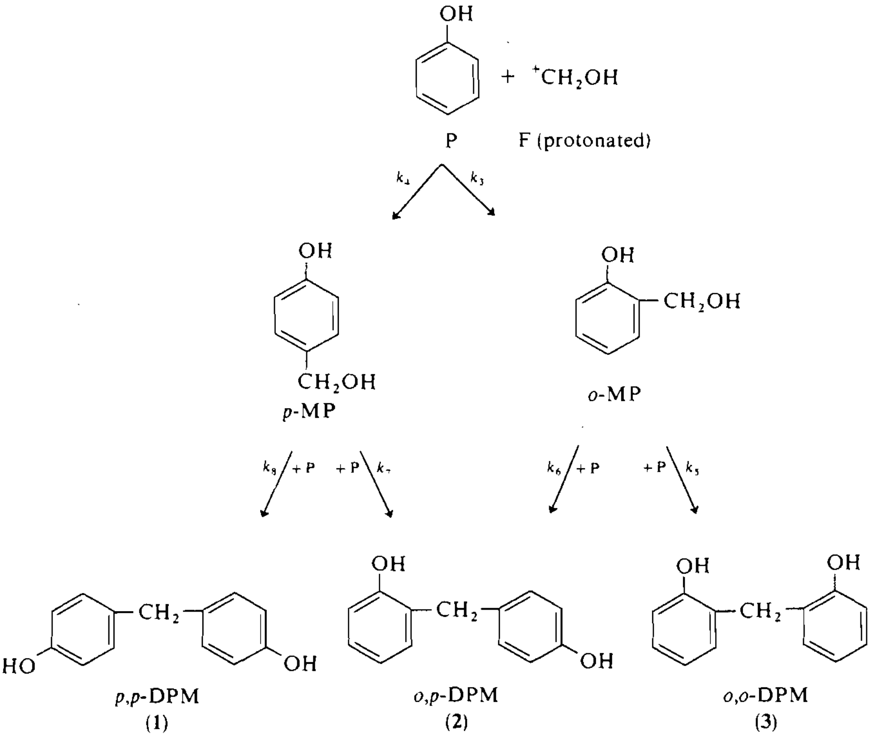


Fig. 3. Formation of novolacs.

although work with phenol and formaldehyde was also performed under conditions common for novolac formation: $N_F/N_P = 0.7$, molarity = 4.5 in phenol and 3.1 in formaldehyde, pH < 3, 100°C. The conditions used (*29*) for the formation of (**1**), (**2**), and (**3**) were a mole ratio of $N_P/N_{MP} = 10$, pH < 3, 70°–90°C. We will not be more specific as the discussion proceeds, unless necessary to the understanding of the conclusions. For the reactions in Fig. 3, there is fair qualitative agreement between investigators (*26*, *29*, *33*). The differences are difficult to reconcile because of the difference in experimental procedures used, but some judgment may be allowed. The most pertinent conclusions will be summarized.

To rationalize the relative concentrations of DPM's initially, it is necessary to know the concentrations of *o*- and *p*-methylol phenol. The reaction of formaldehyde with phenol to form *o*-MP and *p*-MP favors formation of the *o*-isomer in the ratio *o*-MP/*p*-MP > 1.0 (*29*) and though the total amounts may change during subsequent reactions, *o*-methylol phenol is always in excess (*33*). Peer (*26*) finds that this ratio is ≤ 1. For reasons to be given later, we are inclined to agree with Finn and James (*33*) at least to the extent that o-MP/p-MP > 1. Reference (*29*) may show a ratio too high since 80°C was the reaction temperature while Refs. (*26, 33*) used 90°C; also it is estimated that the pH in Refs. (*26, 33*) may have been slightly lower than in (*29*). These conditions do not favor formation of o-methyl phenol but it is doubtful whether o-MP/p-MP should be < 1, at least in the early stages of the phenol–formaldehyde reaction. According to Ref. (*29*), Eqs. (24) and (25) represent reaction rates and activation energies for formation of o- and p-methylol phenol. Once formed, MP's react with P to produce DPM's.

$$k_3 = 1.5 \times 10^{-5}/\text{sec} \qquad E_3 = 22.35\ \text{kcal/mole} \tag{24}$$

$$k_4 = 1.8 \times 10^{-5}/\text{sec} \qquad E_4 = 19.08\ \text{kcal/mole}. \tag{25}$$

The p-MP is more reactive toward phenol than o-MP and condenses preferentially with the p position on phenol. Steric factors favor p condensation to some extent also. Self condensation is thoroughly suppressed at pH < 3 as long as an excess of phenol moieties exists (*33*). There is no evidence of methylol DPM's nor would one expect ether formation in this large excess of phenol or at low pH. The reaction of methylol phenols with phenol is very rapid. The previous estimate (*34*) of the ratio of the rate of methylol reaction to the rate of phenol–formaldehyde reaction was (5–8)/1 while there is evidence (*29*) that it is as great as 42.

Based on these considerations one would expect (**1**) and (**2**) to be present in about equal amounts and (**3**) in much less quantity. Peer (*26*) and Yeddanapalli and Kuriakose (*29*) find this to be true although there is evidence that (**1**) is favored during early stages of the reaction of MP's with phenol. Finn and James (*33*) do not concur. They find that the order of occurrence of DPM's was (**2**) $>$ (**3**) $\gg$ (**1**). It was suggested that this is reasonable because to form (**1**), only one p position is available and there is less p-methylol phenol than o-methylol phenol. On this basis (**2**) and (**3**) have greater probability of formation. However, under the experimental conditions used, we are more inclined to believe that (**3**) would be present in the least amount and that the smaller concentration of p-methylol phenol is due to the fact it is reacting faster than o-methylol phenol with phenol.

The only quantitative information on the formation of DPM's is offered in (*29*): phenol–formaldehyde reactions were conducted at 70°, 80°, and 90°C with 0.1N H_2SO_4 and an $N_F/N_P = 0.1$. The products of reaction were isolated and the rates of formation and disappearance measured. For a summary of the results of this study see Table 6.

Again, first-order kinetics are favored owing to the large excess of phenol. The reaction at 80°C (the only one tabulated) was completed to a degree of reaction of approximately 0.47 in formaldehyde in 300 minutes. In our

Table 6
RATE CONSTANTS AND ACTIVATION ENERGIES FOR FORMATION OF DPM'S (29)
(PSEUDO-FIRST-ORDER REACTIONS)

From	to	E, kcal/mole	k (1/sec) × 10^5 at 80°C	
P + F	o-MP	22.35	k_3	1.5
	p-MP	19.08	k_4	1.8
P + o-MP	(3)	22.88	k_5	5.9
	(2)	18.60	k_6	14.8
P + p-MP	(2)	18.88	k_7	35.6
	(1)	17.35	k_8	83.9

opinion the time taken for this reaction seems long. As would be expected, the rate of formation of all reaction products increases with temperature.

Both o- and p-methylol phenol reach their maximum concentration in a shorter period of time as the temperature increases and their rate of disappearance follows the same pattern. The o-methylol phenol is always in excess and p-methylol phenol decreases to zero in 75 min at 90°C, in 150 min at 80°C, and in 240 min at 70°C. Compound (**3**) can be formed only by reaction of o-methylol phenol with phenol in the o position. This reaction has the largest value for E and smallest value for k of the four competing reactions forming DPM's. This is reflected in the slow rate of formation of (**3**) and relatively very low concentration under all conditions.

The rate of formation of (**1**) and (**2**) closely parallel one another but (**1**) is in excess during early stages of the reaction, particularly at lower temperatures, apparently because of the low E and relatively high rate of formation. At higher temperatures, the concentration of (**2**) surpasses that of (**1**).

There are two modes of formation of (**2**): P + o-MP by p substitution and P + p-MP by o substitution. Each has a slightly higher activation energy than the reaction forming (**1**) and the respective k's are smaller than k_8. Under conditions representing those for usual novolac preparation (100°C), one would expect $[1] \geq [2]$. From Table 6, it may be deduced also that the relative reactivity of the p and o positions on phenol toward MP's is $p/o = (11\text{–}12)/1$. Recalling that the reactivity ratio $p/o = 2.4/1$ for the reaction of formaldehyde with the o and p positions of phenol, one can easily recognize why (**1**) would be expected to be in excess. It is evident also that the rates of reaction of MP's far exceed the rate of formaldehyde reaction with phenol.

The formation of a phenol-formaldehyde novolac proceeds through the reaction of o-methylol phenol and p-methylol phenol with DPM's (**1**), (**2**), and (**3**) to form polynuclear products. The first group of isomers in this series contains the trinuclear materials, TPM's. There are seven possible isomers. No quantitative analytical or kinetic data are available beyond the formation of DPM's. Some qualitative work has been performed by Peer (*26*) and Finn and James (*33*) and this will be reviewed. Other conclusions will be drawn by inference and from data which have relation to these reactions but are not directly comparable.

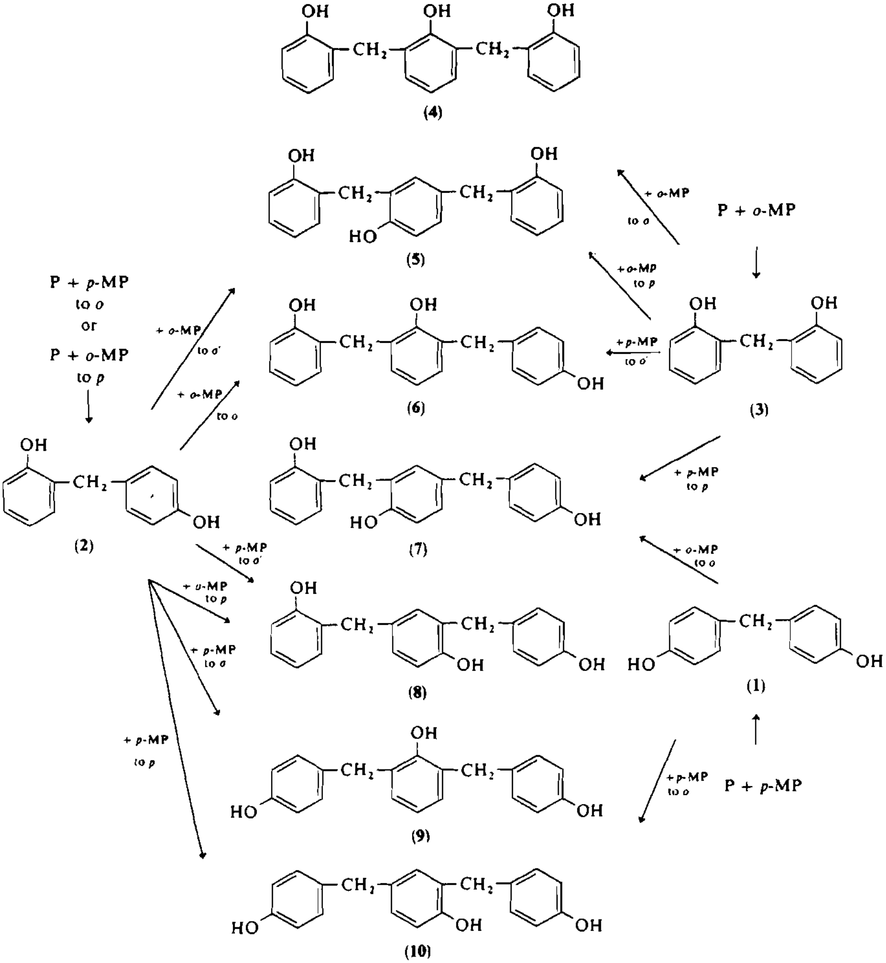


Fig. 4. Formation of trinuclear novolacs through the dihydroxyphenylmethanes.

For reference purposes, Fig. 4 is provided to show all reactions which are possible to generate the seven TPM's by the reaction of (**1**), (**2**), and (**3**) with *o*- and *p*-methylol phenol. Peer (*26*) and Yeddanapalli and Kuriakose (*29*) agree that [1] $\cong$ [2] $\ggg$ [3] throughout the reaction to form a phenol–formaldehyde novolac. Finn and James (*33*) disagree, but as suggested earlier, we are forced to accept the former conclusion as being more plausible.

It has been shown that *o*-methylol phenol is always present in excess of *p*-methylol phenol and that both disappear at about the same rate as the reaction proceeds at 90° although [*p*-methylol phenol] reduces to zero. Also, the rates at which *o*-methylol phenol and *p*-methylol phenol are formed are almost equal but *E* for the latter is significantly less. Table 7 summarizes these initial observations.

Table 7

CONCLUSIONS ON RELATIVE REACTIVITIES DURING FORMATION OF NOVOLAC DINUCLEAR SPECIES (*29*)

F + P	*p* Position 2.4 times as reactive as *o* position
o-MP + P	Reacts with *p* position 12 times as fast as with the *o* position
p-MP + P	Reacts with *p* position 11.3 times as fast as with the *o* position
o-position on P	Reacts with *p*-MP and *o*-MP in the ratio 2.5/1
p-position on P	Reacts with *p*-MP and *o*-MP in the ratio 2.4/1

The immediate conclusions may be reached that *p*-methylol phenol and *o*-methylol phenol react in the ratio of 2.5/1 toward either position on phenol although *o*-methylol phenol may be slightly more reactive relatively at the *p* position (k_6/k_5 and k_8/k_7). Also the *p* position of phenol is about 12 times as reactive as the *o* position in the reactions with methylol groups. In Table 7, small differences are shown (*29*) in relative reactivities of *o* and *p* positions of phenol with *o*-methylol phenol and *p*-methylol phenol but we are inclined to consider them insignificant when dealing with the formation of higher molecular weight materials, although Peer (*26*) concurs that a relative difference does exist.

The factors reviewed above form the basis for understanding the work of Peer (*26*) and Finn and James (*33*) and to indicate qualitatively the composition of the TPM fraction of novolacs. Both sources extracted and identified resinous components from the bulk reaction of phenol with formaldehyde under conditions close to those used for the synthesis of novolacs. The complexity and number of products prevented little more than a highly qualitative conclusion. In an effort to be more specific, it was required for each to revert to reactions which were more selective and which allow a semiquantitative estimate of reaction products to be made.

Peer (*26*) observed that at 100°C, $N_F/N_P = 0.7$ and with HCl as catalyst (**10**) was present in the largest amounts while (**5**), (**7**), (**8**), and (**9**) were present in smaller amounts. Finn and James (*33*) observed that (**8**) was formed in largest amounts followed by medium amounts of (**5**), (**6**), and (**10**); the resin was synthesized at 90°C, pH 1.4, and $N_F/N_P = 0.5$, approaching the conditions used in (*33*). The major differences in results are the absence of (**6**) in Peer's work and of (**9**) in the study by Finn and James.

Compound (**6**) can result from two routes: (1) reaction of (**3**) with *p*-methylol phenol and (2) of (**2**) with *o*-methylol phenol. Both involve an *ortho* substitution. Some (**6**) might be expected, even if in small amounts. Compound (**9**) results from only one reaction: (**2**) with *p*-methylol phenol by *o* substitution. Since (**2**) is present in large amounts, the concentration of (**9**) should at least equal that of (**6**). We would expect both to be present.

Peer observed that the results did not change when different acid catalysts were used but that the rates were slower with weak acids. An increase of N_F/N_P to 1/1 (*29*), at constant pH, did not materially change the trinuclear products formed but did generate di- and trimethylol phenols. This is consistent with the formation of a gel, under these conditions, as the reaction approaches completion.

To pursue the details of TPM formation, both investigations studied specific or "artificial" reactions which would minimize the competitive reactions and give some indication of the over-all mechanism of resin formation. The first observation by Peer was at $N_F/N_P = 0.2$ (large excess of phenol); other conditions being equal, trinuclear products formed in the order (**10**), (**8**), (**7**), (**5**), and (**9**). At the same mole ratio, but at pH 0, Finn and James reported large and about equal amounts of (**3**) and (**5**) and medium and about equal amounts of (**6**) and (**7**). The discrepancy in this case exists because Finn and James detected a relatively large amount of (**3**). We cannot deny these data but find it difficult to accept that (**3**) will be present to any significant extent during novolac formation except where specific catalysis is used. A pH 0 may provide such conditions but there is evidence to the contrary to be presented later.

Both studies (*26*, *33*) involved specific reactions between (**1**), (**2**), and (**3**) with *o*-methylol phenol and *p*-methylol phenol under conditions favoring reactions with the DPM's and minimizing self condensation of the methylol phenols: strong acid and an excess of DPM. In this way some measure of selectivity of reaction was established. Their results are generalized in Table 8.

The conclusions in (*33*) are predictions, supported by some evidence, on the composition of a typical novolac. Peer (*26*) isolated from resin mixtures the compounds predicted by Finn and James. Experimental results by these investigators from the specific reactions of DPM's with methylol phenols are essentially identical. The conclusions of Finn and James are based on evidence that very little (**1**) is present and (**3**) is formed in reasonable quantities. Peer (*26*) and Yeddanapalli and Kuriakose (*29*) showed that (**1**) $\approx$ (**2**) $\gg$ (**3**) in concentration as indicated earlier. With the data available this appears to be reasonable.

Table 8

THE FORMATION OF TPM'S BY SPECIFIC REACTION[a]

Reaction	Finn and James (*33*)	Peer (*26*)
	(Relative concentrations—qualitative)	
(3) + *o*-MP	(5)	(5) $\ggg$ (4)
(2) + *o*-MP	(8) $\ggg$ (6, 5)	(8) > (6) $\gg$ (5)
(1) + *o*-MP	(7)	(7)
(3) + *p*-MP	(7)	(7)
(2) + *p*-MP	(10), trace (9)	(10)
(1) + *p*-MP	(10)	(10)
Conclusions	(8) > (5) > (10) > (6) > (7), (9)	(10) > (8), (7), (5) at $N_F/N_P = 0.7$
		At $N_F/N_P = 0.2$
	(Based on (2) > (1) $\gg$ (3) and *o*-MP > *p*-MP)	(10) > (8) > (7) > (5) > (9)

[a] See Fig. 4 for structures.

To test this conclusion, a commercial novolac manufactured under conditions typical of those used in practice, was examined in this laboratory by gas–liquid chromatography. The ratio of (1)/(2)/(3) was found to be 7.2/5.7/1 in the solid resin. This result is not conclusive, but certainly indicative.

No reports of analytical work which go beyond that reviewed above were found. Thus novolac compositions beyond the trinuclear compounds have not been delineated. Differences in conclusions have been noted and judgments which are certainly open to question have been made. The investigators (*26, 29, 33*) have performed careful and arduous research to provide the results upon which this discussion is based. Each may be correct according to procedures used and conditions of resin formation. Now that new analytical tools are available, another step forward may be possible.

D. THE FORMATION OF HIGHER MOLECULAR WEIGHT COMPONENTS

The previous discussion was limited to the early phases of the phenol–formaldehyde reaction. It was observed that "higher molecular" weight materials were in evidence during these studies. It must not be concluded that steady-state conditions exist during novolac formation. Even though one would expect low molecular weight products to predominate early in the reaction sequence, the DPM's would be expected to disappear as the reaction proceeds through formation of trinuclear then higher molecular weight products. Yeddanapalli and Kuriakose (*29*) showed that the rate of formation of (1) and (2) began to decrease with time although the concentrations of reactants were ample to promote their formation. Finn and

James (*33*), in isolated cases, showed a decrease of TPM's with time. These decreases in concentrations are the result of further condensation.

Molecular growth of a novolac can occur by continued reactions of methylol phenols with chains as described for the early phase of the reaction. It may occur also by reaction of formaldehyde with chain positions and condensation of the resulting methylolated compounds. A combination of the two is most probable since there is every reason to believe that formaldehyde will react with a chain if positions are available and the probability is favorable. As the concentration of phenol decreases and that of higher molecular weight products increases, the number of available functional positions on the polynuclear compound (even if of reduced reactivity) becomes great enough to make reaction highly probable. When this occurs, the molecular weight increases by larger increments and the chances of gelation are greater.

A further complication exists in that both the formaldehyde entity and phenol have groups of unequal reactivity during the course of reaction. In formaldehyde, the second functional position is not equally reactive during the course of phenol–formaldehyde reactions. Under acid catalysis, the reaction of one position of phenol with formaldehyde increases the reactivity of the other. With phenol, the *p* position is more active than either *o* position; also there is some indication that reaction of one position alters the reactivity of the others and that the position of a reactive site on a chain (internal or end) has a bearing on its reactivity. To illustrate properly the mechanism and kinetics of molecular growth, these factors require quantification.

Analytical data are not available in sufficient quantity (or quality) to allow an accurate definition of the molecular structure or the molecular weight distributions of novolacs. Kinetic data do not allow projection of the reaction mechanism to any useful extent and there are no methods available to provide a quantitative comparison of calculated and measured results. It would be most desirable, from a scientific point of view, to know the exact mechanism for molecular growth in novolacs. This would involve knowledge of the structures and distributions of an enormous number of theoretically possible isomers. For the present, it is necessary to limit our discussion to more general terms. Convenient means are available to determine number average molecular weights ($\overline{M}_n$) through proton magnetic resonance spectroscopy (PMR) and weight average ($\overline{M}_w$) by gel permeation chromatography (GPC). These measurements can be adjusted to allow comparison and give some measure of confidence in the molecular weight distribution provided by GPC. This latter technique has its limitations, as will be indicated.

Before examining data or reaching conclusions, a few comments are necessary to describe the nature of the reaction being considered. It would be a simple matter to define the molecular weight distribution of a novolac if conditions satisfied those required by Flory (*23*). There are several deviations, however, which have not been quantified to allow suitable modification of Flory's expressions for the most probable molecular weight distribution. Perhaps the most limiting is the nonequal reactivity of like functional groups and the probability that the reactive species changes as the reaction proceeds. In addition, it must be recognized that kinetic measurements are confounded by phenomena occurring near the final stages of reaction. In aqueous systems, there are at least two phases, each containing reactants. Molecular weight is increasing by large units, thus a viscosity increase occurs. The diffusion of reactants and reaction products have a bearing on the measurements of reaction kinetics. No effort has been made to quantify these factors during novolac formation, although they have been considered mathematically by Secor (*34a*) as a general case in condensation polymerization reactions.

It will be shown that certain assumptions allow some mathematical treatment of molecular weight distribution, but their validity has not been tested. This limits the confidence one can have in such proposals.

The difficulty in adapting phenol–formaldehyde systems to Flory's treatments becomes obvious when it is recalled that the reaction of formaldehyde with phenol encompasses mechanisms which are not readily separable.

1. Formaldehyde reacts with phenol which has *o* and *p* positions of unequal reactivity; reactivity changes as substitution continues. Thus $f_P \neq 3$.
2. During the early stages of molecular growth, the reactive species is a methylol phenol (one or both of two) which reacts with phenol or a polynuclear material. The molecular weight increases by 106 per step. If this reaction were infinitely fast compared to that of formaldehyde with phenol, the problem would be easier, but as this ratio is less than 10/1 both reactions must be considered. Thus $f_F \neq 2$.
3. Molecular growth occurs mainly by the reaction of "end" groups. Branching is not common at most molecular weights typical of novolacs ($\overline{M}_n < 600$), but then again is not readily measurable. Thus the reactivity of branching sites appears less than "end" sites.
4. At some time during the reaction, dinuclear, then trinuclear, and higher novolacs must react with formaldehyde to some degree and the molecular weight could begin increasing by 212 at each step, then 318, etc.
5. Sooner or later gelation will occur if N_F/N_P is sufficiently large, but in the case of formaldehyde–phenol reactions it occurs at a point beyond that predicted by Flory. This indicates that the "effective" functionality of phenol is less than 3, or rather, $N_F f_F + N_F f_P \neq 2N_F + 3N_P$.

Serious limitations apply to the prediction of molecular weight distribution with existing data. Attempts by Imoto et al. (*36*) to predict molecular weight distribution have met with little success. Poisson's distribution is not appropriate. Humberger (*37*) suggests a method for calculating ultimate chain length of condensation polymers prior to gelation. It is oversimplified for our purpose, but does agree with observations that $\overline{M}_{\mathrm{n}} = 600\text{–}700$ is the upper limit for many novolacs. It is our purpose here to explore a means of predicting molecular weight distributions which involves data available and allows incorporation of new information as developed. Comparison with experimental evidence will be given.

Two general theoretical methods for determining the molecular weight distribution (MWD), resulting from polyfunctional condensations, have been examined in relation to the acid–catalyzed phenol–formaldehyde system by MacDonald and Drumm (*38*). One method is a kinetic approach involving the two types of condensation reactions: (1) the reaction of formaldehyde with phenol and all higher mers; (2) The reaction of these methylolated products with any *n*-mer. The other approach is an adaptation of Stockmayer's probabilistic method (*39*) for the MWD in three-dimensional polymers.

Equations (26) and (27) symbolically depict the two reactions referred to above and are related to Fig. 2:

$$\mathrm{P}_n + \mathrm{F} \xrightarrow{k_{\mathrm{a}}} \mathrm{Q}_n \tag{26}$$

$$\mathrm{P}_m + \mathrm{Q}_n \xrightarrow{k_{\mathrm{c}}} \mathrm{P}_{m+n}. \tag{27}$$

The structures for P and Q polymers are shown in Fig. 5 and are written in a form convenient for this discussion. The specific rate constants for the reaction of formaldehyde and of the methylol group, k_{a} and k_{c}, can be calculated from the corresponding rate constants per unit reaction site (k'_{a} and k'_{c}) and the total number of reaction sites (S_n) using Eqs. (28)–(30).

$$k_{\mathrm{a}} = k'_{\mathrm{a}} \cdot S_n \tag{28}$$

$$k_{\mathrm{c}} = k'_{\mathrm{c}} \cdot S_n \tag{29}$$

$$S_n = 4 + \theta(n - 2). \tag{30}$$

In Eq. (30) the first term "4" is the total number of exterior reaction sites that are available for either type of the two basic reactions. It can be shown that the steady state ratio of the more reactive *p* positions to the less reactive *o* positions is higher for the 4 exterior reaction sites than it is for the $(n - 2)$ interior sites as shown in Fig. 5. In addition both *p* and *o* interior sites are less reactive than their exterior counterparts as pointed out earlier. The factor θ in Eq. (30) is less than unity.

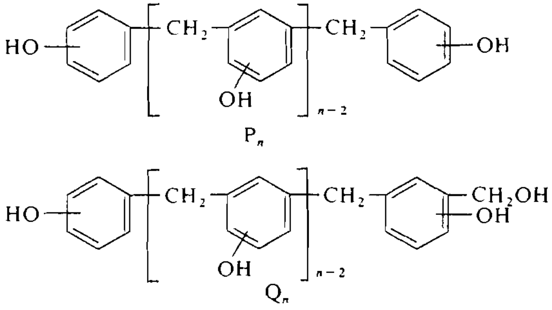


Fig. 5. Novolac structures referred to Eqs. (26) and (27). n = number of mers.

The N-fold pairs of differential equations resulting from the kinetics of Eqs. (26) and (27) are indicated by Eqs. (31) and (32).

$$dP_n/dF = \frac{1}{FT}\,[S_nP_nF + B(S_nP_nV - W_k] \tag{31}$$

$$dQ_n/dF = BQ_n/F - S_nP_n/T, \tag{32}$$

where

$$T = \sum_{n=1}^{N} S_nP_n \qquad V = \sum_{n=1}^{N} Q_n \qquad W_1 = 0.$$

$$W_k = \sum_{n=1}^{k-1} S_nP_nQ_{k-n} \qquad \text{where } 2 \leq k \leq N \quad \text{and} \quad B = k'_c/k'_a.$$

Equations (31) and (32) were solved numerically for a 40-mer system on an IBM-1130 computer. In addition to the initial conditions, the input requires estimates for the two parameters B and θ. Kakiuchi and Otsu (*34*) quotes a value of 5–8 for B. The value 8 was used in the preliminary investigation. The parameter θ can be selected on the basis of providing the best fit for experimental MWD's.

Flory (*40*) suggested that the phenol–formaldehyde reactions could be viewed as the polycondensation of trireactive phenol. It is necessary to regard phenol as the structural unit, with formaldehyde merely supplying the interunit linkage. Stockmayer (*39*) derived the weight distribution function, Eq. (33), for such a system. It is important to stress the assumptions underlying this distribution function. It is assumed that all units are of the same functionality, f, and that all functional groups have the same reaction probability, ρ.

$$w_x = \frac{(1-\alpha)^2}{\alpha}\left[\frac{(fx - x)!f}{(x-1)!(fx - 2x + 2)!}\right]\beta^x \tag{33}$$

where, $\beta = \alpha(1 - \alpha)^{f-2}$.

The number of units in a molecule is x, f is the functionality, and α is the probability that one "leg" of a branch unit is connected to another branch unit. The extent of reaction $\rho = \alpha$, can be viewed as the probability of reaction for any functional group. The number average value ($\bar{x}_n$) and the weight average value ($\bar{x}_w$) of x for the Stockmayer distribution are given in Eqs. (34) and (35):

$$\bar{x}_n = 1/(1 - \tfrac{1}{2}\alpha f) \tag{34}$$

$$\bar{x}_w = (1 + \alpha)/[1 - \alpha(f - 1)]. \tag{35}$$

If it is assumed that an experimental MWD can be described by the Stockmayer distribution function, the two parameters (α and f) in this function can be calculated by experimentally measuring $\bar{x}_n$ and $\bar{x}_w$. Equations (34) and (35) are both functions of α and f. When these equations are solved for α and f, Eqs. (36) and (37) result.

$$\alpha = 2\left[\left(\frac{\bar{x}_n - 1}{\bar{x}_w - 1}\right)\frac{\bar{x}_w}{\bar{x}_n}\right] - 1 \tag{36}$$

$$\frac{1}{f} = \left[\frac{\bar{x}_w}{\bar{x}_w - 1} - \frac{\bar{x}_n}{2(\bar{x}_n - 1)}\right]. \tag{37}$$

If the values of α and f are calculated for a number of novolacs made from different formaldehyde/phenol ratios, it would not be unreasonable to expect the f values to be relatively constant. The values of α would be higher for the higher molecular weight products. If the values for α and f, calculated from Eqs. (36) and (37), are inserted in Eq. (33), the entire distribution can be calculated and compared to experimentally derived values.

Three phenol–formaldehyde resins, prepared prior to the two theoretical studies, were used to test the kinetic and combinatorial models. All resins were synthesized by mixing phenol, formaldehyde, and catalyst, then refluxing to the same residual formaldehyde. The acid strength was varied, but not measured; the pH of the reaction mixtures was in the order resin II < I < III. Table 9 lists some of the MWD characteristics as measured by GPC of these resins. The $\bar{M}_n$ and $\bar{M}_w$ values are the average values for the entire distribution, i.e., including the unreacted phenol.

Table 9
MODEL TEST RUNS FOR MWD

Resin	N_P/N_F (initial)	$\bar{M}_n$	$\bar{M}_w$	Residual phenol (%)
I	1.667	213	375	24.5
II	1.227	360	930	8.5
III	1.176	442	1226	7.6

In order to use Resins I, II, and III as test cases for the Stockmayer distribution, the two parameters, α and f, must be calculated via Eqs. (36) and (37). Table 10 lists these parameters and the molecular weight indices ($\bar{x}_n$ and $\bar{x}_w$) used for their estimation. The average number of units in a molecule ($\bar{x}_n$ or $\bar{x}_w$) is related to the corresponding average molecular weights ($\overline{M}_n$ or $\overline{M}_w$) by Eq. (38):

Table 10

CALCULATED STOCKMAYER DISTRIBUTION PARAMETERS FOR RESINS I, II, AND III

Quantity	Resin I	Resin II	Resin III
Phenol/formaldehyde	1.667	1.227	1.176
$\bar{x}_n$	2.12	3.51	4.28
$\bar{x}_w$	3.64	8.89	11.68
α	0.455	0.611	0.677
f	2.32	2.35	2.27

$$\bar{x}_i = (\overline{M}_i + 12)/106 \qquad (i = n \text{ or } w). \tag{38}$$

The mean value of the parameter f is 2.31. The extreme values (2.35 and 2.27) lie within 2.31 ± 2%. It can be shown that an error $\leq 4\%$ in $\overline{M}_n$ can account for the 2% variation in f. The constancy of f is a necessary but not a sufficient condition for continuing to entertain this model as a reasonable mathematical description of the MWD. In addition the cumulative weight distribution must be closely approximated by the summation of Eq. (33). This equation can be evaluated by inserting the values of α and f. Since the values of f are fractional, the factorials are replaced by the appropriate gamma function.

The combinatorial Stockmayer method (CS) and the kinetic representation (KR) are compared to the experimental MWD for the three test resins in Table 11. The CS model fits very well the experimental points shown in Table 11. The nonoptimized KR model is somewhat inferior to the CS model on a point-to-point basis, and is perforce inferior in estimating $\overline{M}_n$ and $\overline{M}_w$ because of the procedure involved in deriving the parameters of the distribution.

The values used for the two parameters in the KR model are $B = 8$ and $\theta = 0.125$. The MWD for resin I depends strongly on B and is not very sensitive to the choice of θ. It is apparent that a value of $B < 8$ would give a better fit for this resin. In addition, the $\overline{M}_n$ for the KR model is higher than the experimental $\overline{M}_n$ for all three resins. This also points to a lower value of B. In order to achieve higher $\overline{M}_w$ values for resins II and III it is necessary to increase θ.

Table 11

COMPARISON OF EXPERIMENTAL AND THEORETICAL MWD
(CUMULATIVE DISTRIBUTIONS)

	Resin I			Resin II			Resin III		
Mer	Exp.	CS[a]	KR[b]	Exp.	CS	KR	Exp.	CS	KR
1	0.245	0.245[c]	0.168	0.085	0.110	0.067[c]	0.076	0.077[c]	0.056
3	0.516	0.615	0.497[c]	0.270	0.325	0.228[c]	0.201	0.249	0.192[c]
5	0.805	0.806[c]	0.730	0.490	0.486[c]	0.399	0.359	0.392	0.343[c]
7	0.932	0.901[c]	0.862	0.630	0.603[c]	0.546	0.461	0.504	0.478[c]
10	0.993	0.998[c]	0.951	0.773	0.724	0.708	0.577	0.628[c]	0.640
20	1.000	0.999[d]	0.999[d]	0.957	0.903	0.938[c]	0.816	0.841[c]	0.901
30	1.000	1.000[d]	1.000[d]	0.991	0.961	0.987[c]	0.923	0.924[c]	0.973
40	1.000	1.000[d]	1.000[d]	0.998	0.983	0.997[d]	0.968	0.961[c]	0.983
50	1.000	1.000[d]	1.000[d]	1.000	0.993	1.000[c]	0.991	0.980	0.993[c]
$\overline{M}_n$	213	206	249	360	346	430	442	424	481
$\overline{M}_w$	375	374	443	930	917	898	1226	1174	1024

[a] Combinatorial Stockmayer method.

[b] Kinetic representation method.

[c] Gives better fit with experimental.

[d] Equal fit with experimental.

The physical interpretation of the KR model is straightforward. In terms of the functionality of phenol, one could say that $f \geq 2.125$, with the 2 arising from a bifunctional condensation, and with one out of eight phenolic nuclei having a branch, i.e., a fraction of phenol units with a functionality of 3.

The CS model is more difficult to interpret physically. Stockmayer assumed all units to have the same functionality, in deriving Eq. (33). All units do not have a functionality of 2.31, because this is meaningless. Therefore, the f in Eqs. (33), (36), and (37) must be viewed as an "average" functionality for the system, i.e., a mathematical artifact of the process for calculating f. One should resist the temptation to assume that 69% of the phenol units have $f = 2$ and 31% have $f = 3$. The KR model indicates that the branching frequency is between 12.5 and 20%. Thus, the two models are not necessarily in disagreement on the extent of branching as one might initially assume.

The CS model offers the possibility of predicting the conditions for gelation. If the critical value for α can be calculated from Eq. (39), the maximum $\bar{x}_n$ can be calculated using Eqs. (34) and (39):

$$\alpha_c = 1/(f - 1) \tag{39}$$

$$\bar{x}_n(\max) = 2(f - 1)/(f - 2). \tag{40}$$

When $f = 2.31$ is inserted in Eq. (40), $\bar{x}_n(\max) = 8.45$ and $\overline{M}_n = 896$. This is in accord with actual experience and a previous conclusion (*36*) that the number average molecular weight ($\overline{M}_n$) has never exceeded and cannot exceed 1000.

The reader might find it interesting to consult Jonason (*40a*) who offers a determination of α_c for a system glycerol/dibasic acid. Unequal reactivity of hydroxyl groups was considered. He points out that, to be significant in α_c, differences in hydroxyl reactivity must be about 20/1. His case is not directly applicable to novolac chemistry as we understand it, but bears further study.

An examination of branching in novolacs offers some basis for our uncertainties regarding the mechanisms of molecular growth. A general, rather simplified treatment will be given. Initially it is convenient to consider the structural aspects; for this purpose let it be assumed that all positions on the phenol nucleus are equally reactive.

One position on phenol must react with formaldehyde to form a methylol phenol. Any position is satisfactory for our purpose. A methylol phenol reacts with a phenol or any *o* or *p* position on a polynuclear molecule according to their frequency of occurrence. Thus a DPM is from phenol and a methylol phenol. Formaldehyde may react with this and the methylol DPM can react with any phenolic ring position. Likewise a DPM can react with a methylol phenol to form a TPM. Branching can occur once a TPM is formed but the branching probability (BP) is 1 in 5. Not until a hexamer is reached is the BP 1 in 2. If a branch is formed by condensation of a methylol phenol on the internal phenolic ring position the product from a TPM is a tetramer with a BP = 0 for an additional branch. If each successive linear polymer branches with a methylol phenol, the tetramer (BP = 1 in 3) becomes a pentamer (BP = 1 in 7); a straight chain pentamer (BP = 3 in 7) becomes a hexamer (BP = 1 in 4). It is readily seen that if the branching unit is a methylol phenol, the probability of branching is not great until a hexamer is reached and in any case, once a branch is formed, the probability for a new branch to form decreases markedly. Also the internal phenol positions are less reactive than end positions because the more reactive position of the phenol nucleus would be used in bond formation to form the mer. Furthermore, steric factors may contribute to a reduction in accessibility of the internal reactive positions. Therefore, branching to a major extent would not be expected under normal conditions.

At this point it is necessary to recognize that branching via an MP cannot lead to gelation. Yet we know novolacs gel at $N_F/N_P \approx 0.85$ and even lower with strong mineral acids at temperatures approaching 120°C. Dijkstra and de Jonge (*41*) substantiate that α_c, the critical branching coefficient of Flory (*23*), is about 0.56 for a phenol–formaldehyde novolac. Flory shows that $\alpha_c = 1/(f - 1)$ where f = functionality of the branching unit; if all positions are of equal reactivity, $\alpha_c = 0.5$. With a novolac, however, $\alpha_c = 0.56$, thus $f_P = 2.78$ (observed) compared to $f_P = 3$ with all positions equally reactive. This is oversimplified since we have made the further assumption that $f_F = 2$, and this is not true.

Using methylene glycol as a model, the second hydroxyl is reported to be 5–8 (*34*) to 40 (*29*) times as reactive as the first under conditions of novolac synthesis. And as Dijkstra and de Jonge (*41*) point out, formaldehyde and phenol react closer to a "3–3" reaction than a "2–3". (These are functionalities of coreactants.) If the reactivity of the second —OH is infinitely faster than the first, phenol would react as a simple trifunctional molecule, formaldehyde being only a linkage which joins the phenol units. Any deviation would then be attributed to a change in reactivity of a position on a phenol unit.

If branching by a methylol phenol cannot lead to gelation, if the reactive positions on internal phenols are less reactive than end positions, and if one branch lowers the probability of an additional branch on the same molecule, there must be a more suitable explanation of the molecular growth and gelation of a novolac.

The only way in which gelation can occur is by formaldehyde attacking a position on an internal phenol ring to form a methylol group. This must be followed by condensations which ultimately lead to a three-dimensional network. At $N_F/N_P = 0.85$ this network has a very high swelling index and generally constitutes a very minor portion of the resinous mass.

The reaction of formaldehyde with an internal phenol position is not likely until the number of these positions is approximately the same as the number of end groups. This will not occur early in the reaction. By the time the molecule chain is long enough to compensate for the unfavorable ratio of numbers of internal to end positions and for the lower reactivity of these internal positions, it would be reasonable to expect formaldehyde to be nearly consumed. At this time, remaining formaldehyde molecules would have considerable choice of available phenol positions. Those reacting with higher molecular weight components (above hexamer) could well react with an internal phenol position and if a gel does not (or cannot) form, condensation can occur which raises the upper end of the molecular weight distribution. This would be reflected more by an increase in $\overline{M}_w$ and would help to account for the residual low molecular components (phenol and DPM's) always present in novolacs at the end of the reaction and for the relatively low $\overline{M}_n$ compared to $\overline{M}_w$.

Megson points out (*18*) that phenol–formaldehyde novolacs are not straight chain or planar, and have restricted rotation about the methylene bridge. Bond-angle studies and models were used to arrive at these conclusions. On this basis, he suggests that any crosslink would further restrict rotation and limit the probability of reactive sites being in a favorable position for further crosslink formation. Thus the theoretical combined $N_F/N_P = 1.5$ would be most unlikely in the final system. Megson expects few crosslinks under general curing conditions for novolac/hexa mixtures or resoles.

We might agree that cure under isothermal conditions (at high temperature) would be quick and less time would be available for molecular rotations. Reaction for long periods or with a controlled temperature/time balance can change the results substantially. For example, Drumm et al. (*42*) point out that a crosslinked novolac (with hexa) resulting from treatment at 175°C for one hour (slow by most standards) decomposed before it reached its heat distortion temperature. Little difference was noted after exposure of the product to 100% relative humidity for one month. The crosslinked structure showed considerable heterogeneity, however. All products from those with low degrees of crosslinking to those with high crosslinking density showed a low swelling index with acetone. However, except in the most highly crosslinked materials, extractable polymer was high in relation to the swelling index.

Thus, although these structures contain a larger number of crosslinks, the molecular weight distribution is broad; relatively low molecular weight fractions are present. Also, unless ample crosslinking agent is used and the reaction carried out under conditions favoring a large percentage of crosslinks, the resulting structure is affected by high humidity and indications are that the data complement the Megson proposal (*43*) regarding the structure of crosslinked novolacs.

It has been suggested that $\overline{M}_n$ of a phenol–formaldehyde novolac never exceeds 1,000. This is difficult to accept and the tendency is to search for exceptions. However, in no case have we observed values above 1,000 from reactions of formaldehyde with phenol in aqueous media unless operations are performed which change the course or results of random polymerization. For example, dehydration without precautions to remove all unreacted phenol will obviously raise $\overline{M}_n$ but still not above 1,000. On the other hand, the reaction of mono-substituted P with F followed by removal of the substituents on P and of the by-products of the reaction can result in $\overline{M}_n > 1{,}000$. Here, however, the system has been intentionally adjusted.

Higginbottom (*44*) observed that novolacs, synthesized from *p*-chlorophenol—followed by dehalogenation according to Burke et al. (*45*)—resulted in $\overline{M}_n \approx 2{,}800$ by GPC. Molecular dimensions and heterogeneous isomeric structures (chains, coils, H bonding, branches) can influence GPC results. For the case in point, PMR was not used since results are less accurate at high $\overline{M}_n$.

To find the true limit of $\overline{M}_n$, if there is one, reactions should be performed at a N_F/N_P as close to the critical value (0.85) as possible, at low temperature, at low pH, for a long period of time and under conditions which eliminate any loss of reactants.

Under practical conditions ($N_F/N_P = 0.83$), a $\overline{M}_n = 700$–800 can be achieved (PMR) including unreacted phenol after 98% reaction of formaldehyde. A typical PMR analysis of a commercial novolac before removal of unreacted phenol is shown in Table 12. More commonly, however, the $\overline{M}_n$ is in the range 300–500. And in fact Stockmayer (*39*) would predict by Eq. (34) a $\overline{M}_n = 400$ if $f_P = 3$ and $\alpha = 0.5$; this would be the highest $\overline{M}_n$ before gelation would occur.

The molecular weight distribution of a phenol–formaldehyde novolac would not be expected to be narrow or follow the Poisson distribution, as

Table 12

COMMERCIAL NOVOLAC—
PMR ANALYSIS (*44*)

N_F/N_P reacted	0.85
Unreacted phenol	6.15%
Rings/molecule	6.8
Hydrogens/ring	3.29
$\overline{M}_n$	711

the necessary conditions do not prevail. These conditions are (1) growth of each polymer chain must proceed exclusively by consecutive addition of monomers to an active terminal group, (2) all the active termini, one for each molecule, must be equally susceptible to reaction with monomer, and (3) all active centers must be present at the outset of polymerization and there must be no termination. Theoretically, monosubstituted phenols could meet these conditions at $N_F/N_P = 1$. Imoto and Nakadi (*46*) found that this was not the case with *p*-chlorophenol novolacs until "rearrangements" took place, when the novolacs were heated at elevated temperatures in the presence of strong acid. The new resin seemed to approach Poisson's distribution but we cannot place much significance on these preliminary data.

Imoto and Nakade (*46*) also consider the *p*-chlorophenol novolacs in the light of an equation which is said to apply to molecular weight distribution of novolacs and is based on the limitation of $\overline{M}_n \leq 1{,}000$. We can find no justification for this equation and in fact most experimental evidence shows exception to it. It is necessary, therefore, to refrain from further discussion until more data are available. A key point made by Imoto and Nakade (*46*) is that the molecular weight limit may be owing to the intramolecular rearrangements in a novolac as the reaction with formaldehyde is "forced." Surely a change occurs, and in fact gels form in special cases.

Most of the evidence on molecular changes comes from the schools of Imoto and Nakade (*46*) and Burke et al. (*47–49*) working with *p*-substituted phenol, usually *p*-chlorophenol. Burke's intent was to prepare model novolacs of known structure. Imoto searched more for $\overline{M}_n$ characteristics. The major facts which limit the application of the data to usual F–P reactions include nonaqueous conditions, use of *s*-trioxane as a source of formaldehyde, the presence of a strong acid catalyst, and the use of sealed tubes for the polymerization. This work forms a very special and interesting phase of condensation chemistry, but is not truly applicable to this discussion. Some general evidence for the apparent "rearrangements" will be given, but this is for the convenience of the interested reader.

The "rearrangement" of novolacs or some form of thermally induced change takes place under strongly acid conditions, particularly in nonaqueous systems. Peer (*26*) found that the reaction of (**1**) with *o*-methylol phenol in the presence of HCl produced not only the expected trinuclear compound (**7**) but *p*-methylol phenol and (**2**). He calls this an "alcoholytic" breakdown. The mechanism is not at all clear. It is significant, however, that this apparently anomolous reaction occurred principally with the least reactive pair in Fig. 4, (**1**) and *o*-methylol phenol. It would be expected that if (**2**) and *p*-methylol phenol were formed they would react quickly to form (**8**), (**9**), and/or (**10**) but no mention of this was made.

Using rather severe synthesis conditions, for example those used by Burke and co-workers (*47–50*) for chlorophenol novolacs, Rosenthal et al. (*51*) found that novolacs from *p*-alkylphenols decreased in specific viscosity when heated at 180°C. He ascribed this to decomposition of benzyl ethers but it is difficult to perceive their formation at all under conditions of low pH. Some evidence is provided that ether groups are present, but the reduction in specific viscosity is by a factor of 10 with the *p*-cresol novolac; large indeed.

In studying the thermal properties of a novolac ($N_F/N_P = 0.82$) catalyzed with HCl, Popov et al. (*52*) observed an endotherm at 230°–285°C in differential thermal analysis (DTA) studies with no weight loss. Learmonth and Searle (*52a*) give evidence of free radical formation from a phenol–formaldehyde novolac followed by rearrangement under conditions which favor thermal degradation. Hosada (*53*) claims that a rearrangement and polymerization involving the benzyl cation occurs when a novolac or DPM is heated with a strong acid. Raskina and Kogan (*54*) propose that the molecular weight of a novolac changes during dehydration and that the disappearance of phenol is inconsequential since it is present to a maximum extent of about 0.5%. Unfortunately, insufficient information is presented regarding preparation of the resin to allow evaluation of the data. The N_F/N_P was 0.83 and hydrochloric acid was used as the catalyst.

If one assumed bulk reaction (i.e., all ingredients added initially) followed by atmospheric reflux and dehydration as against the metered formaldehyde addition, some conclusions can be reached. Under the conditions used by Raskina and Kogan (*54*), particularly the end temperature of dehydration, some molecular weight change can occur. If atmospheric dehydration is maintained at an active rate, a four-hour period could result in a temperature of 160°C. The same could be true with vacuum dehydration, a technique which is most effective when it is required to remove the last traces of phenol and low molecular weight components.

It is not unusual for a novolac to increase in molecular weight at temperatures above 130°C when a mineral acid (strong) is used as the catalyst at an N_F/N_P greater than 0.8. These conditions are normally avoided since gelation can occur unless extreme care is taken in controlling the N_F/N_P. Increases are reported in $\overline{M}_w$ from 500 to 810 and in $\overline{M}_n$ from 460 to 670 (*54*).

Evidence exists, therefore, which indicates some structural change, other than oxidative, occurs when novolacs are heated in the presence of strong acids. The mechanism of this change is unknown and data are fragmentary. Since the synthesis of commercial novolacs encompasses these conditions, we feel that this area is fruitful for further study.

Throughout this discussion, the influence of pH and the type of acid used has been indicated but not emphasized. Actually these are most critical with regard to kinetics and mechanisms. Unfortunately no study has been made to quantify the contributions of acid type and strength. It is known, however, that strong acids (HCl, H_2SO_4) at concentrations typical of commercial practice (often pH < 1), favor *p* substitution of formaldehyde on phenol and *p* reaction of *p*-methylol with phenol. Thus the first dinuclear material to be formed is often felt to be (**1**) and *p* reactions are favored throughout.

We feel that this area must be studied in more detail. We expect it will be observed that almost all *p*-positions have been reacted under these conditions. The ratio of reactivities of *p* and *o* positions would be expected to be much larger than presently indicated and that the ratio k'_c/k'_a in Eq. (32) would be large. Also, it may not be unreasonable to consider the reactive species to be compound (**1**) when predicting the course of novolac formation.

E. THE STRUCTURE OF NOVOLACS—HYDROGEN BONDING

Megson (*43*) pointed out that phenol–formaldehyde chains would be expected to be sterically nonplanar and coiled. Bond angles of P—CH_2—P would lead to free rotation, but not without hindrance in some cases. These steric effects have an influence on the kinetics and mechanisms of chain propagation. One result of molecular geometry is the relative ease with which some structures may form H bonds. These can have an electronic effect on the reactivity of the molecule. To gain a very approximate idea relative to the general steric configuration of novolac molecules, structures (**1**)–(**10**) were examined as Fisher–Hirschfelder–Taylor models. Recognizing the limitations of such models, they do provide an over-all perspective. Some general conclusions were drawn.

Compounds (**1**)–(**3**) (Fig. 4) have positions which are relatively unhindered for H-bond formation although the molecules are quite nonplanar. (The planes of the aromatic rings cannot lie in the same plane.) Compound (**3**) has definite possibilities for OH···OH H bonding because the open *o* and *p* positions are unhindered. Compounds (**1**) and (**2**) are likewise unhindered in the *o* and *p* positions, but there is little opportunity for OH···OH intramolecular H bonding. In (**3**), H bonding would favor a steric position which makes it more difficult for the benzyl ion to enter the molecule at the *o* position. One might expect also a stabilizing effect on the resonance form favoring an inductive effect on the *p* position.

Geometric characteristics are seen more clearly in models for the tri-, tetra-, and pentanuclear chains. The trinuclear compounds (**6**), (**7**), (**9**), and (**10**) are the most freely rotating and have less-hindered open positions. Structure (**10**) can acquire a position which might favor OH···OH bonding; if so, the open *o* position on the central ring is unhindered; however, any inductive effect would favor reactivity on the end rings. It should be noted that (**10**) can react only through *o* positions. The central ring position in (**8**) is quite hindered in comparison to the end groups. Structures (4) and (5) have a preponderance of *o* links and thus are prone to H bonding between adjacent rings. In (4) all phenolic —OH groups can form a "chain" of OH···OH H bonds. The *p* positions are particularly unhindered, while the two remaining *o* positions are involved in H-bond stereochemistry. Structure (5) has the potential for H bonding both from adjacent phenolic —OH groups and from the —OH groups on end rings. This, incidentally, is typical of all chains terminating with a *p*-benzyl unit. The *p* linkages also facilitate free rotation of the chain and H-bond formation.

The ability of novolac chains to coil and even approach a cyclic configuration is pointed out by Imoto et al. (*36*). Using *p*-cresol, novolacs were prepared containing 1–8 cresol units. As the chain is built up, only the *o* positions on the end rings can be involved. Discounting the difficulties inherent in working with molecules of limited solubility, the data are summarized in Table 13. They were obtained at 55°C by reacting F with the cresol compound in 80% dioxane using perchloric acid as catalyst. The activation energy *E* was determined by measuring *k* over a temperature range of 40°–80°C.

Table 13

THE REACTIVITY OF *p*-CRESOL NOVOLACS WITH FORMALDEHYDE (*36*)

Compound	$k \times 10^4$ liters/mole-sec[a]	Relative k[b]	Activation energy E, kcal/mole
p-Cresol (*p*-C)	6.8	1.0	20.5
$p\text{-C}\!+\!\text{CH}_2\text{—}p\text{-C})_n$			
$n = 1$	7.3	1.1	20.4
$n = 2$	8.1	1.2	20.4
$n = 3$	7.5	1.1	20.5
$n = 4$	3.3	0.5	23.2
$n = 5$	3.3	0.5	22.4
$n = 7$	2.6	0.4	22.9

[a] Units of *k* converted by authors from liters/mole-min to liters/mole-sec.

[b] Value of relative *k* as given in Ref. (*36*).

Considerable significance is attached to the abrupt decrease in *k* after $n = 3$ and to the increase in *E*. Imoto and co-workers rationalize this shift by a coiling of the molecule after $n = 3$, which hinders the reactive site at one end of the chain, and by a reduction in acid strength of the —OH's owing to intramolecular H bonding. Significantly, however, at $n = 0$, 1, and 2, the concentration of cresylic compounds in the reaction mixture was 0.1-*M*; from $n = 3$, 4, and 5, it is 0.05-*M*, and at $n = 7$, 0.02-*M*. In all cases, formaldehyde was present at 0.1-M. Thus, not only did the mole ratio of reactants change, but the concentration changed.

Thus the data for the two groups, $n = 0$–2 and $n = 3$–5, cannot be compared. Data within each group, however, may be considered on a relative basis.

Under the same conditions, it would be expected that $k_{n=3} \geq k_{n=2}$; in fact, the increasing trend observed from $k_{n=0}$ through $k_{n=2}$ would continue. It is recognized that even with this qualification the data of Imoto and coworkers would show a significant change in behavior after $n = 3$. If, as they suggest, the k's of the end groups decrease by a factor of 2 because of steric effects hindering a reactive site, one would expect the same behavior from chains synthesized from phenol. In addition, branching would be expected to occur readily on a phenol–formaldehyde novolac when the number of phenol moieties per molecule reaches four units. Of course this analogy can be made only for novolacs with predominently *o,o* links. This cyclic structure exhibited by the tetranuclear material is not uncommon with *p*-substituted phenols. A tetranuclear cyclic novolac from *p*-cresol was synthesized by Hayes and Hunter (*55*).

An examination of the models of tetranuclear phenol–formaldehyde novolacs shows that the end positions can come within proximity regardless of the ratio of *o*/*p* links, and H bonding would seem possible. Only in the polymer connected by all *o,o* links would conditions be so favorable for preferred formation of hindered end positions, stabilized by H bonds. Even in this case, *o,o*-P–F novolacs would be prone to branching and this has yet to be defined. Steric factors alone do not adequately explain the route by which novolacs are formed, nor does H bonding, although both are influential.

The H bonding has become the subject of considerable interest in P–F chemistry. Its existence in novolacs has been accepted as a partial explanation for experimental evidence relative to kinetics and mechanisms. It is equally important in base-catalyzed reactions.

There have been two approaches to the study of H bonds in molecules related to phenol–formaldehyde resins. Most work has been with novolacs. One was a chemical approach dealing with "hyperacidity" or the effect on acid dissociation of a phenol hydroxyl owing to H bonding. The other emphasized spectrophotometry, usually infrared. Both offer conclusive evidence that H bonding in phenol–formaldehyde reaction products exists, is in a number of forms (some quite strong), and has a definite influence on chemical and physical behavior. The most dramatic evidence has been gathered on *o,o*-linked novolacs or sterically hindered polymers, but ample evidence is available to conclude that H bonding occurs generally and can be identified in randomly linked phenol–formaldehyde units. General

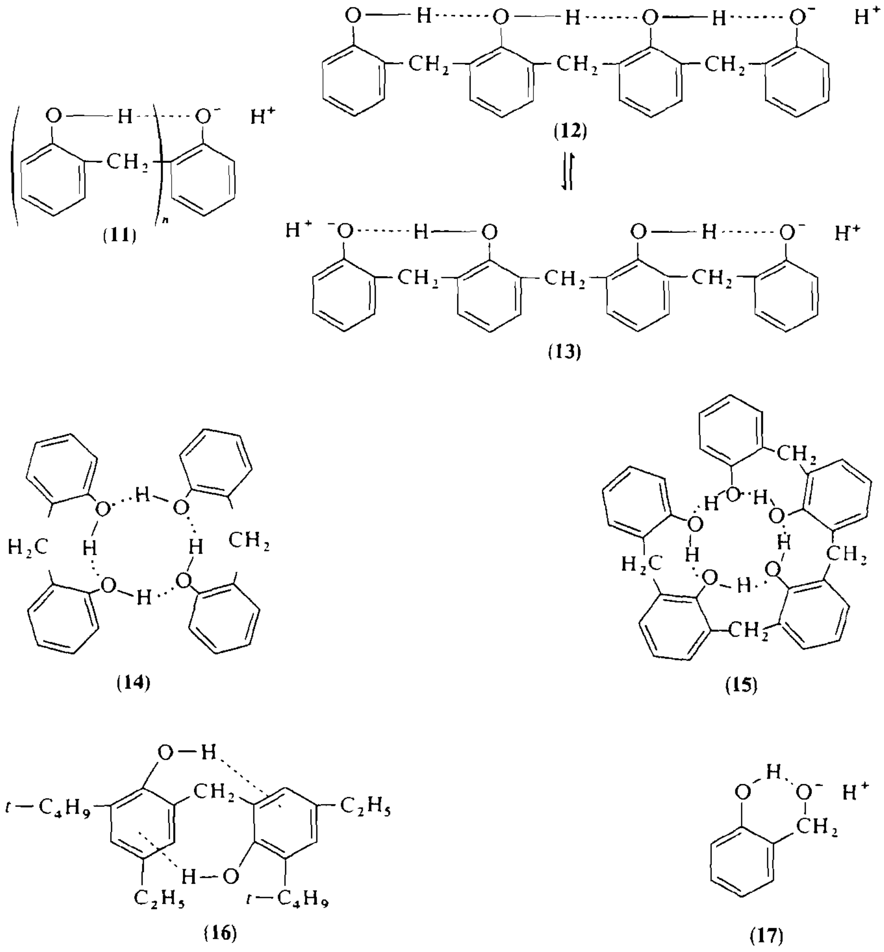


Fig. 6. Some proposed stereo forms of phenol–formaldehyde reaction products.

conclusions will be presented, as will some substantiating evidence where warranted. Figure 6 should be used as reference.

The H bonding exists as intramolecular OH···OH as in **(11)**, **(13)**, and **(15)**, intermolecular OH···OH as in **(14)**, and intramolecular OH···benzene ring as **(16)**. In most cases, unassociated hydroxyls are likewise present. Intramolecular bonds are between adjacent OH groups on *o*-bonded novolacs or through OH groups which come into proximity through molecular mobility. Intermolecular bonds are formed as single OH···OH bonds between molecules or as multiples forming ring structures. These bonds can occur between molecules or segments of molecules. Although weak and generally not competitive except in molecules with unusually hindered positions, the OH· · ·ring bond as in (**16**) has been suggested.

It is seen therefore that H bonds can influence ionization of a phenol —OH, cause hindrance of an end reactive position by cyclization, reinforce inductive effects on reactive positions, and have a bearing on physical behavior in the melt or in solution. Hultzsch (*56*) was among the early intensive investigators of phenol–formaldehyde chemistry to recognize this and he used it freely in explaining the formation of phenol–formaldehyde resins.

Bartlett and Dauben (*57*) report that phenols increase the acid strength of HCl in dioxane, a convenient solvent for novolac preparation. This effect is in direct relationship to the acid strength of the phenol, except for *o*-substituted phenols where intramolecular H bonding can occur. It was pointed out that rates of acid-catalyzed reactions of *o*-substituted phenols should be less, owing to an *o* effect resulting in restricted rotation of the ring–oxygen bond.

Sprengling and Lewis (*58*) investigated dissociation constants of various phenols and found that the acidity was ideed influenced by H bonding; thus reactivity of the phenol moiety is effected. Using ultraviolet spectra to determine the anionic form, several conclusions were reached. The electronic effect of $—CH_2OH$ is small, but H bonding in *o*-methylol phenol, as in (**17**), would favor the resonance transfer of negative charge to the ring, increasing its reactivity to cationic attack, especially in the *p* position. Sprengling (*59*) continued this work and showed that *p,p*-phenolic —OH groups and other phenolic groups separated by more than one methylene linkage exhibited typical phenolic acid behavior in solution. The two hydroxyls did not differ in acidity. Compounds similar to (**3**) [(**11**) at $n = 1$] showed unusual behavior when titrated, which indicated a great difference in the acidity of each —OH group. This was true not only in dinuclear materials, but was seen in tri- and tetranuclear *o*-linked novolacs from *p*-cresol. This work has some interesting concepts and will be discussed in more detail.

It was pointed out that molecular models show the possibility that (**3**) has intramolecular H bonds and it will be shown that, in solution as well as in the solid form, (**3**) shows IR absorption for intramolecular H bonding (*60*). To explore this further, Sprengling examined the compounds (**11**) at $n = 1, 2$, and 3 [shown as (**12**) and (**13**) in Fig. 6].

The *o,o*-linked phenol structures, e.g., (**3**), show different acidities for each phenolic —OH. If the chain is extended to three units as in (**11**) at $n = 2$, one hyperacid hydroxyl is observed which is a little more acidic than the first —OH of (**3**). The remaining —OH groups differ in acidity, but not by much. Continuing to a tetranuclear structure, (**12**) or (**13**), there are two possibilities in equilibrium for hyperacid formation. One hyperacid —OH is found with a second —OH at slightly greater acidity than phenol. It is significant to note that this equilibrium is sterically possible and is obviously owing to increased mobility of the chain, as pointed out earlier. The structure is being approached in which intramolecular bonding will occur in segments of a molecule and likewise intermolecular bonds will become more probable and presumably from between segments of different molecules. Thus evidence continues to mount that physical and chemical behavior of a novolac might be expected to change at a molecular weight of 400.

Insufficient data are available to attribute great significance to "end effects" except where the end rings are *o,o* and can form intramolecular bonds. In this case, hyperacidity seems to be associated with the end —OH and thus this ring would be activated for further cationic attack. This is a partial explanation for linear chain growth being favored and few branched structures formed. Where *p* links are involved, molecular mobility at the tetranuclear stage and beyond allow intra- and intermolecular H bonds. If the end —OH's are favored as hyperacids, weight is added to the explanation of why most novolacs have no or very limited amounts of branching.

Burke et al. (*49*) observed the influence of H bonding on the behavior of novolacs prepared from chlorophenols. Linear *o*-chlorophenol novolacs were not completely dehalogenated with sodium in liquid NH_3, nor were they appreciably soluble in liquid ammonia in direct contrast to *p*-chlorophenol novolacs. Even with a mutual solvent, dechlorination was more difficult. There is a striking difference in structure between these two novolacs. That from *o*-chlorophenol would be linked by *o,o*, *p,p*, and *o,p* bridges while the novolac from *p*-chlorophenol has only *o,o* linkages. This makes the latter prone to a high level of intramolecular H bonds which would enhance acidity (thus solubility in liquid ammonia) and activate the *p*-chlorine toward removal by $Na{\cdot}NH_3$ (liquid).

Keane (*61*) indicated further evidence of intramolecular H bonding in *o,o*-linked novolacs. In performing chromatographic separation of such polymers, he noted that HCl depressed the chromatographic movement of the *o,o*-linked materials as contrasted to other isomers. He concluded that the hyperacidic *o* form [(**11**), Fig. 6], as an anion, has greater mobility in water than does the less-dissociated isomers. It was observed also, that acetyl numbers were larger than expected. The strong hyperacid from *o,o*-linked novolacs gave rise to an inflection in the titration curve which indicated a higher acetyl number. This was true through the heptanuclear novolac [(**11**), $n = 1$–6] beyond which coiling [similar to (**15**)] was presumed to interfere with the intramolecular H bonding that caused hyperacidity. Thus ionization of the phenol moieties is influenced by H bonding sufficiently to provide evidence not only of its existence, but of some of its effects on molecular behavior.

Spectrophotometric studies (mainly IR) have provided most of the information on the stereochemistry of H bonds in phenol–formaldehyde reaction products. Spectral assignments have been quite consistent, at least in the general absorption ranges. Spectral shifts owing to changes in the character of the bonds are not in absolute agreement, but all investigators are in good agreement with regard to the nature of the bonds. Spectral assignments in the IR by several investigators are given in Table 14.

Table 14

IR SPECTRAL ASSIGNMENTS FOR H BONDING (cm^{-1})

Unassociated —OH	Intermolecular H bond	Intramolecular H bond	Intramolecular OH··· ring	Ref.
3,615	3,200–3,350	3,450		*60*
3,620	3,400	3,510		*62*
3,611	3,200	3,476	3,516	*63*
3,610		3,465		*64*
3,610	3,300	3,460		*66*

In phenolic resins the H bonds have certain general characteristics which aid in determining the structural parameters associated with them. The intramolecular OH··ring bond is weak and any competition from other H bonds or from a polar solvent will prevent its formation except in cases of highly hindered structures (*66*, *67*). In these cases unassociated —OH groups often are not observed by IR.

Under most conditions the unassociated —OH is present at least to some extent in all phenolic resins and resin intermediates. Intermolecular bonds generally decrease in intensity upon dilution and may be replaced by intramolecular bonds. Particularly strong intermolecular bonds may persist on dilution and even at elevated temperatures but this requires favorable steric configuration. Intramolecular bonds are not influenced by concentration changes. Some of these observations will be documented because of the importance that H bonding is believed to have on the chemistry and behavior of phenol–formaldehyde materials.

Richards and Thompson (*60*) observed that *p* substitution on a phenol or a *p* bond in a P–F novolac favored the presence of unassociated —OH in dilute solution. In solid phenolic resin there is intermolecular H bonding. If *o*-linked materials are examined, the free —OH is present in dilute solution and another IR band is observed which is generally unaffected by dilution and persists in the solid form. This is considered typical of intramolecular H bonds. In the solid form, *o*-linked materials show intermolecular H bonds.

Compound (**3**) shows unassociated —OH in solution. In the solid form intermolecular H bonds are observed. The unassociated —OH is absent in the solid state for (**1**), (**2**), and (**3**). In solution, (**1**) and (**2**) show only unassociated —OH. In the solid form, (**1**) exhibits intermolecular H bonding. Compound (**2**) shows definite evidence of intermolecular bonding. No evidence of intramolecular bonds in (**1**) or (**2**) is given, nor would it be expected.

Phenol–formaldehyde resins, by acid or by alkali catalysis, showed evidence of H bonds of various types and strengths. The data suggest that most of the H bonds are intramolecular and all resins show the unassociated —OH. Since these intramolecular bonds can theoretically "open" when sufficiently activated, intermolecular bonds could form which would require further energy to cause complete dissociation. Thus one might expect intramolecularly H-bonded molecules to have lower melting points and they could conceivably change their viscosity characteristics as they become intermolecularly bonded. Examination of molecular models shows that unless there is a high proportion of adjacent *o,o*-hydroxyls, intramolecular H bonding does not become facile until the tetranuclear compound is reached. In this case, the end rings come in close proximity and could form intramolecular bonds. Perhaps this is a partial explanation of the sudden shift in viscosity-vs-$\overline{M}_n$ relationships to be discussed later.

Coggeshall (*62*) has studied the effect of H bonds on the ionization of phenol with relation to steric factors. As steric hindrance increases, intermolecular H bonds and unassociated —OH decrease. Highly hindered structures show only OH···OH bonds. All materials examined were *o,o*-DPM's. Hindrance reduces the acidity of the phenolic —OH; the addition of base has little effect on OH···OH bonds but neutralizes unassociated —OH readily.

The steric effects on H bonding as related to phenol–formaldehyde derivatives have been examined, but strategically placed substituents are required for the effects to be clearly identified. This would be the exception rather than the rule in phenol–formaldehyde chemistry.

Cairns and Eglinton (*63*, *65*), Goddu (*64*), and Pshenitsyna et al. (*66*) studied these effects in various degrees and reach general accord. Briefly, the conclusions indicate that all types of H bonds shown in Fig. 6 are formed depending on the steric configurations and positions of substituent groups. They emphasize the concentration (solution) dependence of intermolecular bonds, the stabilization of cyclic intra- and intermolecular bonds by steric factors, and, in extreme cases of steric hindrance, the formation of intramolecular H bonds with the benzene ring. Nonpolar solvents are particularly effective in promoting H bonding in novolacs (*63*, *66*).

It is proposed that tetra, penta, and hexanuclear novolacs are intramolecularly H-bonded cyclic monomers such as (**15**). These hydrogen bonds are not concentration dependent. The di- and trinuclear molecules have bonds which are concentration dependent but show self association at low concentrations, the trinuclear material being more strongly associated. For this work novolacs which were completely alkylated in the *p* positions were studied. This, of course, facilitates H bonding. This is the first real suggestion that *o,o*-novolacs exist as cyclic intramolecularly bonded molecules when the number of phenol units equals 4–6 (mol wt 415–629 for a phenol–formaldehyde novolac). Pshenitsyna et al. (*66*) obtained results by IR studies in CCl_4 solution that confirm the inter- and intramolecular H bonds associated with *o*-bonded novolacs (3) and (2). For (2), no intramolecular H bonds exist, but intermolecular bonds are in evidence as well as unassociated OH. The intermolecular bond does not disappear upon dilution. This is contrary to expectations unless association is very strong indeed. This is claimed to be the case.

As pointed out earlier, chain mobility of tetra-, penta- and hexanuclear novolacs is sufficient to allow formation of cyclic structures. Cairns and Eglinton (*65*) believe that these structures predominate over bimolecular materials. The di- and trinuclear molecules are not capable of intramolecular ring formation, other than rings between adjacent nuclei of the same molecule; thus intermolecular H bonds are favored. They go on to indicate that these novolacs are influenced by an electronic effect of the intramolecular H bond on the terminal hydroxyl. Such an effect would activate the terminal rings rather than the branching positions.

In studying the melt viscosity of novolacs, Jones (*67*) noticed that between 100° and 250°C the energy of activation for viscous flow decreased rapidly as the temperature was increased, but tended to be almost linearly related to $\overline{M}_n$ at high temperatures. A plot of $\ln \eta$ vs $1/T$ was thus nonlinear (η = viscosity). The temperature coefficient of cubical expansion had great dependence on $\overline{M}_n$ until $\overline{M}_n = 400$, where it approached an asymptotic value. The temperature effect on η was greatest with high $\overline{M}_n$. These observations led to the conclusion that phenol–formaldehyde novolacs are strongly associated molecules which are highly ordered in the nonactivated state.

At lower temperatures, flow is thought to be by intermolecularly associated molecules resulting from H bonding between chains. Thus "segmental" flow occurs. These complexes can apparently absorb and distribute greater energy than that required to move one molecule or an associated dimer or trimer. As the temperature increases, intermolecular bonds are broken and the polymer behaves as might be expected for a viscous material, although this does not occur until well over 200°C. For example, a plot of $\log \eta$ vs $\overline{M}_n$ shows nonlinearity over the entire range of $\overline{M}_n$ at 150°C, whereas at 200°C linearity begins at $\overline{M}_n \approx 400$ and at 250°C there is some indication that it exists at lower $\overline{M}_n$. In general, explanations would be expected for behavior at $\overline{M}_n < 400$ at all temperatures and at $T < 200°C$ for all $\overline{M}_n$. The latter is rationalized on the basis of association owing to H bonding. The apparent critical nature of $\overline{M}_n = 400$ is more difficult to rationalize.

Imoto et al. (*36*) showed that a definite change occurred in reaction rate between formaldehyde and *p*-cresol chains when the chain increased from 4 to 5 cresol units. This was attributed to an "end effect" and Jones (*67*) proposed that this may be the case in his viscosity studies although he did not elaborate. Sprengling (*59*) pointed out that dinuclear and trinuclear *o*-novolacs show only one ionization constant but the tetranuclear shows two with one predominating. An equilibrium is indicated. It is interesting, too, that all compounds through trinuclear novolacs are isolated as crystalline solids while the tetranuclear compounds are almost invariably resinous. Thus the H bonding undergoes some change in character at $\overline{M}_n \approx 400$.

Jones (*67*) was particularly careful to avoid oxidation of the novolac during measurements at elevated temperatures. He was equally thorough in removing unreacted phenol and water, both of which are present in commercial novolacs and influence the $\overline{M}_n$ and viscosity to a major extent. For example, a 1% increase in water content decreases the viscosity by about five times. Phenol is very influential as a plasticizer and as a factor in determination of $\overline{M}_n$. The data of Jones (*67*) relating N_F/N_P to $\overline{M}_n$ are of interest. Resins were synthesized using purified raw material. Molarities were consistent with usual practice, HCl was the catalyst, and the reaction at 100°C was continued until the degree of reaction of formaldehyde was 1.0. Table 15 shows the results. As would be expected, the major factor limiting $\overline{M}_n$ is the N_F/N_P and the fact that N_F/N_P must be less than 0.86 to avoid gelation.

Under conditions of reaction to achieve $\overline{M}_n = 400$, branching would not be expected to occur to a great extent. This surely becomes more probable as N_F/N_P increases. Jones eludes to the possibility of branching but does not credit it with any of the observations on η vs $\overline{M}_n$ data. Branching, coiling, and intertwining of molecules owing to their nonlinear and nonplanar configurations all may contribute to molecular mobility (or lack of it), but

Table 15

VISCOSITY VS $\overline{M}_n$ FOR PHENOL–FORMALDEHYDE NOVOLACS (*67*)

N_F/N_P	$\overline{M}_n$	η, poise 150°C	200°C
0.5	395	2.15	0.244
0.67	471	5.07	0.465
0.75	587	19.9	1.30
0.80	722	84.1	3.31
0.83	776	232	4.80
0.86	867	684	10.10

we must agree with Jones that association through H bonding is a major stabilizing factor at the least.

A closer examination of H bonding is justified. Its full influence on reaction kinetics and mechanisms is not known. It is a plausible explanation for some phenomena during synthesis of novolacs, and the very nature of phenol–formaldehyde chains makes H bonding a high probability. Thus some understanding of this property of novolacs will be beneficial as future research is considered. It will be found that H bonding can be influential in both acid- and base-catalyzed phenol–formaldehyde systems. The H bonding by the phenolic —OH is not a new concept. There are many cases which can be cited and much data worthy of review. This discussion was limited to subjects related to materials which have a relationship to phenol–formaldehyde chemistry. As we have just seen, the ways in which H bonding shows itself in phenol–formaldehyde resins are the important factors.

F. DIRECTIVE CATALYSIS—*o*-LINKED NOVOLACS

It has been pointed out that strong acids, low pH, and low temperatures favor the formation of *p* bonds both in the reaction of formaldehyde with phenol and of the methylol phenol with phenol or phenol–formaldehyde novolacs. With the pH in the range of 4.0–6.0, the rates of reaction are relatively slow and an excess of phenol favors formation of *o,o*-linked novolacs. This is also the pH range where benzylethers form and are relatively stable and where the reaction of methylol phenols with phenol or other phenol moieties usually requires forcing for completion.

It has been known for some time that, in basic catalysis, formaldehyde reacts with phenol in the *o* position to a greater extent when the catalyst is based on a divalent alkaline earth metal. Of course in this case methylol phenols are formed. Bender et al. (*68*) observed that the use of divalent metal compounds (ZnO was very effective) as catalysts under conditions favoring novolac formation resulted in a large preponderance of *o* links. This meant that structures were synthesized in which most of the remaining unreacted groups were *p*. These are very reactive and thus the novolacs crosslink at much accelerated rates compared to compounds with random linkages. These novolacs are referred to as *o,o* novolacs or high-*o* novolacs. Structurally, they are often represented in one form as (**11**) (Fig. 6). This is a highly selective catalytic effect in phenol–formaldehyde novolac chemistry.

As often occurs, investigators do not agree completely on the mechanisms of this directive effect although there is little doubt about the general conditions to achieve high *o* bonding. Before examining the information available, it might be well to consider the unusual circumstances under which *o,o* bonds form and how they differ from common practice in the synthesis of novolacs and methylol phenols (resoles).

Novolacs are synthesized at pH < 3, using strong acids. The initial reaction is between a formaldehyde cation ($^+CH_2OH$) and an electron-rich position on phenol. Development of the novolac occurs by reaction of a benzyl cation with electronegative positions on phenol moieties. The reaction occurs under conditions favoring an ionic mechanism and inductive and resonance effects on phenol regulate the positions attacked. These are mostly *p*.

Resoles are synthesized at pH > 7.0. The reactive species are the phenate ion and an un-ionized source of formaldehyde. Usually, strong bases are used for catalysis. An ionic mechanism is again indicated. Directive effects of the catalysts are observed under alkaline conditions but always there is a broad distribution of substituted positions. As resoles polymerize, the phenate ion reacts with methylol groups in a ring position. Ether formation is not favored except under special conditions.

The only comment made so far relative to specific catalysis for *o* links was that the reactions were favored at pH 4.0–7.0, generally 4.5–6.0. This would seem to be of major significance. At this pH, the concentration of phenate ion is the equilibrium concentration for the ionization of phenol, and very nearly that for ions postulated for aqueous formaldehyde.

To be totally effective, any effect must be general. It must direct formaldehyde to an *o* position on phenol and must control the condensation of *o*-methylol phenol with phenol, in chains or other forms. It is difficult to rationalize that a catalyst could control all factors, each in a specific manner, which would result in only *o* links. Something must exist in common with the reactions of formaldehyde with phenol and the subsequent condensations, which allows the catalytic influence to be consistent.

The first step in the *o,o*-novolac synthesis is the reaction of formaldehyde with phenol. This must be in the *o* position. The growth reaction can occur in a number of ways. The *o*-methylol phenol can react with phenol in an *o* position, followed by continued condensations of this type. Self condensation of *o*-methylol phenol is possible, either on the open *o* position or by benzyl ether formation with itself or another methylol phenol. We have found little evidence in the literature or in our own laboratory that the concentration of the dibenzyl ether of *o*-methylol phenol is ever large enough to be significant in the formation of *o,o*-linked novolacs. Many authorities believe that this ether is an important intermediate. We have yet to be convinced and will accept the major initial mechanism as being one of condensation of *o*-methylol phenol with 2,6-DMP to form the ether and with the possibility of self condensation of methylol phenol forming initially *o*-methylol DPM (*o*-methylol derivative of (3), Fig. 3), which condenses further. Finally, decomposition and resinification take place.

The evidence will be examined with the preceding in mind, but certain facts must be apparent regardless of the actual mechanism. Without the addition of any other materials, phenol and formaldehyde are virtually unreactive. Under normal conditions the pH of an uncatalyzed mixture of phenol and formaldehyde in proportions typical for novolac formation is about 3–3.5 depending on the amount of formic acid in formaldehyde and inhibitor in phenol. At this same pH, the addition of divalent metal ions causes reaction to occur, slowly to be sure, in a manner which favors *o,o* links.

It is necessary that the *o* positions on phenol derivatives be activated in relation to the *p* positions under the conditions of reaction. Thus any effect which can be transferred around the benzene ring by resonance must be discounted. Inductive effects are probably not at work here. The specificity must be owing to interactions with the phenolic —OH that can be transferred only to the *o* position. One such possibility is a rearrangement through complex formation.

The most complete report on *o,o* novolacs is a series of two papers by Fraser and co-workers (*69*, *70*). About the same time, Peer (*26*) published his data in thesis form to be followed by a formal disclosure of results (*71*). Finn and Musty (*72*) were among the first to examine the distribution of *o* and *p* bonds in novolacs. The most controversial conclusion comes from them, "... pH is the controlling factor and the presence or absence of ZnO at any given pH makes little difference." Unfortunately this statement is often taken too broadly to indicate that pH is controlling in all circumstances. It is known that *o* substitution is favored even without a catalyst at high temperatures and pressures.

A large excess of phenol is often favored in preparing high *ortho* novolacs but $N_F/N_P = 0.7$ is successful (*26*, *69*, *70*, *71*). Finn and Musty (*72*) used $N_F/N_P = 0.182$, ZnO concentration 1.92 g/mole formaldehyde, and reaction conditions reaching a maximum of 160°C after the removal of unreacted phenol. The pH was varied from 0 to 6. The maximum occurrence of (**3**) was at pH 4–5, for (**2**) at pH 0.5–1.0, and for (**1**) at pH 0. As Finn points out, however, the amount of total DPM's [(**1**), (**2**), and (**3**) in Fig. 3] found represents the isomers remaining unreacted, not the amount formed; the total was never very large and, interestingly, a minimum existed at pH $\approx$ 2.9 for total concentration of all isomers. It was suggested that this may be the optimum pH for condensation to longer novolac chains. We are inclined to think that this may be a transition region from an ionic to a nonionic or other type of mechanism. As the pH goes from 2.9 to 4.5, the quantity of (**3**) increases rapidly while (**1**) and (**2**) decrease to virtually zero. Finn and Musty (*72*) acknowledge that this work was preliminary and "suggested" rather than "concluded" from the results.

The other investigators acknowledged the significance of metal ions although some disagreement is evident. Only the major conclusions will be dealt with here. In beginning their work on *o,o*-linked novolacs, Fraser et al. (*69*) were interested more in qualitative descriptions of the many variables which influence this directive effect. Unfortunately, the methods by which the relative degrees of *o,o* bonding were determined were not particularly analytical. Cure characteristics (crosslinking) were used with some assistance from IR analysis. The measurement of cure rate, degree of cure, etc., was indicative but not conclusive. There are too many interactions which cloud the results. As a start, however, there was logic in this approach since *o,o*-linked novolacs were known to be fast gelling. The second paper (*70*) was more definitive. Products were isolated by paper chromatography and results were more analytical. Since these two papers are part of the same research, they will be viewed as one.

Concerning general catalysis which favors *o,o* bonds in novolacs, Fraser and co-workers found that both the rates of reaction and the proportions of *o,o* links decreased in the order given for the effective catalysts:

$$Mn^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Co^{2+}, Ca^{2+}, Ba^{2+}.$$

It was stated further that only divalent metal ions were conveniently effective (without solubility and side-reaction complications). Trivalent or other transition elements showed little or no effect. Fraser reported that there was no relationship between chelating ability of the ions, their magnetic moment, ionic radius, etc., and the *o*-directing influence.

The initial step in the reaction of phenol with formaldehyde is methylolation to *o*-methylol phenol and 2,6-DMP followed by condensation to ultimately form chains. The directive influence of the catalyst is effective throughout the reaction. It is felt that the dibenzyl ether is important in this reaction at temperatures of 100°–150°C. We hold some reservation here and will discuss this more thoroughly. The $\bar{M}_n$ increases with pH and N_F/N_P, but *o* substitution tends to decrease. Molecular weight distribution is inclined to be narrower with increasing *o,o* bonding. Any deviation from pH 5–6 or any change from the catalysts listed decreases *o,o*-bond formation. The most favored catalyst is zinc acetate [$Zn(OAc)_2$]/acetic acid (HOAc); a pH 5.5, atmospheric reflux reaction (100°C), and distillation to 160°C are typical of preparative methods.

Under the preceding conditions, Fraser observed the course of reaction during reflux and distillation by paper chromatographic separation and qualitative identification of reaction products. At 100°C and less than 50-min reaction time, only *o*-methylol phenol was found in quantity although 2,6-DMP was reaching a maximum. After 50 min, and during the distillation when the temperature increased from 100° to 160°C in 85 min, several simultaneous reactions occurred; *o*-methylol phenol decreased to zero in 80 min; 2,6-DMP reached a maximum in 40 min, but disappeared in 70 min;

concurrently, resin formed very quickly beginning after 40 min (as temperature began to increase); tri- and tetranuclear novolacs were observed in later stages of the process in quantities less than the amount of (3). The dibenzyl ether (**18**) is reported as beginning to form after 50 min; at 100°C and as the temperature rose to 160°C, (**18**) increased in concentration to a maximum of 5%, then decreased to zero at $T = 160°C$. We find it difficult to rationalize these observations on the ether (**18**) and comments will be made later.

Peer (*71*) likewise found the strong *o*-directing influence of the divalent alkaline earth-metal ions. He differed with Fraser in a number of respects. For example, Al_2O_3, MgO, and other alkaline earth-metal hydroxides were found to be rather weak *o*-directing catalysts, while $Cu(OH)_2$ and hydroxides of other transition metals were strong. He concluded also that the catalytic influence of the metal ions is in direct relation to their chelating strengths. A $N_F/N_P = 0.7$ was found to be effective in achieving *o*-directed reactions. These observations are in contrast to Fraser's. Peer worked also with boric acid and other catalysts in nonpolar solvents and found a strong *o*-directing effect.

It is interesting that Peer's original work (*26*) was performed at about the same time as Fraser's. Obviously independent, it was unfortunate neither could expand on the work of the other. It thus remains for us to examine and evaluate these results in view of the conditions used. This often leads to a third opinion. Some comparison is required owing to the major differences in conclusions by these workers. Both authors used paper chromatography to separate and identify the reaction products qualitatively.

Peer favored a value for N_F/N_P of 0.7 while Fraser used 0.5. Except for pH, all other conditions of reaction and condensation were much the same. Reflux was at 100°C, distillation and condensation were carried out up to 160°C, and pH = 4.0–6.0. Peer, although measurements were approximate, favored pH 4.0–5.0 while Fraser favored 5.0–6.0. A third set of conditions will be interjected here which represents unpublished work from this laboratory. At reaction conditions similar to the preceding $N_F/N_P = 1.0$ can be used effectively. We prefer, however, to use a pH 5.0–5.5 (Fraser preferred 5.5). In our work, just as for other workers, ZnO/HOAc was an effective catalyst.

There is general agreement that the first step in the reaction must be the formation of *o*-methylol phenol. This must be followed by ether formation by condensation of methylol groups on *o* positions on phenol under conditions which do not decompose the ethers prematurely. Finally, the ethers are decomposed at elevated temperatures to form *o* novolacs. The significant factor is that the mechanism involves mostly ethers, with some condensation of *o*-methylol phenol with phenol or polynuclear novolacs. Although Peer

(*71*) suggests strongly, and Fraser et al. (*70*) offer some evidence, that (**18**) is significant in this mechanism, our analytical information from nuclear magnetic resonance and gas–liquid chromatography shows no evidence, at any time during the reaction, of the existence of (**18**).

We conclude that the reactions in Fig. 7 predominate: *o*-methylol phenol is formed first, and in large quantity; 2,6-DMP forms next; ether formation occurs during reflux. The ethers are quite stable at pH 5.0–6.0 and must be heated to 160°C before complete decomposition and resinification take place. This last step must be carried out in unreacted phenol to avoid gelation.

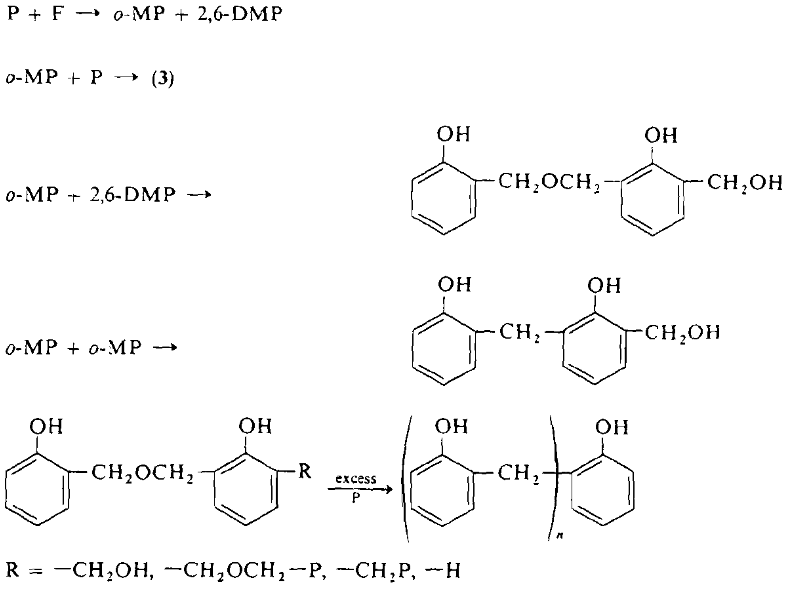
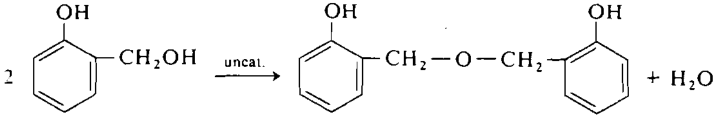


Fig. 7. Some reactions during formation of *o*-linked novolacs.

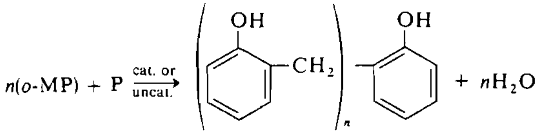
It is our opinion that the material isolated by Fraser as (**18**) is another ether. It is well known that substituted methylol phenols readily form ethers which are relatively stable. Condensation of *o*-methylol phenols with phenol also occurs readily although it is not favored under the conditions for synthesizing *o* novolacs. It is obvious that ethers of many possible structures can form. Ultimately this mixture of ethers decomposes to form *o,o* novolacs. Formaldehyde can be liberated which can methylolate an open-ring position or crosslink the structure if the probability of branch formation is high (low phenol concentration). In addition, however, benzyl cations may form without formaldehyde evolution and react with open-ring positions, although pH may be limiting in this reaction.

Since we offer doubt as to the importance of intermolecular ether formation by two molecules of *o*-methylol phenol in the formation of *o,o* novolacs, an examination specifically of this point may serve to clarify our position. Sprung and Gladstone (*73*) showed that only the uncatalyzed condensation of pure *o*-methylol phenol resulted in the dibenzyl ether as in Eq. (41). When catalyst (triethanolamine) or phenol was present, resinous materials resulted. These are thought to be according to Eqs. (42) and/or (43). It was further observed that the presence of phenol decreased the rate of self condensation of *o*-methylolphenol. The reactions in Eqs. (41) and (42) were shown to be second order; that in Eq. (43) was first order.



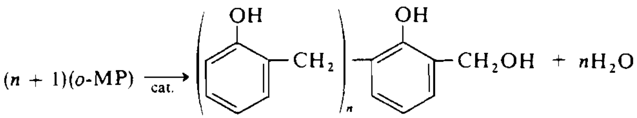
(18)

(41)



(19)

(42)



(20)

(43)

Finn and James (*33*) showed that phenol and DPM's suppressed the self condensation of *o*-methylol phenol. Also, at 90°C, with N_F/N_P from 0.2 to 5.0, and at pH ≈ 5, no ether was reported in the reaction mixtures over a range of 10 min to 80 h of reaction time. If there had been a significant amount of (**18**) present, it would have been detected even though the authors were not searching for it. It was interesting also that Finn and James (*33*) observed that the reaction at pH 6.0 and 90°C between *o*-methylol phenol and phenol required 14 h for completion. The products of reaction were not identified but a mixture of DPM's is inferred.

The work of Fraser et al. (*69*, *70*) emphasized the role of (**18**) in resin formation. Analytical results during the reaction of phenol and formaldehyde indicated that (**18**) formed well after the reaction generated resinous materials and that its concentration was a maximum of 5% which decreased with heating at 140°–160°C. Since resinous components formed very quickly and were still forming when evidence of (**18**) appeared, a significant role of (**18**) in resin formation is not indicated. It did not "decompose" until the temperature reached 140°C. Higher molecular weight resins had already formed by this time; low molecular weight materials showed evidence of increasing in concentration after 140°C. These could be formed in any number of ways including formation of (**18**), but indications are that this is a minor factor.

The complete absence of *p*-methylol phenol in Fraser's work is confusing since *o* bonds seldom are formed exclusively. Fraser et al. (*69*) showed also that with an excess of phenol (the conditions for novolac formation), (**18**) reacts to produce some *p* bonds. With $Zn(OAc)_2$ as catalyst at 150°C and 100% molar excess of phenol, over one-half of the compounds isolated contained *p* bonds. Of the total bonds identified, however, *o* was still 88% of the total number of methylene linkages.

The differences in conclusions by Peer (*26*, *71*) and Fraser et al. (*69*, *70*) relative to the activity of metal cations cannot be resolved from the information available. Generally, the conditions used by Peer showed small differences from those used by Fraser. Peer used a higher N_F/N_P and lower pH. It would be expected that a lower pH would extend the number of catalysts which are effective. For example, transition metals might well be more active catalysts at pH 4.0–5.0 while the alkaline earths are best at pH 5.0–6.0. A higher N_F/N_P favors increased substitution and more ether formation. It would seem that Peer used conditions favoring catalysts which are "weaker" by Fraser's standards. Actually, reaction conditions were sufficiently different that direct comparison of results is not possible.

Mechanisms for the directive catalytic effect are suggested by both Peer (*71*) and Fraser et al. (*69*). Neither mechanism was studied in detail, but both involved chelate formation. That suggested by Peer stops with the formation of *o*-methylol phenol while Fraser and colleagues go on to show the continuing *o*-directing influence through the formation of (**3**). Both omit ether formation.

Dijkstra (*70a*) points out, however, that the formation of a salt by methylene glycol in the presence of the stronger acid phenol is not likely. He also proposes that formation of complexes of methylene glycol and divalent metals is feasible and is a reasonable mechanism. Peer (*26*, *71*) offers such a mechanism. Both mechanisms are illustrated in Fig. 8.

G. NOVOLACS FROM NON-AQUEOUS SYSTEMS

The chemistry of phenol–formaldehyde reactions would be expected to change in nonaqueous media. In the presence of alcohols, for example, formaldehyde is known to exist as a mixture of formals in equilibrium. In nonpolar solvents ionization of reactants and of catalysts is influenced, and H bonding becomes more prevalent. Chelation and other complex forming

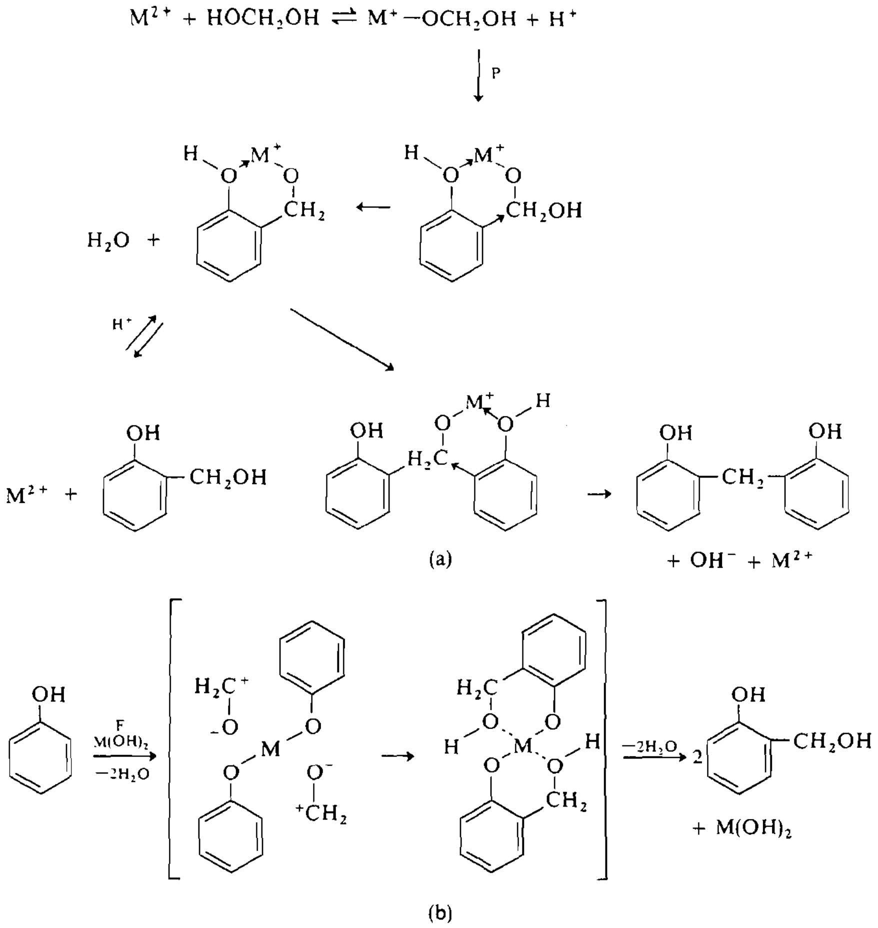


Fig. 8. The *o*-directing effect of divalent metal ions. (a) From Fraser et al. (*70*); (b) from Peer (*26, 71*).

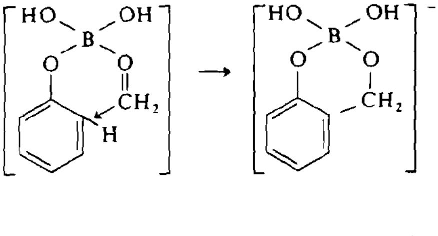
mechanisms vary. Conventional catalysts alter in influence and other catalysts become effective. Hence the kinetics change in the nonpolar media used. Generally phenol–formaldehyde reactions are not performed in nonaqueous solvents. It is not necessary. Even cresols and some modified phenols are reacted with formaldehyde in an aqueous medium if desirable. Unfortunately, the expense and annoyance of using organic solvents have caused neglect of an interesting area of research for phenol–formaldehyde chemistry.

Little has been published on phenol-formaldehyde chemistry in nonaqueous medium which is designed to give the same products as from water systems. Some limited work has been done where special synthesis was desired and the materials used required organic solvents to maintain homogeneity. We are interested here in comparing the effect of reaction media on phenol-formaldehyde chemistry, thus the special cases will not be reviewed.

Perhaps the two best examples of catalytic effects as influenced by nonaqueous media are those given by Peer (*26*, *71*) and by Partansky (*74*). Both dealt with *o*-directing catalysis in the synthesis of novolacs. One most interesting conclusion is that once the reaction conditions are adjusted so that phenol and formaldehyde are virtually un-ionized, reaction takes place exclusively in one *o* position, even without a catalyst. Toluene, *p*-xylene, and cyclohexane were particularly effective as solvents in this case. Thus the full effects of intramolecular H bonding of *o*-methylol phenol and of the *ortho* transition state are felt without interference from the *p* position.

Without a catalyst, only *o*-methylol phenol was formed and resin formation occurred exclusively through the ethers. It was found also that some transition metal compounds not highly active as *o* directors in water (but expected to be) were more active in benzene [$Fe(OH)_3$ and $Zn(OH)_2$ are examples]. Apparently, complex formation by these ions in aqueous media does not occur with phenol. The $Pb(OH)_2$ was a more effective *o*-directing catalyst in benzene than in water.

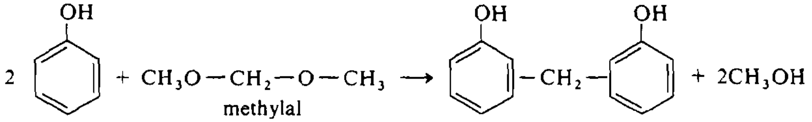
The most unusual case is H_3BO_3. It is an *o*-directing catalyst, only in nonpolar media. Peer found no effect in water; however, it is known that an *o*-directing effect exists if the temperature of the reaction is raised to 125°–140°C and the water content is a minimum; however no organic solvent is necessary (*75*). A mechanism for Peer's observations was offered and account was taken of the fact that water must be absent. The mechanism proceeds through a monophenyl borate formed by the nonaqueous reaction of phenol with H_3BO_3. Formaldehyde adds to phenyl borate and is directed to the *ortho* position as in Eq. (44).



$$H^+ \xrightleftharpoons[H_2O]{} o\text{-MP} + H_3BO_3 \qquad (44)$$

Partansky (*74*) observed that monovalent alkali metal hydroxides, in small amounts, favored *o,o* links in nonpolar solvents only. The paraformaldehyde and phenol were reacted in solvents of various polarities and the *o*/*p* ratio was determined by IR analysis. The N_F/N_P was generally 0.2, a large excess of phenol. Several catalysts were evaluated. Weak acids in nonpolar solvents gave a mixture of 80–83 % *o* bonds to 20–17 % *p* bonds. As the strength of the acid increased and/or the solvent became more polar, the percent of *o* bonds decreased to as low as 10–20 % (with HCl in ethanol/water). With those catalysts which are generally very effective as *o* directors, nonpolar solvents caused little enhancement; however, they did increase the *o*-directing effect of catalysts normally giving more *p* bonds, e.g., HCl, oxalic acid, triethylamine. The ratio of *o*/*p* bonds in these cases never equaled that from catalysis by alkaline earth metal ions. The best yields of *o* bonds was by conventional techniques with MgO, ZnO, $Zn(OAc)_2$ (zinc acetate)/HOAc, and $Mg(OAc)_2$ in nonpolar solvents. No mechanism was offered but it was pointed out that under acid conditions, the reaction of formaldehyde with phenol to form *o*-methylol phenol deactivated the other *o* position. Also, ethers formed most easily from methylol phenols substituted in at least one other position. This observation is consistent with our experience in aqueous systems.

Concerning a more general formation of novolacs, Murayama (*76*), in a series of three papers, has attempted to describe fully the kinetics and mechanisms of the phenol–formaldehyde reaction in nitromethane. A large excess of phenol was used, formaldehyde was in the form of dimethylformal (methylal), and the catalyst was $(C_2H_5)_2O{\cdot}BF_3$. The course of the reaction was followed by gas chromatography and the rate of formation of methyl alcohol was significant in kinetic considerations. Interactions of reactants and intermediates were examined. The general reaction for the preparation of novolacs by this method is shown in Eq. (45) and the overall kinetic equations proposed by Murayama are in Eqs. (46) and (47). It should be noted that the reaction rate is dependent on the catalyst concentration.



(45)

$$\frac{d(CH_3OH)}{dt} = \frac{k[P]^2\,[\text{methylal}]^0\,[\text{catalyst}]}{[CH_3OH]^3} \qquad (46)$$

$$E = 18.6 \text{ kcal/mole.}$$

Unfortunately we are unable to rationalize all the conclusions reached regarding the kinetics of this system. Equation (46) is suggested for application at low conversion of methylal. Equation (47) is said to operate at conversion >30 %.

$$\frac{d[\mathrm{CH_3OH}]}{dt} = \frac{k[\mathrm{P}]\,[\mathrm{methylal}]^0\,[\mathrm{catalyst}]}{[\mathrm{CH_3OH}]^{2.5}}. \tag{47}$$

Murayama acknowledges the apparent complexity of the system. The theoretical treatment of the kinetics is interesting but too little data exist for an accurate description. On the other hand, the chemistry is better defined, at least qualitatively.

The principal reactions between phenol and formals in nonaqueous media are the acetal exchange (reversible) and substitution on the aromatic ring (irreversible). At up to 30 % conversion, the rate of consumption of phenol is equal to the production of methyl alcohol and twice the consumption of methylal. The general conclusions reached are that: the reaction rate is fast initially, but slows down as it proceeds; reaction products and intermediates have a rate-reducing effect; also, high proportions of phenol in the initial reaction media decrease the rate, while the methylal concentration has little effect; methyl alcohol, on the other hand, decreases the rate.

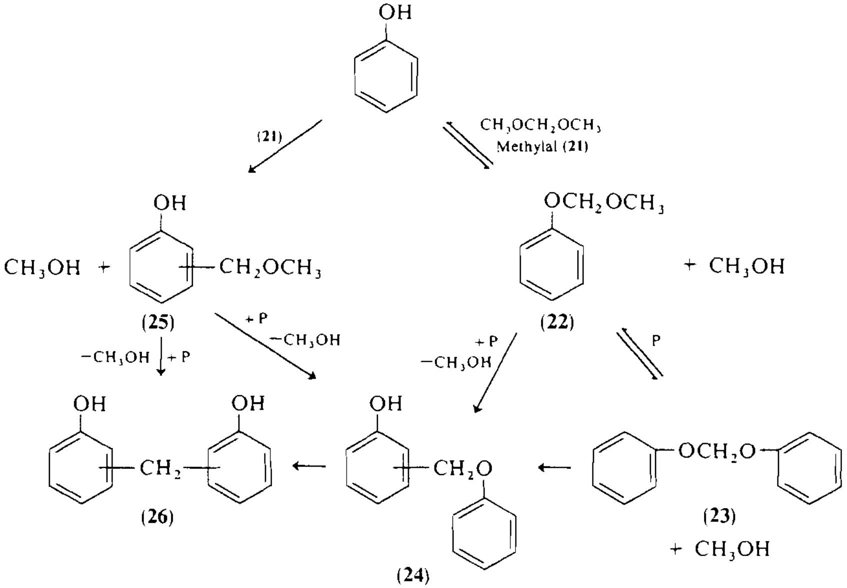


Fig. 9. Reaction of formaldehyde with phenol under nonaqueous conditions (*76*).

By studying, quantitatively, the effects of the above variables and with the use of paper and gas chromatography, a reaction scheme has been suggested; this is shown in Fig. 9. Phenol, **(22)**, **(25)** (as *p* isomer), and **(26)** (as *p,p'* and *o,p'* isomers) have been identified. The presence of methylphenylformal, (**22**), led the author to suggest that the route involving (**22**), (**23**), and (**24**) is an important part of the reaction mechanism. He indicated equilibrium among phenol, CH_3OH, (**22**), and (**24**) which is not consistent with acetal exchange and involves aromatic substitution. We have altered his scheme to be consistent with his earlier statements regarding equilibria,

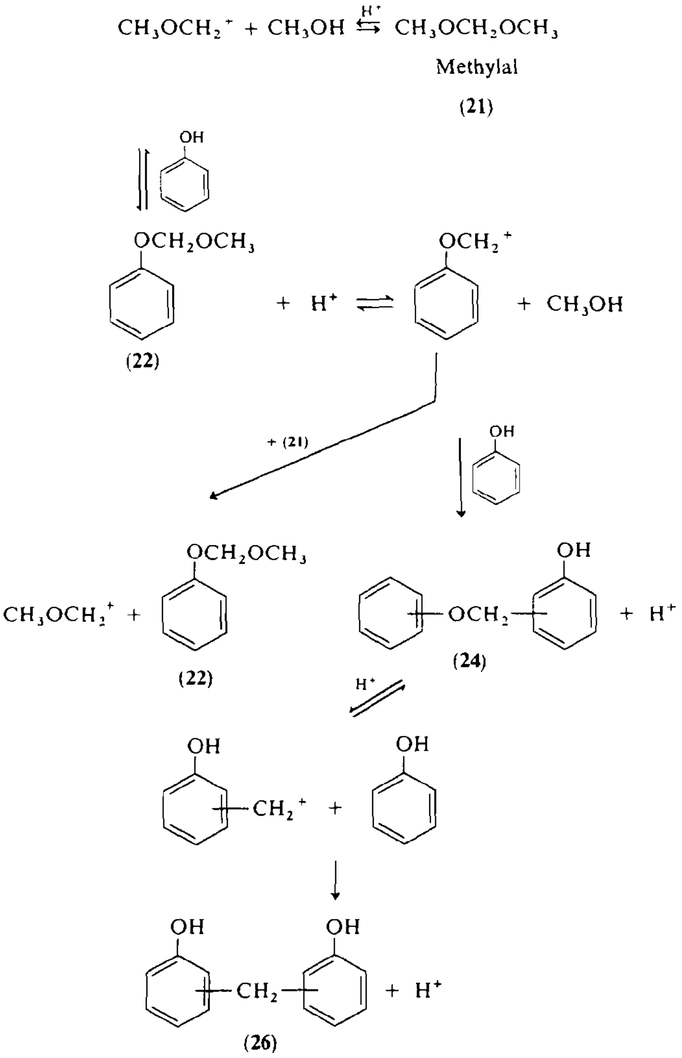


Fig. 10. Reaction of phenol with methylal in nonaqueous medium; most probable route to novolacs (*76*).

thus showing the preceding reaction to be nonreversible while indicating a reversible reaction involving phenol, (**22**), CH_3OH, and (**23**). In this manner, (**26**) may be formed without competition from equilibria involving the suggested, but undetected, intermediates (**23**) and (**24**). This is justified on our part since Murayama ultimately discounted the participation of (**23**).

The identification of (**24**), however, must be made before the suggested course of reaction can be accepted. He places great significance on the importance of methylphenylformal, (**22**), in the over-all mechanism, but in our opinion this has not been substantiated. We have observed that in nonaqueous media, phenol ethers (e.g., **22**) rearrange irreversibly under the influence of strong acid to an aromatic substituted isomer. Thus it might be suggested that (**24**) is formed directly from (**22**).

Finally, the summary of suggested mechanisms in this system was dependent on the presence of H^+ ions and benzyl cations. It is indeed unfortunate that the entire reaction scheme in nonaqueous media depended upon the presence of "traces of water" to form H^+. This may be the actual case or the active cations could form by interactions of BF_3 with the variety of complexes possible in this system, phenol for example. In any case, the mechanism of Murayama is given in Fig. 10. Note again that the formation of (**24**) is essential. We still favor the rearrangement of (**22**) to (**25**) even though Murayama does not favor the path through (**25**) (Fig. 9) relative to the alternative through (**22**) (Fig. 10).

Lest we be too critical regarding the presence of (**24**), it should be recorded that Finn and Musty (*72*) and Baekeland (*77*) have considered its presence in other reaction schemes. This does not, however, remove the necessity for isolation and identification.

Owing to the meager data available, further comment on the reaction of phenol with formals is not justified. It is a branch of phenol–formaldehyde chemistry, however, which offers an attractive opportunity for research.

IV. The Alkaline-Catalyzed Reaction of Formaldehyde with Phenol

A. GENERAL CONCEPTS

This area of phenol–formaldehyde chemistry has received a great amount of study, only slightly less than the chemistry of selectively substituted phenols. To be sure, the kinetics of the reaction of formaldehyde with phenol to form resoles is well understood, particularly in comparison to those of acid-catalyzed reactions. The reasons, of course, lie in the development of analytical techniques and the fact that most alkaline-catalyzed products in useful form are limited to mono- and dinuclear materials; they are relatively low in molecular weight. Even after the methylolation reaction is nearly complete, the products are essentially all mononuclear components of which there are only five excluding phenol and formaldehyde.

Freeman (*19*) developed paper chromatographic techniques which separated all methylol derivatives of phenol. Reese (*78*) extended this technique to two-dimensional paper chromatography which separated isomers of higher molecular weights. The technique has been refined and adapted by many and has become the basis for much of the work on kinetics.

More recently, new quantitative methods have been developed. Lower molecular weight products (dinuclear) from phenol and formaldehyde in both acid and alkaline systems can be quantitatively characterized by gas–liquid chromatography (GLC) (*79*) and by nuclear magnetic resonance (NMR) spectroscopy (*80, 81*).

The tools are available, thus a kinetic description of alkaline-catalyzed systems is possible, even after more than 70% conversion of phenol. Novolacs are too complex and are too high in molecular weight to succumb to these techniques beyond the early phases of the reaction—at least for the present. Early work on kinetics of alkaline-catalyzed reactions relied on the rate of disappearance of formaldehyde and that on mechanisms relied on work with selectively substituted phenols. Without adequate analytical tools, there were no other means available.

In both acid- and alkaline-catalyzed reactions of phenol and formaldehyde, the functionalities of the reactants are the same; so are the reactive sites. Thus ideally, $f_P = 3$ and $f_F = 2$, although for the synthesis of resoles (methylol phenols) it is usually preferred that formaldehyde react as $f_F = 1$. Also, the first step in the reaction is formation of methylolphenol. Here the similarity ends. At $\text{pH} < 3$, the reaction to form methylol phenol is slow compared to the reaction of methylol phenol with phenol or phenol moieties. At $\text{pH} > 8$, where resoles are synthesized, the condensation reaction is slow enough to be controllable, thus the molecular weight and the distribution of methylol phenol can be regulated within limits.

Since the condensation of a methylol phenol with phenol or with itself is relatively slow, it is highly probable that DMP's (dimethylol phenols) and TMP's (trimethylol phenols) will form. It is necessary also to recognize that the probability of branching becomes very high as the molecular weight increases, even at a low N_F/N_P. In an alkaline system, the methylol groups do not condense quickly enough to initiate chains favoring reaction with formaldehyde or a methylol phenol at end positions. Gelation becomes of definite concern as the condensation reaction proceeds.

Until recently (*30*) the significance of hemiformals in phenol formaldehyde resoles was overlooked and their formation was not accounted for in kinetic studies. Their presence is undeniable as shown through use of GLC (*79*) and PMR (*80*). A resole synthesized at 64°C for 4 h from a mixture of 1 mole phenol, 1 mole formaldehyde, and 0.05 mole $Ca(OH)_2$, contained monohemiformals of *o*-methylol phenol, *p*-methylol phenol, 2,6-DMP, 2,4-DMP, and 2,4,6-TMP as well as the dihemiformal of 2,4,6-TMP. This phase of the mechanism of formaldehyde–phenol reactions under alkaline conditions surely justifies further work if the total reaction kinetics is to be quantified. Lack of information prevents further discussion here.

B. FORMATION OF METHYLOL PHENOLS

The initial reaction of phenol and formaldehyde at $pH > 8$ to form methylol phenols proceeds according to seven simultaneous routes shown in Fig. 11. Under conditions typical of resole synthesis, condensation to multinuclear materials does not begin until after the degree of reaction of phenol is about 0.7 (*30*). These low molecular weight materials are often of commercial importance. The reactions in Fig. 11 have been well defined kinetically.

There are three schools of study which provide early approaches to the problem of kinetics and mechanisms of these reactions. The major handicap under which they worked was the lack of a quick, reliable analytical technique to determine the rate of change of concentration of the products of reaction. In addition, it was necessary to simplify the chemical approaches to minimize or eliminate undesirable (competing) side reactions. Furthermore, if all variables were considered, the mathematics would have been prohibitive to handle. Each school in its own way has provided a basis for more current work.

Debing et al. (*82*) worked under conditions typical of commercial practice and offered some of the first analytical kinetic data. Using $N_F/N_P = 1$, pH 8.1, and NaOH as a catalyst, they observed that the reaction was between first and second order. Recognizing that phenol had positions of different reactivity and that substituted phenols react at a rate different from phenol, allowances could be made to show that second-order kinetics applied. It was observed that the pH changed during the course of the methylolation reaction from pH 8.1 to 7.5; although not recognized at the time, the acid dissociation constants of methylol phenols are greater than those of phenol.

De Jong and de Jonge (*28*) emphasized the early stages of the reaction of phenol and formaldehyde without attempting to delineate between *o* and *p* substitution. Dilute solutions were used. The reaction was shown to be second order, and the rate was directly proportional to $[OH^-]$ in the range pH 5–8. It was logical to conclude that the reactive species is the phenol anion.

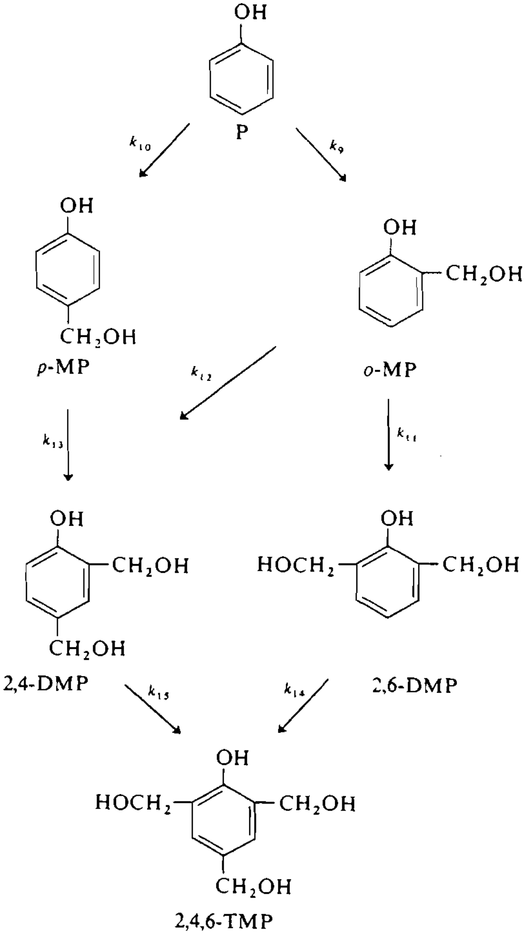


Fig. 11. The initial reaction of formaldehyde with phenol under alkaline conditions (each step assumes addition of 1 mole of formaldehyde).

Freeman and Lewis (*83*) were first to describe the kinetics of the seven reactions involved in the synthesis of methylol phenols (see Fig. 11). Using paper chromatographic techniques developed by Freeman (*19*), it was possible to determine the rate of change in connection of each MP throughout the reaction, but prior to formation of dinuclear materials. Even here, however, it was required to use some simplifying adjustments to the reaction system so that the mathematics could be handled and the analytical technique used conveniently. Thus, sufficient base was used to convert all of the phenol components to the ionic form; this eliminated the need to incorporate ionization constants.

As individual reaction sequences were studied, N_F/N_P was adjusted to provide an equivalence of formaldehyde (at $f_F = 1$ in this case) for available reactive positions of phenol ($f_P = 3, f_{o\text{-MP}} = 2, f_{2,4\text{-DMP}} = 1$, etc.). This overcame the difficulties experienced by Debing et al. (*82*) in reconciling kinetics of "fractional order." Paper chromatographic techniques were not easily adapted for studying the kinetics of the total reaction shown in Fig. 11. The individual reactions were studied and by the use of ratios of rate constants and absolute values for the initial reactions it was possible to calculate each rate constant and to construct a chart showing the rate of change of concentration of each component throughout the reaction period.

As expected, simplifying steps generally have some associated disadvantages. The high concentration of sodium hydroxide, unless carefully controlled, could lead to a lower reaction rate for a number of reasons. Also, working with individual reactions with equivalence of functional groups is not totally representative of the actual reaction being simulated. In addition, all reactions were stopped by cooling and the addition of a large amount of methanol. Hemiformals of the methylol phenols were not taken into account during subsequent analysis; their significance in phenol–formaldehyde chemistry was unknown at the time. The reaction conditions of 30°C, pH > 11.0, and molarities 0.8–1.8 in formaldehyde and phenol are not typical of usual practice.

Without repeating actual values of the rate constants, conclusions from this work are most meaningful. The reactions are second order. An *o* position of phenol is less reactive than the *p* position, the substitution ratio (*o*/*p*) being about 1.7. In *o*-methylol phenol the *o* position is more reactive than the *p* position. A *p*-methylol phenol is less reactive than phenol indicating a deactivating effect by the *p*-methylol groups in general. Relative reactivities are given in Table 16. They are compared to those of Zavitsas and co-workers (*30*) obtained under similar conditions but at a much lower pH. Agreement is fair considering that Zavitsas and Beaulieu (*88*) showed a decrease in *o*/*p* substitution ratio at high pH. This may account for the difference in relative values for 2,4-DMP and for the generally higher *o* reactivity found by Freeman and Lewis (*83*). We could expect catalyst concentration and the type of catalyst to influence *o*/*p* substitution ratios.

Last, the work of Peer and of the school of Yeddanapalli used paper chromatography as the basis for analytical input to kinetic studies but worked under conditions favoring first-order kinetics. They offered general clarification of the mechanisms and will be cited where appropriate.

Our discussion on the kinetics of alkaline phenol–formaldehyde reactions will emphasize the more recent work of Zavitsas and co-workers (*30*). Conditions are those typical of common practice, new analytical techniques are convenient, accurate, and proven, and the use of a computer to handle the mathematics allows consideration of many variables and fast tests for compliance of data to predicted values. Observations of other workers will be included.

Table 16

POSITIONAL REACTIVITIES IN AN ALKALINE-CATALYZED REACTION BETWEEN PHENOL AND FORMALDEHYDE

Compound	Position	Relative positional reactivities: Ref. (*83*)	Relative positional reactivities: Ref. (*30*)
p-MP	*o*	1.0	1.00
P	*o*	1.4	0.93
P	*p*	1.7	1.33
o-MP	*p*	2.0	1.69
o-MP	*o*	2.3	2.33
2,4-DMP	*o*	2.4	1.19
2,6-DMP	*p*	11.1	4.98
All data at pH		~11.3	8.5
N_F/N_P		3/1 to 1/1	2
Molarities		0.8 to 1.8 in P or MP 0.8 to 6.0 in F	1.0 in P 2.0 in P

Zavitsas and co-workers (*30*) generated a kinetic model of the reactions shown in Fig. 11 which in various stages are competing, parallel, simultaneous, and consecutive. The reacting species were taken as the phenate ion and formaldehyde monohydrate (as methylene glycol). Knowing the rate constants for each reaction, the kinetics of the scheme in Fig. 11 was simulated on a computer and verified experimentally. Full account was taken of the concentration of each phenate ion, the formaldehyde equilibria, and the dielectric influence of the solvent (water). Thus the composition with time could be determined of any reacting system as a function of initial concentrations of phenol and formaldehyde, catalyst, and total water.

Data of earlier workers such as Debing et al. (*82*), Freeman and Lewis (*83*), and Dijkstra and co-workers (*84*, *85*) were found to fit the kinetic equations of Zavitsas and co-workers (*30*) with up to 50% of the phenolic components neutralized with a catalyst if allowances were made for the various factors suggested in the following paragraph.

Zavitsas showed that, in order for kinetics to be adequately defined under conditions typical of practical resole preparation, several factors had to be considered which had been unnecessary or overlooked in much of the earlier work. The general characteristics of these reactions are summarized by Zavitsas.

1. The reactions are kinetically second order.

2. The reactive species are the phenate ion and formaldehyde monohydrate.

3. Formaldehyde equilibria in aqueous media have a major effect on the reaction rates. Obviously the concentration of reactive species depends upon these equilibria. At high dilution, more formaldehyde as percent methylene glycol is available.

4. At alkaline pH, formaldehyde reacts with alcohols (methylol phenols) to form hemiformals. Equilibria are established which influence the concentration of methylene glycol. This becomes most significant as the reaction proceeds toward completion.

5. The dielectric constant of the reaction medium is important. Concentrations of reactants govern this. A low dielectric medium (high concentration of phenol and formaldehyde) generally gives higher reaction rate constants.

6. The acid ionization constants of the methylol phenols and phenol itself have an effect on reaction rates. A high ionization constant (low pK) favors higher rates of reaction.

Zavitsas stopped his reactions when dinuclear components began to be formed (< 2 mole %), thus this study is limited to the formation of methylol phenols. As with all previous workers, condensation was avoided for simplicity. Illustrative results are given in Table 17 for two catalysts and under conditions typical of usual practice.

Table 17

EXAMPLE OF RATE CONSTANTS FOR REACTIONS IN FIG. 11 (*30*) AND ACTIVATION ENERGIES (*88*)

Catalyst	MgO	NaOH	
Temp., °C	57	57	
$[F]_0$	9.963	9.456	
$[P^-]_0$	0.2320	0.09615	
$[P]_0$	4.815	4.680	
$[H_2O]_{total}$	21.0	20.8	
pH	8.7	8.3	
Fraction F as $HOCH_2OH$	0.24	0.25	
	$k \times 10^4$ liters/mole-sec		(NaOH) *E*, kcal/mole
k_9	12.86	14.63	21.1
k_{10}	2.37	7.81	20.6
k_{11}	19.35	13.50	20.4
k_{12}	4.82	10.21	19.0
k_{13}	12.38	13.45	21.1
k_{14}	9.91	21.34	19.3
k_{15}	7.08	8.43	19.2
k_9/k_{10}	5.43	1.88	

A general rate equation was given as Eq. (48) (*30*),

$$\text{Rate} = k[P^-][F]\gamma. \tag{48}$$

In this expression, k is the reaction constant, $[P^-]$ the concentration of a phenol anion, [F] the concentration of the unreacted formaldehyde as determined analytically, and γ the fraction of aqueous formaldehyde in the form of the monomeric hydrate. The term γ is a function of total analytical [F], concentration of available water from all sources, the quantity of methylol groups, and two "equilibrium" constants describing the formaldehyde and hemiformal equilibria in a particular system.

The calculations of rate constants were performed by the solution of seven simultaneous rate equations which were related through six simultaneous algebraic equations involving the acid ionization constants of each phenolic species. In addition, the fraction of aqueous formaldehyde as methylene glycol was calculated at each step during the numerical solution of the rate equations. The equilibrium constant represented in Eq. (19) at $n = 2$ was used in this calculation. Also, the effect of hemiformal equilibria was considered, and accounted for the apparent decrease in reactivity of the system at higher degrees of reactions. Eqs. (49) and (50) illustrate hemiformal equilibria:

$$ArCH_2OH + nHOCH_2OH \rightleftharpoons ArCH_2O(CH_2O)_nH + nH_2O \tag{49}$$

$$K = \frac{[ArCH_2O(CH_2O)_2H][H_2O]^2}{[ArCH_2OH][HOCH_2OH]^2} \quad \text{at } n = 2. \tag{50}$$

Although great emphasis was placed on the "concentration of aqueous formaldehyde as methylene glycol," Zavitsas points out that $[HOCH_2OH]$ and $[CH_2O]$ are essentially proportional in his treatment, thus the kinetic model would have been successful if CH_2O were the reactive species. Some thought must also be given to the possibility that formaldehyde equilibria at very low and very high pH shift toward formation of unhydrated monomer. Once studied in more detail we may indeed find that these equilibria are rate determining under these conditions since formaldehyde would surely react at a fast rate.

It is not within the scope of this discussion to include the mathematical details of the rate calculations used by Zavitsas and co-workers (*30*), but it is of interest to observe that a digital computer was used to perform a linearization procedure as an approximate method to determine the rate equations. The method is based on a knowledge of the concentration of each reacting species at several times during the reaction and of the rates of reaction of each species at those times. This required the solution of algebraic equations for ionization constants of the phenol species. The seven rate equations could be solved, once a set of rate constants had been obtained. Experimental verification of the solutions was quite good.

In general, there were two steps in the development of the rate equations. An estimate of each rate of reaction was made at several points on plots of concentration vs time of each species involved. A linear regression analysis of rate equations in the differential form was used to establish the first approximation of the rate constants. Converged values were obtained by using nonlinear least squares coupled with numerical solutions of the rate equations. This is an iterative technique. The rate constants from linear regression equations were used as initial values in the iterative procedure. The fit of the curves (moles/liter vs time) to experimental data is amply illustrated in the original article (*30*).

Dijkstra and de Jonge (*84*) showed that the ratio of *o* to *p* substitution during the methylolation reaction was independent of temperature (30°–90°C) and pH (5.5–9.8), but influenced by the metal ion of the basic catalyst. Thus $o/p = 1.4$ with Na^+ and 1.8 with Mg^{2+} in a reaction system of 0.4 molar in phenol and $N_F/N_P = 0.25$; that is, dilute conditions with an excess of P to maximize formation of methylol phenols. In direct contrast, however, Yeddanapalli and Gopalakrishna (*95*) observed an $o/p = 0.94$ at $N_F/N_P = 0.25$ at 80°C and 0.8 molar in phenol. This is not too different from a value suggested by Zavitsas and Beaulieu (*88*) at high pH but the value by Yeddanapalli and Gopalakrishna cannot be reconciled on this basis.

Zavitsas and Beaulieu (*88*) made additional observations of general significance to the methylolation reaction. In contrast to the published work (*30*) the ratio of *o* to *p* substitution decreases at $pH > 10$ and the rate constants likewise decrease. At $pH \approx 8$, $o/p = 1.4$; at $pH \approx 11$, $o/p = 1.0$. The rate constants k_9 and k_{10} decreased 40–50% at $pH \approx 11$. Peer (*26*, *86*) indicated also that the rate constants k_9 and k_{10} began decreasing at $pH > 10$, and that the *o/p* decreased. He attributed the latter to metal ion clusters about the phenol anion shielding the *o* position. Zavitsas and Beaulieu (*88*) and Peer (*86*) provide evidence that k_9 and k_{10} reverse in relative magnitude at $pH > 11$.

The reaction rates at pH 11 may be influenced also by the Cannizzaro reaction (see Section II). The rate constant for the Cannizzaro reaction is great enough to compete for formaldehyde with condensation reactions, where first- and second-order rate constants are of the order of 10^{-5}, even under optimum conditions. The Cannizzaro reaction follows second-order kinetics with respect to F and the rate constant is reported to be 1.25×10^{-3} liter/mole-sec at 50°C in 50% aqueous NaOH (*87*). If rates are determined by measurement of the rate of disappearance of formaldehyde, it would be expected that the Cannizzaro reaction would give the effect of an increase in rate.

On the other hand, formic acid would compete for the base and the methanol is known to have a rate-reducing effect on phenol–formaldehyde reactions. The dissociation constant for formic acid at 25°C is 1.76×10^{-4} which is several magnitudes greater than any of the phenolic species present (see Table 19). Cupit (*11*) shows that methyl alcohol has a definite rate-reducing effect on the Cannizzaro reaction through formation of hemiformals. The equilibrium constant for hemiacetal formation by methanol is 395. The consequence of this reaction has not been studied in any detail with regard to the phenol–formaldehyde reaction in alkali. We feel it warrants investigation.

Dijkstra et al. (*85*) observed the decrease in the rate of the reaction of formaldehyde with phenol at high pH and suggest that from pH 10–12 formation of the inactive ion $HOCH_2O^-$ is responsible for this decrease. At pH > 12 a slight increase in apparent rate is attributed to the Cannizzaro reaction. The data are preliminary. Making allowances for these changes, kinetic equations were developed which fairly accounted for experimental results obtained at pH 5–13, a temperature of 30°C, a very low degree of reaction of formaldehyde, and using an excess of phenol at low molarity of reactants. Even though the method and equations of Zavitsas seem to accommodate data and results from other workers, it is significant to offer the approach of Dijkstra et al. (*85*).

These workers explained the anomaly of rate reduction at high pH as owing to formation of the inactive $HOCH_2O^-$ ion, the complete ionization of phenol, and the Cannizzaro reaction. Each will have an effect of changing the rate constant which is inversely proportional to $[H^+]$ from pH 4.5–9.0. It was shown that Eq. (51) for the reaction rate accounts for the kinetics of the formaldehyde–phenol reaction in a range of pH 5–13, at 30°C, with an excess of phenol and under dilute aqueous conditions:

$$v = \frac{6.9 \times 10^{-5}[P^-][F][P]}{0.006 + [P]} \quad \text{g-moles/liter-sec.} \tag{51}$$

The valid assumptions were made that the reactive species in alkaline systems are P^- and $HOCH_2OH$. In the dilute reaction medium used, more than 99% of aqueous formaldehyde exists in the form of methylene glycol. Un-ionized phenol and ionized methylene glycol ($HOCH_2O^-$) are considered unreactive. The value 6.9×10^{-5} represents the rate constant for formation of an "active ionized intermediate" through an equilibrium reaction of P^- and F, Eq. (52):

$$P^- + F \xrightarrow{k} I^- \tag{52}$$

The term $[P]/(0.006 + [P])$ in Eq. (51) represents a rate-reducing effect of phenol molecules at high pH. This term compensates for the unexpected decrease in reaction rate at $\mathrm{pH} > 10$ compared with $\mathrm{pH} > 12$, as predicted by dissociation constants. The factor 0.006 was determined experimentally. At pH 4.5–9, the rate constant is inversely proportional to $[\mathrm{H}^+]$ as expected. The reaction is second order. In the range pH 9–12.5, the rate is proportional to $[\mathrm{P_a}]^n$ where $n = 1.7\text{–}1.9$ and $\mathrm{P_a}$ is the analytical value for phenol which includes $[\mathrm{P}^-]$. Over the range pH 5–13, Eq. (51) applies.

This outline, though representing limited conditions of reaction which are not typical of commercial practice, serves to illustrate the factors which influence the mechanisms of formaldehyde–phenol reactions and which undoubtedly limit the control of total inherent versatility of the system.

Continuing the discussion of *o*/*p* substitution, it was observed that media with lower dielectric constant increased *o*/*p* (*88*). Using a large excess of phenol, $N_\mathrm{P}/N_\mathrm{F} \approx 12$, in an aqueous system of reactants increased *o*/*p* to 4. In a concentrated system (high molarities) the metal ion is influential in the mechanism of formation of *o*- vs *p*-methylol phenols. This is just one more piece of evidence that *o*-chelate structures will exist where conditions allow. It is not surprising, therefore, to learn that at high molarities of reactants, divalent metal ions favor *o* substitution. Catalysts Ca^{2+}, Ba^{2+}, and Mg^{2+} lead to higher *o*/*p*. A comparison of relative positional reactivities is given in Table 18 (*30*).

Table 18

RELATIVE POSITIONAL REACTIVITIES (*30*)

Phenol + Formaldehyde: Catalysts Na^+, Mg^{2+}

		30°C		57°C		
Compound	Position	Na^+ (Dil.)	Na^+ (Conc.)	Na^+ (Dil.)	Na^+ (Conc.)	Mg^{2+} (Conc.)
P	*p*	1.00	1.00	1.00	1.00	1.00
	o	0.70	0.87	0.75	0.94	2.71
o-MP	*p*	1.27	1.62	1.06	1.31	2.03
	o	1.75	1.77	1.46	1.73	8.16
p-MP	*o*	0.75	0.80	0.82	0.86	2.61
2,6-DMP	*p*	3.74	3.24	3.18	2.73	4.18
2,4-DMP	*o*	0.89	1.29	0.78	1.08	2.99
k_9/k_{10}	*o*/*p*	1.41	1.74	1.51	1.88	5.43
$k_{10} \times 10^4$ liters/mole-sec (reference rate)	*p*	0.275	0.479	3.39	7.81	2.37
pH		8.5	8.3	8.1	8.3	8.7
$N_\mathrm{F}/N_\mathrm{P}$		2	2.1	1.96	2.03	2.05

The relative reactivities of various ring positions govern the *o*/*p* substitution ratio in the resole. Starting with the reaction of formaldehyde with phenol, it is important therefore to understand the factors affecting this distribution if any structural control is to be achieved. We understand what occurs under a variety of conditions but unfortunately do not know completely the controlling factors, nor have we a quantitative measure of their influence. This uncertainty is clearly pointed out above. It is further illustrated by consulting the works of Eapen and Yeddanapalli (*99*), Freeman and Lewis (*83*), Minami and Ando (*94*), and Peer (*26*, *86*). Each worked under reaction conditions sufficiently different to give different ratios of *o*/*p* substitution. Thus absolute values differ but relative positions in the reactivity comparison do not change greatly. Since Zavitsas and co-workers (*30*) worked under conditions closely approximating commercial practice, their data may be of more current interest.

The reaction mechanism for the formation of methylol phenols is dependent on the reactivity of ionized phenol and un-ionized methylene glycol. Peer (*26*, *86*), Dijkstra et al. (*85*), and de Jong and de Jonge (*28*) agree that the reaction proceeds through an active ionic intermediate. The mechanism is shown in Fig. 12. Peer retains the phenate ion throughout his mechanism and Dijkstra and colleagues agree that this ionic product does exist but

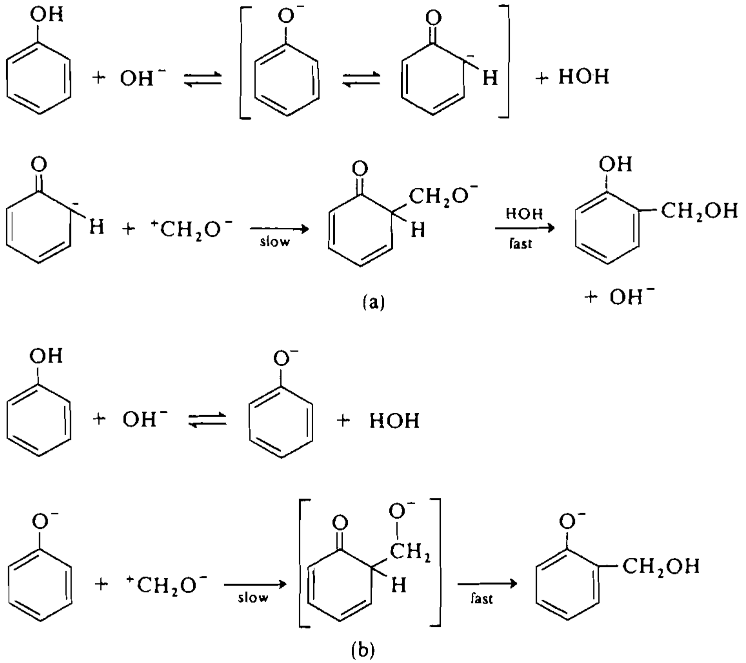
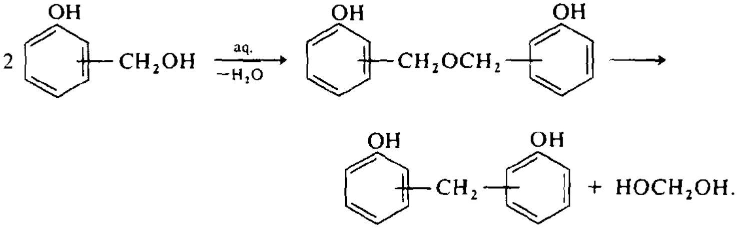


Fig. 12. The formation of methylol phenols in aqueous alkaline solution. (a) From de Jong and de Jonge (*28*); (b) from Peer (*26*, *86*).

suggest that protonization is very rapid at pH < 9. One might assume that the ionic species would surely be present in many systems since the ionization constants of phenol, *o*-methylol phenol, and *p*-methylol phenol are very nearly equal.

C. Formation of Polynuclear Compounds

It was clear from the work of Zavitsas and co-workers (*30*) and Woodbrey et al. (*80*) that polymerization at pH > 8 resulted in some DPM's. No ethers were in evidence at any time up to a concentration of 50% dinuclear and polynuclear components. Rate equations were also extrapolated to conditions beyond 70% conversion of phenol and show that the disappearance of P was only through reaction with formaldehyde. Formation of polynuclear products would be expected to occur preferably through condensation of $-CH_2OH$ groups. These observations demand ether formation followed by decomposition to generate a $-CH_2-$ link and evolve formaldehyde. Equation (53) illustrates this. Freeman and Lewis (*83*) offered evidence to this effect.

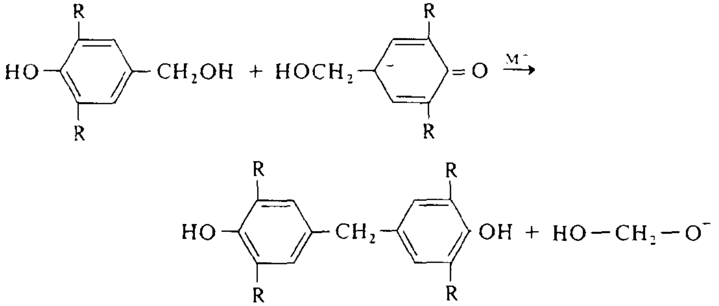


(53)

Formation of methylol-substituted DPM's could occur by a similar reaction but the mechanism is not so clear since quantitative analytical treatment by the latest methods (*79*, *80*) have failed to separate methylolated DPM's except for that formed by the self condensation of 2,4,6-TMP. It is known that the quantity of the very reactive 2,4,6-TMP increases markedly as the phenol/formaldehyde conversion increases, particularly at high N_F/N_P.

Freeman (*89*) confirms that only *p–p* coupling takes place in forming a DPM from 2,4,6-TMP and that this dinuclear compound is not formed by $-CH_2OH$ reacting with a ring hydrogen. He provides evidence that the mechanism involves an equilibrium between ionized and un-ionized 2,4,6-TMP; the reaction rates are thus highly dependent on pH. The reaction is second order and is illustrated in Eq. (54). The second-order rate constant at 40°C is reported to be $\sim 6 \times 10^{-6}$ liter/mole-sec at pH 8.9, reaching a maximum when pH = pK = 9.48. With a large excess of base (pH > 12), the concentration of un-ionized 2,4,6-TMP is so small that the reaction becomes pseudo-first order with a rate constant of about 2.8×10^{-7}/sec.

Most explanations for this high reactivity of 2,4,6-TMP center on the very high ionization constant compared to other mono nuclear methylol phenol derivatives.



(54)

R = $-CH_2OH$

Francis and Yeddanapalli (*89a*) show that even with a large excess of phenol, 2,4,6-TMP condenses intermolecularly to form the *p–p* methylene linkage. Only traces of other reaction products were observed. This is truely a very reactive species relative to self condensation.

This study emphasized the self condensation of all possible methylol phenols and their reaction with large excesses of phenol. Dilute conditions were used and first-order kinetics were favored.

The studies involving large excesses of phenol do not aid our present discussion. The self-condensation reactions (intermolecular) are of interest, however. It can be concluded from this work that *o*-methylols are less prone to self condensation than *p*-methylols. Also, *p*-methylols have a predominant tendency to condense with another methylol rather than react with the nuclear position on phenol or a methylol phenol. These observations are consistent with our previous discussion. Relative positional reactivities are as expected.

Confirming earlier observations, no evidence of ether formation between *o*-methylol groups was observed. Only *p*-methylol groups seemed to enter this reaction.

Frequent reference is made to the acid ionization of each phenol species. Since the reactive form is the phenol anion, the significance of ionization to kinetics becomes obvious. Illustrative values are given in Table 19. Zavitsas (*90*) determined the temperature coefficients of these ionization constants which are obviously necessary for kinetic studies at different temperatures. Details may be obtained from the original reference but two observations are significant. At 25°C, the ionization constant for 2,4,6-TMP is 1.26 times greater than for its nearest rival 2,6-DMP and 2.29 times that of phenol. At 57°C these differences are 1.59 × and 2.42 ×, respectively. These differences in relative values with temperature are not so abrupt as with *o*-methylol phenol.

Table 19

IONIZATION DATA ON PHENOL DERIVATIVES AT 25°C (*91, 58*)

Derivative	pK_1	pK	pK_2	K_1	K	K_2
Phenol		9.85			1.41×10^{-10}	
(1)	7.55		10.80	2.82×10^{-8}		1.58×10^{-11}
(2)	8.00		10.95	1×10^{-8}		1.12×10^{-11}
(3)	7.50		11.60	3.16×10^{-8}		2.51×10^{-12}
o-MP		9.83			1.48×10^{-10}	
p-MP		9.73			1.86×10^{-10}	
2,4-DMP		9.68			2.09×10^{-10}	
2,6-DMP		9.57			2.69×10^{-10}	
2,4,6-TMP		9.47			3.39×10^{-10}	

In general, all mononuclear compounds in Table 19 have similar slopes of plots pK vs *T*°C. However, *o*-methylol phenol has a greater rate of increase in acidity with an increase in temperature than the others. This is attributed to breakdown of the intramolecular H bond. Since this did not seem to occur with 2,6-DMP, some credence is added to the suggestion that a second methylol group on phenol destroys the H bonding, although an increased number of resonance forms might be expected to increase the stability of the chelate structures of 2,6-DMP. Data by Minami and Ando (*93*) were not included in Table 19 since they were obtained on (1), (2), and (3) at a relatively low temperature and could not be compared without temperature coefficients.

A series of studies of the alkaline formaldehyde–phenol reaction by Yeddanapalli and co-workers (*95–100*) was performed under conditions favoring first-order kinetics and at low molarities of reactants. Although useful in showing relative reactivities and the general mechanism of the reaction, it is unnecessary to present these publications in detail in view of the work already discussed. There are data, however, which supplement the current state of knowledge as well as some observations which do not reflect the more current thinking.

Gopalakrishna and Yeddanapalli (*96, 97*) studied the reaction of formaldehyde with phenol ($N_F/N_P = 1.0$) in dilute solution (0.2-*M*) at pH ≈ 8.3 and 70°–90°C. The reactions were terminated before 50% conversion of formaldehyde. Their conclusions (and results) are confusing. It is indicated that several things occur at the same time in the reaction sequence: [*o*-MP] decreases abruptly with a small but incomparable increase in [2,4-DMP]; [2,6-DMP] decreases faster than [2,4,6-TMP] increases; the pH decreases from 8.28 to 8.15; and the reaction rate decreases. At this time in the reaction at 80°C, one would expect significant amounts of dinuclear components to form. Obviously, kinetic measurements on the formation of *o*- and *p*-methylol phenol would be influenced.

It was pointed out by Zavitsas and co-workers (*30*) that the apparent decrease in reaction rate with increased degree of reaction resulted by overlooking formaldehyde equilibria in the calculations, including hemiformal equilibria with methylol phenols. The shift in pH may arise from formation of DPM's, all of which have ionization constants greater than those of phenol and methylol phenols (Table 19). This also would contribute to a reduction in reaction rate.

It has been suggested that the presence of methylolated DPM's in alkali-catalyzed reactions is owing to preferential condensations of methylol groups rather than reaction with a ring hydrogen of phenol. It might be suggested that these methylol derivatives could also be formed by the reactions of (**1**), (**2**), and (3) with formaldehyde, (**1**)–(3) being generated by methylol condensations. We are inclined to discount this mechanism because of analytical evidence by GLC according to the procedures of Higginbottom et al. (*79*). Compounds (**1**)–(3) are found only at $N_F/N_P <$ ~1.25 at pH 7–9, and then in small amounts. At the same time, however, all MP isomers are found with the exception of 2,4,6-TMP. At $N_F/N_P > 1.25$, (**1**)–(3) are not found at any time during the reaction.

Some support for this lack of participation of (**1**)–(3) in most resole chemistry is offered by Francis and Yeddanapalli (*100*). They point out that the rate constants for the reaction of formaldehyde with (**1**), (**2**), and (3) are about the same as for the methylol condensation reactions. The formaldehyde addition reaction rates increase at high pH, and rates of condensation decrease. Minami and Ando (*94*) indicate this ratio of reaction rates as 8/1. In addition, however, by the time condensation takes place, formaldehyde has been consumed to a major extent, thus little remains for reaction with dinuclear materials. Further work is indicated, however, since reaction of two methylol groups generates formaldehyde at a greater rate than is accounted for by analysis for unreacted formaldehyde. This could be reacting with lower molecular weight methylol phenols or with condensation products being formed.

To show an order of magnitude of reaction rates and products which result, should the reaction of formaldehyde with (**1**)–(3) be of major significance, Francis and Yeddanapalli (*100*) provide first-order rate constants at several temperatures. Values at 80°C were chosen as illustrative. Recognizing that the reactions are actually second order, work was done under conditions favoring first-order kinetics. Figure 13 shows the results obtained at 10% conversion of formaldehyde. The distribution of methylolated isomers from (**2**) and (3) is not totally explainable on the basis of *o* and *p* reactivity. Further

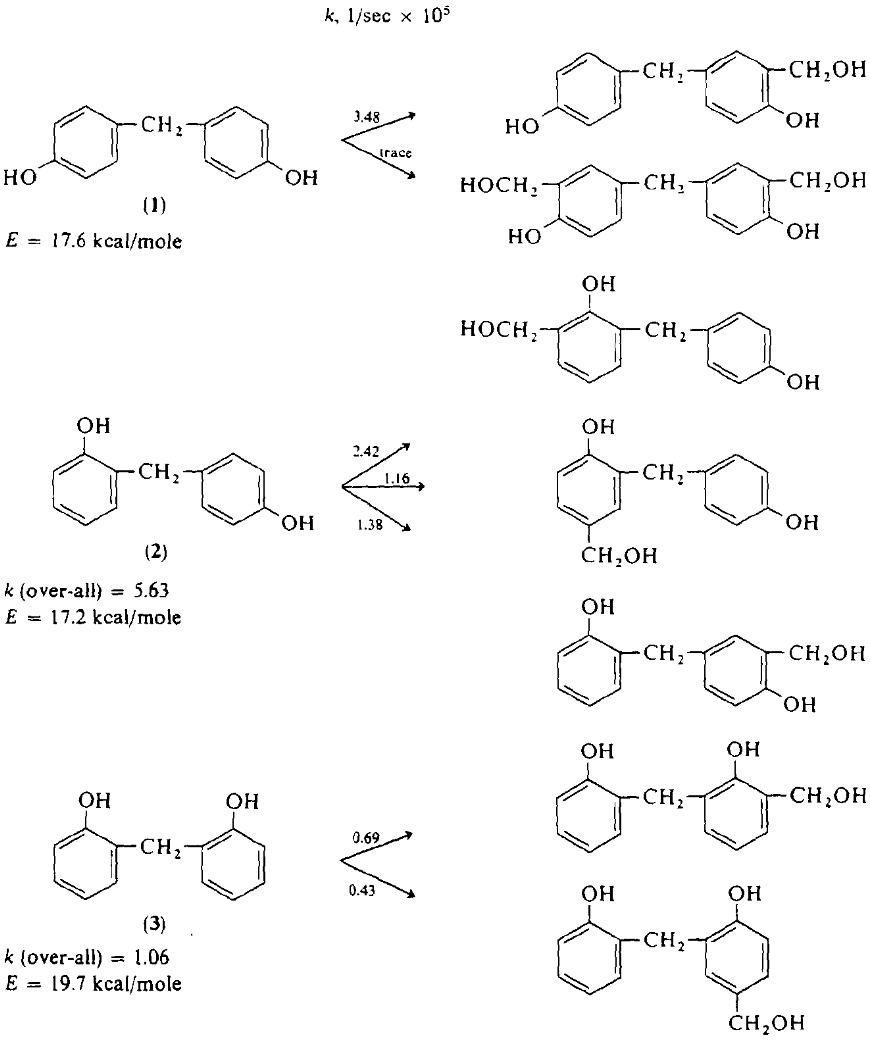


Fig. 13. Kinetic data on the reaction of DPM's with formaldehyde (*100*).

data are required. It is apparent that pK's of the DPM's are of significance (Table 19).

Yeddanapalli and Francis (*98*) showed that the self condensation of the methylol phenols is a much faster reaction than condensation with phenol; the reaction of formaldehyde with DPM's is slower than both. Thus, methylol DPM's result mostly by the self-condensation reactions. The self-condensation reactions in this study were limited to 25% reaction of the methylol phenols. Figure 14 shows these results. In Fig. 14 are qualitative results showing the products obtained by the reaction of methylol phenols with phenol in equal molar amounts.

The work of Finn and James (*33*) was not nearly so descriptive of alkali-catalyzed phenol–formaldehyde reactions as for the formation of novolacs and will not be reviewed here.

In conclusion, it can be said with reasonable confidence that (a) the alkaline-catalyzed reaction of formaldehyde with phenol proceeds through

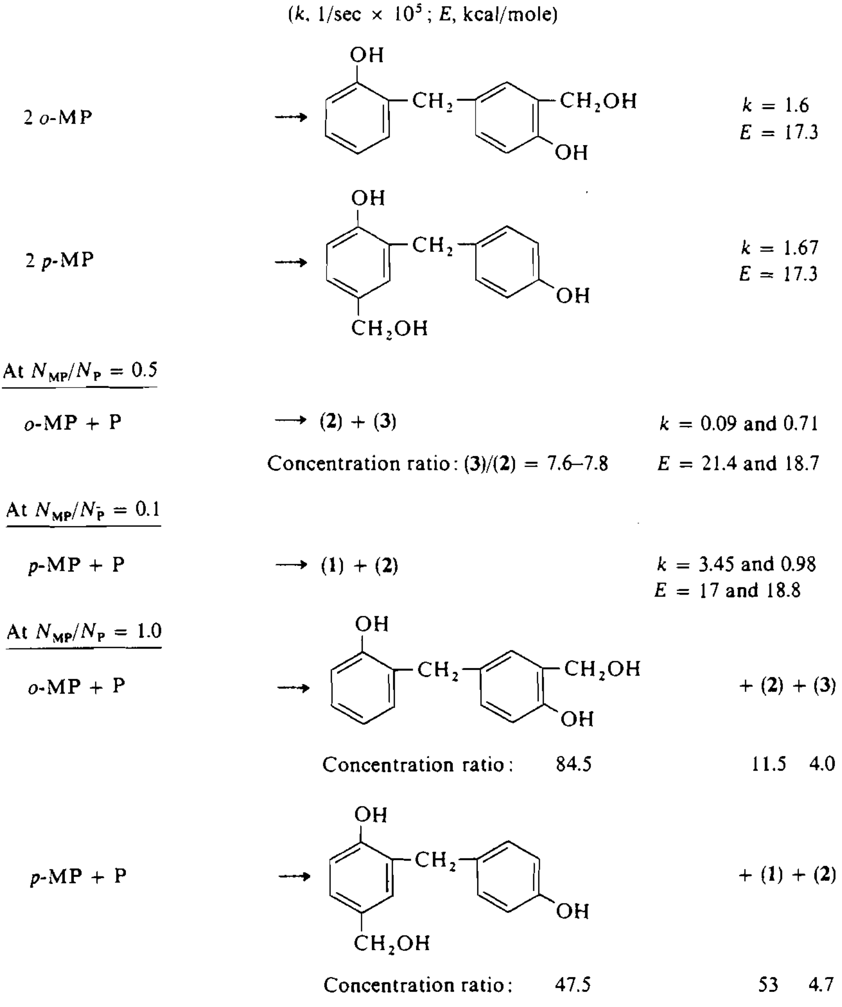


Fig. 14. Reactions of methylol phenols; self condensation and reaction with phenol (*98*).

methylolation of phenol in the *o* and *p* positions, (b) continued methylolation occurs to form the DMP and TMP, (c) eventual self condensation of methylol phenols occurs in preference to condensation with phenol, and finally (d) the formation of branched molecules occurs, ultimately leading to gels. The *p* position on phenol is more reactive than the *o* position, and *p*-methylol phenol is more reactive in the self-condensation reaction than *o*-methylol phenol.

Formaldehyde is given off during self condensation and it apparently reacts with phenol or methylol phenol until mononuclear materials decrease in concentration to the point where the probability of reaction with formaldehyde is less than that for the combination of formaldehyde with a ring position on a DPM.

The over-all rate of reaction decreases at high pH (>11) owing to formation of the inactive $HOCH_2O^-$ and possibly as a result of the Cannizarro reaction. It seems to decrease at high conversions of formaldehyde but this is because of consumption of formaldehyde by hemiformal formation with methylol phenols. A reaction medium of low dielectric constant (high concentration of reactants) favors a larger rate constant. The ratio of *o* and *p* substitution (*o*/*p*) increases with the use of divalent metal hydroxides, a lower dielectric constant of the reaction medium, at pH < 10, and at higher temperatures.

Throughout the reaction, various factors in the reaction environment influence the equilibria which provide the active form of aqueous formaldehyde (the monohydrate) and of the phenolic species (the phenate ion). These must be accounted for in kinetic studies.

V. Epilogue on Phenol–Formaldehyde Reactions

There are many fascinating subjects which are of significance in phenol–formaldehyde chemistry but which could not be reviewed here, mainly owing to the limits we set, but importantly because the subjects are not well understood or reported.

Controlled practical synthesis of novolacs to achieve special properties is important. An example is the faster-curing branched novolac of Dijkstra and de Jonge (*101*) synthesized by condensation of TMP with an excess of phenol. Other cases of "controlled" novolac synthesis are surely possible.

The study of molecular weight growth, particularly in a novolac, but also in a resole system, has been neglected. We are convinced that molecular structure can be simulated with but little more kinetic data on polynuclear novolac structures.

The study of the crosslinking of a phenol–formaldehyde resin is most difficult. With resoles we must assume that the kinetics of gelation are very similar to those of condensation. A beginning of kinetic studies is offered by Little (*92*). Novolacs are particularly challenging; reaction with hexamethylenetetramine (hexa) has not been defined, although an approach to the kinetics is offered by Basov et al. (*101a*) based on the rate of evolution of ammonia. Extension of the work of Kamenskiĭ (*102*) and Orrell and Burns (*102a*) on the anhydrous reaction of hexa with phenol would be most helpful.

And finally, it would be beneficial to know the exact N_F/N_P which causes gelation in a novolac at $\mathrm{pH} < 3$. This would surely improve understanding of branching in novolac molecules and aid in clarifying the relative positional reactivities.

It has been mentioned repeatedly that new analytical procedures have encouraged much of the research in the past twenty years. Paper chromatography has been the mainstay of this effort. More recently new techniques have become useful and are finding favor. Before leaving this section we wish to recall the significance of these procedures.

Freeman (*19*) initiated paper chromatographic techniques for the separation of methylol phenols. Reese (*78*) refined this procedure by expanding resolution through two-dimensional chromatography. These methods and further refinements have formed the entire basis for much of the work reported prior to 1965 (*26*, *29*, *33*, *71*, *83*, *86*, *91*, *95–100*). At that time Higginbottom et al. (*79*) published their gas–liquid chromatographic procedure for quantitatively separating low molecular weight phenol–formaldehyde condensation products.

At the same time Hirst et al. (*81*) and Woodbrey et al. (*80*) presented proton magnetic resonance studies of phenolic resins. This technique provided such structural information as the number average molecular weight $\overline{M}_n$, the ratio of *o*/*p* linkages, the manner in which CH_2 groups were present (that is, methylene link, ether bridge or hemiformal), aromatic —H, and combined formaldehyde/phenol. The use of GLC and PMR has been invaluable in kinetic studies (*30*).

More recently, Gardikes and Konrad (*35*), Quinn et al. (*103*), Armonas (*103a*), and Vasishth et al. (*103b*) have used gel permeation chromatography (GPC) to determine the $\overline{M}_n$ of phenol–formaldehyde novolacs.

The future unquestionably holds great promise for more definitive explanation of the kinetics and mechanisms of the reactions of phenol with formaldehyde and their reaction products.

VI. Reaction of Formaldehyde with Amines and Amides

A. INTRODUCTION

The practical conditions for reacting amines and amides with formaldehyde are much the same as for the reaction of phenol with formaldehyde. Aqueous

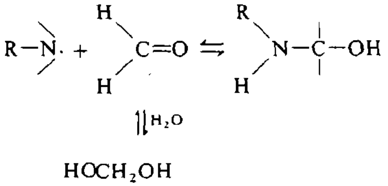
F is favored, an alkaline pH is generally required to form soluble low molecular weight products, and alcohols are used on occasion. In the case of melamine specifically, etherification of methylol groups is often of benefit. For this purpose an aqueous/alcoholic reaction medium is common. Thus not only are equilibria of formaldehyde in aqueous solution significant, but the presence of formals and their equilibria must influence formaldehyde reactions. Unfortunately these factors are ill defined in the chemistry of formaldehyde with amines and amides.

All methylol-substituted compounds in this series can condense by intermolecular reaction and form higher molecular weight products and eventually branched structures. These will ultimately lead to three-dimensional networks if ample formaldehyde is available. These reactions are particularly influenced by acid.

In the case of methylolated urea, condensation through ether formation has been suggested but little evidence to support this has been reported. The case is even less clear with melamine or aniline.

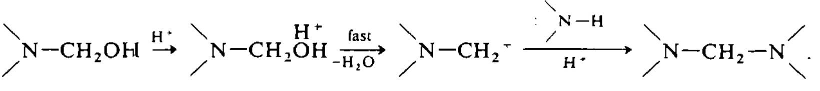
Many of the same comments made about phenol–formaldehyde systems on functionality (real and theoretical) as related to reaction mechanism, kinetics, and branching can be made here. These factors are not nearly so well understood with amines and amides. Recalling the modest state of knowledge in phenol–formaldehyde systems, one recognizes the present difficulties in adequately describing the chemistry of formaldehyde with these amine and amide hydrogens. One can readily understand the complexity of commercially important systems when it is recognized that the functionality toward formaldehyde of melamine is $f_{\mathrm{Me}} = 6$ and that of urea is $f_{\mathrm{U}} = 4$ (Me represents melamine, U is urea).

The initial products of the reaction of formaldehyde with amines and amides are based on reaction of formaldehyde with an electron-rich center. In phenol the electronegative sites are the *ortho* and *para* positions. With amines and amides the reactivity is dependent on the attraction of nitrogen electrons to the positive center of formaldehyde. Equation (55) illustrates the initial reaction in general terms. Just as in phenol–formaldehyde reactions, aqueous media are often preferred, although the presence of significant amounts of alcohols is common in melamine chemistry.



$$\begin{array}{c} R{-}\dot{N}{<} + H_2C{=}O \rightleftharpoons R(H)N{-}\overset{|}{\underset{|}{C}}{-}OH \\ \Big\updownarrow{\scriptstyle H_2O} \\ HOCH_2OH \end{array} \qquad (55)$$

Also similar to phenol/formaldehyde chemistry are the effects of acid and base catalysis. Base catalysis leads to methylol-substituted derivatives, generally called "addition products." In the amine and amide families of products some of these derivatives have been isolated and, at least to some degree, characterized. Some studies with model compounds of methylolated amines and amides have also been conducted. Acid catalysis of the reaction of amine and amide hydrogens with formaldehyde probably proceeds initially according to the general mechanism indicated in Eq. (55). However, in the presence of acid, the methylol species is short lived and undergoes condensation rapidly, combining with another electron-rich site as shown in Eq. (56).



$$>N-CH_2OH \xrightarrow{H^+} >N-CH_2\overset{H^+}{O}H \xrightarrow[-H_2O]{\text{fast}} >N-CH_2^+ \xrightarrow[H^+]{>N-H} >N-CH_2-N< . \qquad (56)$$

Thus in the chemistry of amines and amides the two fundamental chemical reactions appear to be addition and condensation. This has generally been considered the case in phenol–formaldehyde reactions under acid conditions, but our reservations have been indicated. The products that are commercially important are chiefly a mixture of low molecular weight compounds that contain a considerable number of methylol groups. These materials may be crosslinked by the application of heat to form infusible three-dimensional networks. The reaction takes place mainly by a condensation mechanism.

This portion of the chapter is concerned with the kinetics and mechanisms of the reaction of formaldehyde with amide and amine hydrogens. Much of the work on kinetics reported in recent years has been concerned with urea, aniline, and melamine. These materials typify this field of endeavor and illustrate the complexity of the reactions involved. Since they are the most important commercially, we have arbitrarily restricted our discussion to these structures.

Perhaps the first research on the reaction of formaldehyde with amide hydrogens was reported by Tollens (*104*) in 1884. In this work monomethylol urea, the simplest addition product of this family, was isolated. Einhorn and Hamberger (*105*) conducted further research that led to the isolation of dimethylolurea. Practical application of urea–formaldehyde resins was achieved by John (*106*) in about 1920. Uses were found in adhesives, molding, and fabrics. Additional investigators reporting on urea–formaldehyde products included Pollak (*107*), Ellis (*108*), Walter (*109*), Dixon (*110*), Henkel and Cie (*111*), and others. The research by these investigators contributed to the growth of the urea–formaldehyde resin industry in the 1920's.

Melamine (2,4,6-triamino-*s*-triazine) was found to exhibit reactivity toward formaldehyde similar to that shown by urea. Following commercialization of the basic raw material, melamine resins entered the field in 1939 (*112*). Propertywise, melamine–formaldehyde resins exhibited a distinct superiority over urea-based materials in thermal performance as well as moisture resistance; therefore, the uses of melamine resins grew in many areas.

Also important in aminoplast chemistry is the closely related material, benzoguanamine (1,3-diamino-5-phenyl-2,4,6-triazine) (*113*). This product is of interest as a coating resin intermediate.

Urea and melamine are similar in reactivity toward formaldehyde. They both show more amide character rather than amine and are only very weakly basic. More basic is the true amine, aniline, which reacts quite readily with formaldehyde. Reaction of formaldehyde with aniline leads to products such as 4,4′-diaminodiphenylmethane as well as resinous materials.

Also considered part of amide technology are the formaldehyde reaction products with cyanoguanidine commonly referred to as dicyandiamide. These resinous materials are especially important in the bonding of glass fibers.

Although many literature contributions have been made in this complex field, publications on kinetics and mechanisms have been rather limited. This is perhaps owing to the complexity of the products involved. The rapid commercial development of the resin technology has far outdistanced the capability to analyze the products. As new analytical techniques have been developed, research on kinetics and mechanisms has progressed.

De Jong and de Jonge (*114–121*), in a series of papers in 1952–1957, reported research on the mechanisms and kinetics of the reaction of formaldehyde with urea. Confining their experiments to the initial stages of reaction, significant progress was made toward an understanding of both the addition and condensation reactions. Landquist (*122–125*) added to the technology in 1957 by reporting a spectrophotometric method of following the reaction, confirming the rate constants obtained by de Jong and de Jonge over a wide range of conditions. In 1961, Ito (*126*) made a significant contribution by reporting paper chromatographic techniques for separating and measuring the rate of development of the individual hydroxymethyl urea species. The presence of trimethylolurea was also confirmed and strong evidence was obtained for the formation of significant quantities of tetramethylolurea (*127*).

Wagner (*128*) studied the reaction of aniline with formaldehyde and contributed much to our understanding of aniline-based resins. The complexity of the products obtained was indicated. The kinetics of the reaction of formaldehyde with aniline were studied by Ogata et al. (*129*) in 1952. The order of reaction was established and a mechanism for reaction was proposed. Equilibrium studies on acid-catalyzed reaction products of aniline with formaldehyde were conducted by Erickson and Sharp (*130*). Thus, some understanding has been achieved in the field of aniline–formaldehyde chemistry.

The kinetics and mechanisms of melamine reactions with formaldehyde are particularly complex. Initial reaction-rate data were reported by Okano and Ogata (*131*) in 1952. By studying the reaction in the initial stages, rates of reaction were established and rate constants determined. Koeda (*132*) made a most important contribution in 1954 by developing a method for analyzing the reaction products. Paper chromatographic techniques resolved various methylol derivatives and it was shown that up to 6.0 moles of formaldehyde could be combined with melamine. Gordon et al. (*133, 134*) in 1966 conducted investigations of kinetics and illustrated that quantitative estimates of the individual reaction products could be made using C_{14}-labeled formaldehyde. Some deviation from random behavior was noted and parameters were assigned to qualify the rate equations. Validity of these parameters was tested in computer simulations by Aldersley et al. (*135*). In this manner refined values for rate constants and reactivity parameters were obtained.

B. General Concepts

As indicated previously, the reactions of urea, melamine, and other amino-related materials involve the nucleophilic attack of the electron-rich nitrogen upon the positive center of formaldehyde. In the reaction mechanism, we should consider the existence of the aforementioned hydrated species of formaldehyde (methylene glycol) although its role in these reactions appears to have been neglected. It has been effective so far to accept formaldehyde as the source of reactive species in aqueous media.

The reaction of formaldehyde with urea (U) in aqueous solution has been shown (*104–107*) to proceed in its simplest form according to Eq. (57):

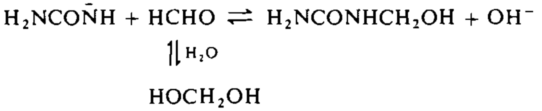
$$H_2NCONH_2 + HCHO \rightleftharpoons H_2NCONHCH_2OH. \qquad (57)$$

This was shown to hold over a wide variety of conditions.

Perhaps more consistent with known formaldehyde equilibria, the reaction is more appropriately described by Eqs. (58)–(62).

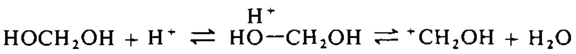
<u>Basic catalysis</u>

$$H_2NCONH_2 + OH^- \rightleftharpoons H_2NCO\overset{-}{N}H + HOH \qquad (58)$$



$$\begin{array}{l} H_2NCO\overset{-}{N}H + \underset{\displaystyle \underset{HOCH_2OH}{\updownarrow{\scriptstyle H_2O}}}{HCHO} \rightleftharpoons H_2NCONHCH_2OH + OH^- \end{array} \qquad (59)$$

<u>Acid catalysis</u>



$$HOCH_2OH + H^+ \rightleftharpoons \overset{H^+}{HO}{-}CH_2OH \rightleftharpoons {}^+CH_2OH + H_2O \qquad (60)$$

$$ {}^{+}CH_2OH + H_2NCONH_2 \rightleftharpoons H_2NCONHCH_2\overset{H^+}{O}H \xrightleftharpoons{-H_2O} H_2NCONH\overset{+}{C}H_2 \qquad (61)$$

$$H_2NCONH\overset{+}{C}H_2 + H_2NCONH_2 \rightleftharpoons H_2NCONHCH_2NHCONH_2 + H^+ \qquad (62)$$

Similar reaction paths for the reaction of formaldehyde with other nitrogen derivatives of basic character can be postulated.

Research on the kinetics has been reported for the reaction of urea, aniline, and melamine with formaldehyde. The rates of the initial reaction with aqueous formaldehyde have been determined in the early stages where condensation is negligible. The latter reaction is sensitive to low pH and therefore pH was controlled above critical levels. The early reaction has been followed by measuring the consumption of formaldehyde. As might be expected, second-order kinetics have been observed.

The reversible nature of the reaction has been demonstrated conclusively by several workers. The reaction rates are affected by ionic strength and the presence of alcohol(s) which retards the reaction. Evidence for general acid and base catalysis has been obtained. Generally second-order kinetics have been observed, thus the rate of methylolation can be determined by the relationship in Eq. (63) where A represents the concentration of the reactive species of formaldehyde, B the concentration of coreactant, and k a rate constant:

$$-dA/dt = kAB. \qquad (63)$$

In terms of the variable x, representing the decrease in concentration of a reactant in a given time, Eq. (63) becomes

$$dx/dt = k(a - x)(b - x). \qquad (64)$$

The integrated form (*136*) can be used to determine the forward rate constant:

$$\left[\frac{1}{(a - b)}\right] \ln\left[\frac{b(a - x)}{a(b - x)}\right] = kt. \qquad (65)$$

Evidence for the dissociation of the methylolated product has also been obtained:

$$H_2NCONHCH_2OH \xrightleftharpoons[OH^-]{H^+ \text{ or}} HCHO + H_2NCONH_2. \qquad (66)$$

The rate of dissociation can be kinetically described by

$$kA/dt = k'C. \qquad (67)$$

Again, in terms of the variable x,

$$dx/dt = k'(c - x). \qquad (68)$$

The integrated form is

$$\ln[c/(c - x)] = k't. \tag{69}$$

In Eqs. (63)–(70), a is the initial concentration of urea (U) or melamine (Me), b the initial concentration of F (formaldehyde), c the initial concentration of MU or MMe (methylolurea or methylolmelamine), x the concentration of MU or MMe produced by the forward reaction or dissociated in the reverse reaction; $a - x$, $b - x$, and $c - x$ are the various concentrations at time t; k is the forward-rate constant and k' the reverse rate constant.

The equilibrium constant K is thus related to rate constants k and k' according to

$$K = k'/k. \tag{70}$$

General agreement for the above has been obtained in the early stages of the reaction where condensation is minimized.

C. REACTION RATES

1. *Urea (U)*

The rate of reaction of formaldehyde with urea was studied extensively by de Jong and de Jonge (*114*). In neutral, acid, and basic aqueous solution, the forward reaction was found to be bimolecular in the early stages. Care was taken to minimize condensation. The reverse reaction was monomolecular. Data were obtained at a pH 2–11 in 0.045 to 0.2-*M* solution at 25°–59°C. Equations (59) and (61) may be used for reference.

The reaction was studied during the initial stages to minimize intermolecular condensation of methylol groups and was followed by determining the consumption of formaldehyde. The total formaldehyde content (unreacted formaldehyde plus methylol) was determined using the alkaline iodine method. The unreacted formaldehyde was determined using the sulfite method and the extent of methylolation was thus obtained by difference. This approach served as a check that methylene bridges were not formed. The reactions proceeded to an equilibrium level of formaldehyde which was established in 20 h at 59°C in a 0.045-*M* phosphate buffer solution at pH 7.0.

Purified monomethylol urea (mp 109°–110°C) was used to determine the reversibility of the urea–formaldehyde reaction and contained 99.7% theoretical methylol content. When this material was placed in aqueous solution, formaldehyde was formed and the equilibrium reaction in Eq. (71) was demonstrated.

$$\mathrm{H_2NCONH_2 + HCHO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{MU}{H_2NCONHCH_2OH}}. \tag{71}$$

Second-order kinetics was established for the initial reaction and first-order kinetics was shown for the decomposition of methylol urea (MU). The rate constants and the experimentally determined equilibrium constants K are shown in Table 20. The equilibrium constants were determined experimentally by studying the decomposition of methylol urea. Good agreement was obtained over a wide range of conditions when comparing equilibrium-constant values obtained with those calculated from k_1 and k_2. At pH 2–11 the equilibrium constant was independent of pH. In more acid solution the equilibrium was affected by the condensation reaction,

Table 20

FORMATION AND DECOMPOSITION OF MU (*114*)

[$K = k_2/k_1$; See Eq. (72)]

Temp. (°C)	pH	k_1 exp. (liter/mole-sec)	k_2 exp. (sec^{-1})	K exp. (moles/liter)
25	7	0.6×10^{-4}	1.2×10^{-6}	2×10^{-2}
35	11	1.6×10^{-3}	5.5×10^{-5}	3.7×10^{-2}
35	7	1.10×10^{-4}	3.2×10^{-6}	3.7×10^{-2}
35	4	4.4×10^{-4}	1.4×10^{-5}	
35	2	1.5×10^{-4}	4.2×10^{-5}	
42	7	1.9×10^{-4}	6.8×10^{-6}	4.1×10^{-2}
59	7	5.7×10^{-4}	3.1×10^{-5}	5.6×10^{-2}

$$H_2NCONH_2 + H_2NCONHCH_2OH \rightleftharpoons H_2NCONHCH_2NHCONH_2 + H_2O. \quad (72)$$

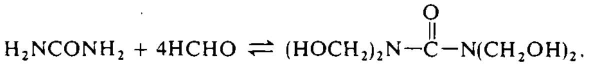
In this work (*114*) two correction factors had to be applied to the kinetic equations. Further addition of formaldehyde to methylol urea to make dimethylol urea (DMU) takes place, and at pH $\cong$ 2.0 some condensation begins to become important. Both factors affected calculations of the equilibrium constant K.

Both the forward and reverse reaction rates were shown to be catalyzed by hydronium ions and hydroxyl ions and to be affected by ionized salts which function as buffers. However, the equilibrium constant was affected only slightly. Neutral salts hardly changed the reaction rates.

The activation energy for the reaction of urea with formaldehyde was obtained by plotting logarithms of rate constants versus 1/°K in the usual way. An activation energy of 13 kcal/mole was estimated for the forward reaction and 19 kcal/mole for the dissociation of methylol urea. The heat of reaction is thus estimated at 6 kcal/mole. It was shown that the equilibrium in Eq. (71) shifts to the left with increasing temperature.

De Jong and de Jonge (*116*) also studied the reaction rate for formaldehyde and urea in more concentrated solution, 4 *M*. Similar kinetics was observed as in dilute solutions. Small differences in velocity constants may be attributable to subtle hemiformal equilibria differences as observed in phenol–formaldehyde reactions. In the latter, differences in concentrated versus dilute solution were rationalized in terms of hemiformal effects and the influence of the dielectric constant of the reaction media.

There are four replaceable hydrogens on urea. Theoretically, $f_U = 4$ and the tetramethylol derivative of urea should be possible, as



$$H_2NCONH_2 + 4HCHO \rightleftharpoons (HOCH_2)_2N-\overset{\overset{\displaystyle O}{\|}}{C}-N(CH_2OH)_2. \qquad (73)$$

The reaction might be expected to proceed stepwise with increasing difficulty. This appears to be the case. While conflicting results regarding isolation of tetramethylol urea have been reported, there is general agreement (*126*, *127*) that dimethylol urea as well as trimethylol urea formation occurs quite readily.

De Jong and de Jonge (*115*) followed the formation and dissociation of dimethylol urea in depth and elucidated the kinetics of the reaction, as

$$HCHO + H_2NCONHCH_2OH \rightleftharpoons HOCH_2NHCONHCH_2OH. \qquad (74)$$

Methylol urea was synthesized and its reaction with formaldehyde to form dimethylol urea was studied under conditions minimizing condensation. Again at $pH > 2$, little condensation was shown to take place.

Equilibria of methylol urea in solution with formaldehyde must involve dissociation of methylol urea as well as reaction of MU with F to form DMU. Thus disappearance of F is described kinetically by

$$-dF/dt = k_1^*[MU][F] = k_2[MU]. \qquad (75)$$

Using the values for k_2 determined previously, k_1^* may be derived from the [formaldehyde]-vs-time (t) plot. The brackets [ ] denote concentration.

By preparing dimethylol urea and following the appearance of formaldehyde, the rate constant for the reverse reaction and the equilibrium constant were obtained. Reversibility was clearly established. The forward rate exhibited second-order kinetics and the reverse reaction was monomolecular. At $pH > 3$ and a temperature of 35°C, the equilibrium constant K was shown to be 0.2–0.16 with a slight dependence on pH. Rates of reaction were increased by both acids and bases. The activation energy determined for formation of dimethylol urea was 14 kcal/mole and for the reverse reaction 19 kcal/mole. Heat of reaction is thus 5 kcal. These results are similar to those on the methylol urea equilibrium with formaldehyde.

De Jong et al. (*117*) studied the reaction of urea with a large excess of formaldehyde. With $N_F/N_U = 4/1$, at 50°C and pH 10, it was shown that 2.5 moles of formaldehyde were combined at equilibrium. Utilizing previously determined equilibrium constants for aqueous solutions of MU and DMU, the equilibrium concentrations of DMU and TMU were estimated algebraically. In this way, K^{**}, the equilibrium constant for TMU formation from DMU and formaldehyde, was estimated as 1.8 at 50°C and by similar experiments as 1.2 at 35°C. This work assumed that no TeMU was formed in the reaction. Thus the ease of formation of nitrogen methylol derivatives is in the order U > MU > DMU. This is illustrated by the equilibrium constants. At 50°C, the equilibrium constants are $K = 0.045$ moles/liter; $K^* = 0.27$; and $K^{**} = 1.8$. The equilibrium constant for the system $\text{TMU} + \text{F} \rightleftharpoons \text{TeMU}$ is expected to be still larger.

Table 21 summarizes some equilibrium and rate constants experimentally obtained in the reaction of formaldehyde with urea. Data were obtained at 35°C in a buffered system at pH 7.0.

Table 21
EQUILIBRIUM AND RATE CONSTANTS IN UF SYSTEM (*117*)

Constant[a]	$\text{U} + \text{F} \rightleftharpoons \text{MU}$[a]	$\text{MU} + \text{F} \rightleftharpoons \text{DMU}$[a]	$\text{DMU} + \text{F} \rightleftharpoons \text{TMU}$[a]
k_1	0.9×10^{-4}	0.38×10^{-4}	0.1×10^{-4}
k_2	2.5×10^{-6}	0.69×10^{-5}	
K exp.	0.036	0.22	1.2

[a] k_1 = forward reaction rate (liter/mole-sec); k_2 = reverse reaction rate (sec^{-1}); K = equilibrium constant (moles/liter); MU = methylol urea; DMU = dimethylol urea; TMU = trimethylol urea.

Landquist (*122–125*) studied the reaction rate of urea with formaldehyde at 20°C. He utilized a spectrophotometric method to determine the concentrations of urea, MU, and DMU. The method was based on a color reaction between these compounds and *p*-dimethylaminobenzaldehyde in the presence of methanolic hydrochloric acid. Utilizing rate constants previously determined, equilibrium data were calculated for N_F/N_U of 1.4, 1.7, and 2.0 in 0.05-*M* buffer solution. These were compared with data observed spectrophotometrically. Good agreement was obtained for various molar concentrations. Some comparative values obtained at initial urea concentrations of 1.0-*M* are indicated in Table 22. Similar agreement was also obtained at initial urea concentrations of 0.5 and 0.33-*M*.

Aqueous formaldehyde that is commercially attainable usually contains measurable quantities of methanol. Methanol and formaldehyde establish

Table 22

EQUILIBRIUM DATA OF REACTIONS BETWEEN FORMALDEHYDE AND UREA (*123*)

Mole ratio N_F/N_U	Buffer	Calculated data[a] [U]	[MU]	[DMU]	[F]	Observed data[a] [U]	[MU]	[DMU]	[F]
1.4	KH_2PO_4	0.13	0.47	0.41	0.13	0.13	0.46	0.41	0.12
1.7	pH 6.70	0.06	0.38	0.56	0.21	0.07	0.36	0.57	0.21
2.0		0.03	0.28	0.69	0.34	0.03	0.27	0.70	0.33
1.4	Borax	0.14	0.43	0.43	0.11	0.15	0.43	0.42	0.11
1.7	pH 9.20	0.07	0.36	0.57	0.19	0.07	0.34	0.59	0.18
2.0		0.03	0.26	0.71	0.32	0.02	0.28	0.70	0.32
1.4	Na_2CO_3	0.15	0.40	0.45	0.10	0.16	0.43	0.41	0.10
1.7	pH 10.00	0.07	0.33	0.60	0.17	0.08	0.32	0.60	0.18
2.0		0.03	0.23	0.74	0.30	0.03	0.24	0.73	0.29

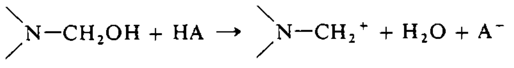
[a] Concentrations in moles/liter. Initial urea concentration, 1 mole/liter.

a hemiacetal equilibrium,

$$HCHO + CH_3OH \rightleftharpoons CH_3OCH_2OH. \tag{76}$$

Landquist (*124*) studied the reaction of urea and formaldehyde in the presence of methanol to determine its effect on reaction rates. A considerable retardation effect on the forward reaction to methylol urea was found, although no effect on the reverse reaction was found. The presence of methanol in formaldehyde can retard the formation of methylol ureas by an amount proportional to the methanol concentration. Since the hemiacetal does not take part in the reaction of urea with formaldehyde, the equilibrium conditions of the hemiacetal are maintained in the reaction mixture. The effective lowering of formaldehyde concentration explains the decrease in the forward reaction rate.

Methylol derivatives undergo intermolecular condensations and can react with available hydrogens. De Jong and de Jonge (*119*) investigated the kinetics of methylene bridge formation from urea and its methylol derivatives. Aqueous solutions of urea, MU, and DMU were studied under various conditions and the reaction scheme shown in Eqs. (77)–(79). Equation (78) was suggested as representing the rate-determining step.



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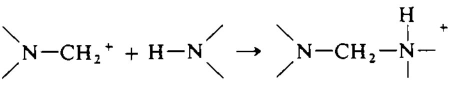

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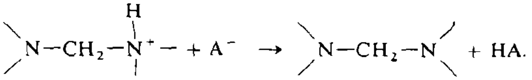


$$>N-CH_2-\overset{H}{\underset{|}{N^+}}- + A^- \rightarrow >N-CH_2-N< + HA. \qquad (79)$$

The reaction was found to exhibit second-order kinetics and to be catalyzed by acid. The reaction velocity was proportional to hydronium ion concentration and therefore could be given by

$$v = dm/dt = k[-NCH_2{}^+][-NH_2]. \qquad (80)$$

The condensation of methylol ureas can proceed in several ways as illustrated:

$$MU + MU \rightarrow U-CH_2-U-M \qquad (81)$$

$$MU + U \rightarrow U-CH_2-U \qquad (82)$$

$$DMU + DMU \rightarrow DMU-CH_2-U-M \qquad (83)$$

$$U + DMU \rightarrow MU-CH_2-U \qquad (84)$$

$$DMU + MU \rightarrow MU-CH_2-U-M \qquad (85)$$

where $M = -CH_2OH$.

These condensations were studied and rate constants were estimated. It was possible to follow the course of these reactions by determining the rate of disappearance of the methylol groups by titration with a hypoiodous acid solution.

The intermolecular reaction of methylol urea was studied in the initial stages at 25°–45°C, over a range of concentrations, and in a range pH 4.1 to 4.95. By choosing conditions that minimize decomposition of MU to U and formaldehyde, the order of reaction was established and a rate constant determined. Second-order kinetics was confirmed and the reaction was found to be proportional to hydronium ion concentration. At a pH > 5.0, dissociation of all methylol derivatives became more important and impaired measurements of the kinetics of the single reaction. The activation energy was established as 15 kcal/mole by conventional means.

Similarly, the reactions of the other methylol urea components were investigated. With acid catalysis the reactions were found in general to exhibit second-order kinetics. Significant reaction rates were found in all systems except for the intermolecular condensation of dimethylol urea. The rate of this reaction was 1/50 of the rate of the other condensation reactions under the conditions used. Based on these data it was theorized that for the condensation reaction to proceed facilely, the presence of at least one $-NH_2$ group is necessary.

A comparison of the rate constants for the bimolecular reaction obtained under similar conditions is shown in Table 23.

Table 23

CONDENSATION REACTION RATE CONSTANTS (*119*)

Reaction	k in liters/mole-sec
U + MU → UCH_2U^a	3.3×10^{-4}
U + DMU → $U{-}CH_2{-}U{-}M$	2.0×10^{-4}
MU + MU → $U{-}CH_2{-}CH_2{-}M$	0.85×10^{-4}
MU + DMU → $M{-}U{-}CH_2{-}U{-}M$	0.5×10^{-4}
DMU + DMU → $DM{-}U{-}CH_2{-}U{-}M$	$<3 \times 10^{-6}$

[a] M = $(-CH_2OH)$. U = urea nucleus: all positions not containing $-CH_2OH$ have —H.

In further investigations (*120*) the reversibility of the condensation reaction was demonstrated. Methylenediurea (UCH_2U) was prepared and its decomposition in aqueous acid solution was followed by determination of the sum of concentrations of methylol groups and unreacted formaldehyde. First-order kinetics was established and the reaction was found to be catalyzed by hydronium ions. Acid catalysis was found to be specific since buffer concentration had no effect on reaction speed. The activation energy was 19.5 kcal/mole. Values of rate constants obtained at 50°C over a pH range are shown in Table 24.

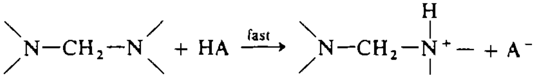
Table 24

METHYLENE DIUREA DECOMPOSITION.
EFFECT OF pH (*120*)

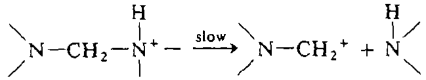
pH	k (sec^{-1})
2.90	4.2×10^{-4}
3.14	2.9×10^{-4}
3.48	1.2×10^{-4}
3.95	4.3×10^{-5}
4.87	6.4×10^{-6}

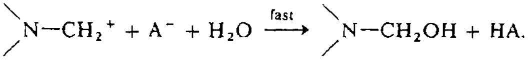
Since side reactions complicated the equilibrium, direct determination of the equilibrium constant was not accomplished. However, estimates were obtained by the use of the ratios of the rates of forward and reverse reactions. At 50°C and a pH 4.05, K was estimated as 0.03 mole/liter in a 0.1-*M* solution. The equilibrium was found to be independent of pH.

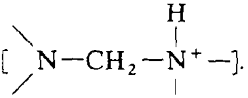
The mechanism of the reverse reaction was thus proposed as shown:



$$>N{-}CH_2{-}N< \; + \; HA \xrightarrow{\text{fast}} \; >N{-}CH_2{-}\overset{H}{\underset{|}{N^+}}{-} \; + \; A^- \qquad (86)$$


(87)


(88)

Equation (87) would be rate determining and expected to follow first-order kinetics described by rate = .

Some insight into the structure and molecular weight of urea formaldehyde condensates was also obtained by de Jong and de Jonge (*121*). A number of condensates were prepared at 25° to 76°C at a pH of 1.8 to 6.6. These materials were reacted to a point where they were no longer soluble in water and were isolated as precipitates. Analysis of these "methylene ureas" showed a mixture of condensates with a molecular weight of 300–500. No evidence for existence of cyclic structures was obtained under the conditions utilized and no ethers were reported.

Under these relatively mild conditions some residual methylol groups were observed. It would be expected that further reactions at higher temperatures could occur. Thus an additional increase in molecular weight with some branching to three-dimensional networks via a methylene bridge would take place. Therefore, the "cure" or high-temperature reaction of urea–formaldehyde products would be expected to follow reaction kinetics similar to that of the condensation reaction of methylolated ureas. Second-order kinetics would be expected to predominate in the crosslinking of these materials and acid catalysis would be particularly effective in accelerating the reaction.

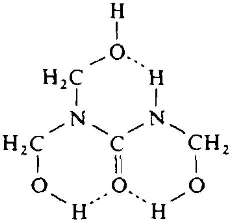
Ito (*126*) characterized the products of the base-catalyzed reaction of urea and formaldehyde. Paper chromatographic techniques were applied to resolve the reaction mixtures into mono-, di-, tri-, and tetramethylol ureas. Although previous authors indicated that tetramethylol urea was not produced, Ito presented some evidence to indicate its formation. Significant quantities appeared to be obtained under the conditions he chose.

A series of reactions was made at 30°C utilizing N_F/N_U of from 2/1 to 20/1 and 0.005-*M* sodium hydroxide gave, initially at least, only unreacted urea, mono-, and dimethylol ureas. At higher mole ratios trimethylol urea was formed as the reaction proceeded. At a temperature of 60°C and with a tenfold increase in catalyst to 0.05-*M* sodium hydroxide, tetramethylol urea was observed chromatographically even in the initial stages of reaction. As the reaction proceeded, larger concentrations of tetramethylol urea were noted.

Ito isolated a product from a urea–formaldehyde reaction mixture by solvent fractionation techniques which corresponded to chromatographic assignments for trimethylol urea. The substance was further characterized by the formation of its trimethyl ether and of thioether derivatives. Therefore, based on this characterization, Ito confirmed his chromatographic assignments for trimethylol urea.

At higher temperatures, high base-catalyst levels, and with increasing N_F/N_U, he also obtained some chromatographic evidence for increased formations of tetramethylol urea. The evidence presented was consistent with the synthesis conditions utilized.

The more stringent conditions required to form tetramethylol urea were explained by Ito as owing to hydrogen-bonding effects. This is illustrated by



(27)

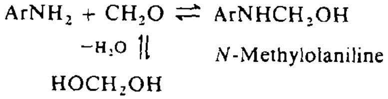
It is seen that the only available amino hydrogen for further reaction with formaldehyde could well be involved in a six-member ring, hydrogen-bonded structure.

Urea–formaldehyde reaction rates have been determined by measuring the consumption of formaldehyde. The reverse reaction rates have been measured by determining [F]. In order to advance the state of the art, complete characterization of the products of reaction and their rates of formation should be undertaken.

Some effort to separate the products of reaction has been made by Ito (*126*). He utilized paper chromatographic techniques and gained some insight into the rates of formation of methylolated products. Further work is needed to define reaction rates and to characterize the products on a quantitative basis. Perhaps conversion of the methylolated ureas to stable products capable of analysis by GLC (gas–liquid chromatography) may be developed in further research efforts. Another probable contribution would involve improvements in liquid–phase chromatography.

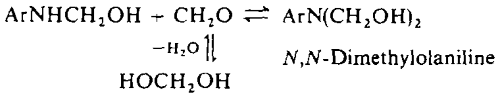
2. *Aniline* (*A*)

Formaldehyde reacts with amines in general under a wide variety of conditions. The reaction has been studied extensively and many contributions have been reported. Considerable research has been performed on the reaction of aniline with formaldehyde (*128*). Commercial products resulting from this reaction are diaminodiphenylmethane, consisting chiefly of the 4,4′-isomer, and aniline–formaldehyde resinous materials. The *N*-methylolaniline, *N*,*N*-dimethylolaniline, bis(phenylamino)methane and the trimer anhydro–formaldehyde aniline have been isolated. All can be explained in terms of the oversimplified reaction scheme,



$$\begin{array}{c}ArNH_2 + CH_2O\\ {\scriptstyle -H_2O}\Big\updownarrow\\ HOCH_2OH\end{array} \rightleftharpoons ArNHCH_2OH \qquad (89)$$

N-Methylolaniline

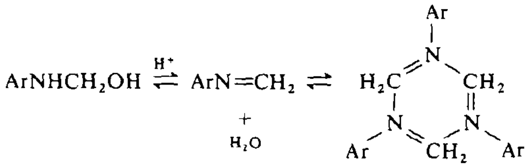


$$\begin{array}{c}ArNHCH_2OH + CH_2O\\ {\scriptstyle -H_2O}\Big\updownarrow\\ HOCH_2OH\end{array} \rightleftharpoons ArN(CH_2OH)_2 \qquad (90)$$

N,*N*-Dimethylolaniline

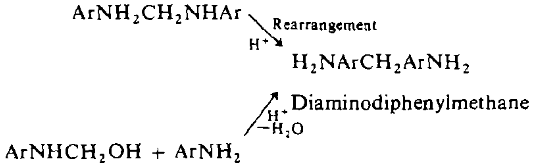
$$ArNHCH_2OH + ArNH_2 \rightleftharpoons ArNHCH_2NHAr + H_2O \qquad (91)$$

Bis(phenylamino)methane



(92)

Anhydroformaldehyde aniline trimer



(93)

$$ArNHCH_2OH + ArNH_2 \xrightarrow{H^+} \text{Resinous poly(methyleneanilines)} + H_2O \qquad (94)$$

The compounds shown are derived from the addition reaction of one mole of aniline with one mole of formaldehyde, proceeding possibly by *N*-methylolation. The products isolated after further reaction will depend upon reaction conditions. The formation of heterocyclic by-products has been reported by Wagner (*128*).

Although much research had been done in this area, little kinetic investigation was reported until 1951. Ogata et al. (*129*) investigated the reaction of aniline and substituted anilines with formaldehyde at a pH of 0.7–7.0. Under these conditions, considerable condensation occurred. They followed the course of the reaction by measuring the rate of formation of insoluble products. The rate-determining step was postulated as involving two moles of aniline and one mole of formaldehyde. An inverse dependence on protonated methylene–aniline concentration was found. Over the pH range of 0.7 to 1.6 the rate increased with higher pH. At a pH closer to 7, precipitation of anhydroformaldehyde aniline trimer occurred and retarded the reaction.

As a means of studying the rate-determining step, the trimer was substituted "in toto" for aniline and formaldehyde. The rate of resinous product development was found to be the same as in the formaldehyde–aniline reaction. This was postulated as evidence that the trimer is in equilibrium with methylene aniline and with formaldehyde and aniline.

Thus, the rate-determining step in the over-all reaction scheme was suggested as the reaction of protonated methylene aniline with aniline,

$$\mathrm{Ar{-}NH{-}CH_2^+ + Ar{-}NH_2 \xrightarrow{slow} (Ar{-}NH{-}CH_2{-}NH{-}Ar + H^+) \longrightarrow NH_2{-}Ar{-}CH_2{-}Ar{-}NH_2 + H^+}. \tag{95}$$

Diaminodiphenylmethane is formed probably through a rearrangement of the bis(phenylamino)methane.

The reaction rate was investigated under conditions resulting in pseudo-first-order kinetics. The effects of varying the mole ratios and concentration of the reactants on the reaction rate at 25°C were calculated utilizing Eq. (96) where [F] is the initial stoichiometric concentration of formaldehyde and $[x]$ is the concentration of formaldehyde at time t:

$$k = 1/t \ln\{[\mathrm{F}]/([\mathrm{F}] - [x])\}. \tag{96}$$

In the calculations, methyleneaniline and trimer concentrations were treated as equivalent to [F]. Table 25 summarizes the results obtained. In all experiments a molar excess of acid was utilized. The reaction-rate constant remained unchanged only when the formaldehyde concentration was varied. Increasing the acid concentration decreased the rate, while increasing the aniline concentration had the reverse effect.

The data suggest that the rate-determining step may involve one mole of protonated methylene aniline and one mole of aniline. However, because of the complexity of the reactions, including possible side reactions to heterocyclic products, etc., some caution in interpretation must be exercised.

Similar rate studies were also conducted with substituted anilines such as toluidines and chloroanilines. In following the rate of consumption of formaldehyde by the sulfite method, the following decreasing order of the effect of substituents on reactivity was obtained:

$$m\text{-}\mathrm{CH_3} > o\text{-}\mathrm{CH_3} > \text{None} > m\text{-}\mathrm{Cl} > p\text{-}\mathrm{CH_3} > p\text{-}\mathrm{Cl}.$$

Table 25

PSEUDO-FIRST-ORDER CONSTANTS IN THE CONDENSATION OF ANILINE WITH FORMALDEHYDE[a] (*129*)

Initial concentration ne (A) arity	CH$_2$O molarity	HCl molarity	$k \times 10^4$ sec^{-1}	pH
00	0.100	0.125	2.31 ± 0.03	1.6
00	0.100	0.200	1.57 ± 0.03	1.0
00	0.100	0.300	1.11 ± 0.01	0.7
00	0.050	0.150	2.08 ± 0.03	1.3
00	0.100	0.150	2.09 ± 0.02	1.3
0	0.200	0.150	2.02 ± 0.04[a]	1.3
50	0.100	0.150	0.42 ± 0.01	1.0
0	0.100	0.150	2.09 ± 0.02	1.3
5	0.100	0.150	3.74 ± 0.05	1.6
0	0.050	0.075	0.62 ± 0.01	1.6
0	0.100	0.150	2.09 ± 0.02	1.3
0	0.200	0.300	7.0 ± 0.2	1.0

h the mole ratio $N_F/N_A > 1$, the first-order kinetics applies only below about 40% ption of F. Temperature of reaction, 25°C.

data appear consistent with the concept of electrophilic attack by a ium ion, i.e., protonated methylene aniline, on the ring carbon as rate determining.

stigations with aniline in a higher pH range (pH 2–7) were also aken. Estimation of rate constants was complicated by precipitation trimer and the consequent retardation in the formation of resinous ts. The concentration of free aniline is also quite high under these ons. In the very early stages of reaction, the maximum rate was found range of 5–6.

son and Sharp (*130*) also studied the reaction of formaldehyde niline at 65°–75°C to form 4,4′-diaminodiphenylmethane. In this 1, molar equivalent quantities of aniline and hydrochloric acid as high aniline-to-formaldehyde mole ratios were utilized.

ious polymethylene anilines were found (*130*) to be in equilibrium dimer, 4,4′-diaminodiphenylmethane. These data further substan- at the rate-determining step in the formaldehyde–aniline reaction y proceeds according to

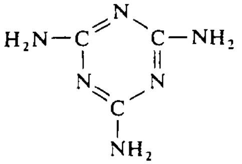
$$\mathrm{ArNH\overset{+}{C}H_2 + ArNH_2 \xrightarrow{slow} ArNHCH_2ArNH_2 + H^+.} \qquad (97)$$

r can react further with protonated methylene aniline to form H$_2$ArNHCH$_2$ArNH$_2$ as well as higher molecular weight members of the series. By increasing the aniline-to-formaldehyde ratio, the distribution of products can be shifted to favor formation of high yields of dimers, e.g., 4,4'-diaminodiphenylmethane.

Thus the kinetic and equilibrium data obtained indicate a possible course of initial reaction. Formaldehyde appears to react with aniline to form *N*-methylolaniline. Under acid catalysis, reaction of protonated methylene aniline can react further to form dimers, trimers, and resinous polymers. Thus, the behavior of anilines toward formaldehyde shows some similarity to the urea–formaldehyde system, at least in the initial stages of reaction. The same two reactions, addition of formaldehyde followed by condensation, are the most important. However, great care must be exercised in additional interpretation, since the system is complex and the possible reaction paths and products are many.

3. *Melamine* (*Me*)

Melamine (Me), 2,4,6-triamino-*s*-triazine, is a weakly basic material that shows reactivity similar to amides. The most widely accepted structure of melamine is

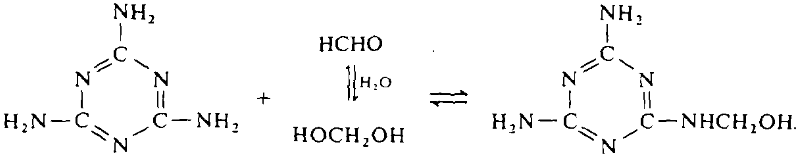


(28)

Formaldehyde can react with all hydrogens; the hexa-substituted product has been isolated. Thus melamine has a functionality of $f_{\mathrm{Me}} = 6$.

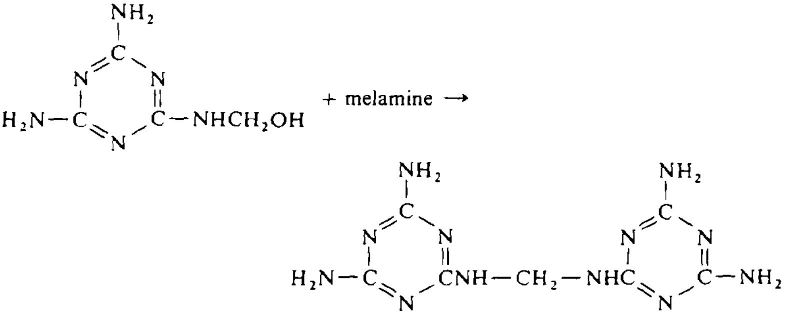
Many have studied the reaction of melamine with formaldehyde. Similar to urea, melamine reacts with formaldehyde over a wide pH range. The products are derived by methylolation of the amine groups to form addition products. The course of further reactions is pH dependent, as is the case with all methylol groups considered in this discussion. Basic conditions promote further addition reactions with formaldehyde until the functionality has been satisfied. Acid conditions lead to rapid condensation reactions. High temperatures and highly alkaline conditions are usually avoided in the synthesis of MeF resins. Rate studies become most difficult under these conditions partly owing to the competing Cannizzaro reaction. Lapina and Zhurina (*130a*) show a substantial loss of formaldehyde by formic acid formation above pH 9. Four percent of the formaldehyde was converted to formic acid at pH 8.6–8.9, while a very abrupt increase was observed at pH 9.6–9.8. This is similar to the experience with phenol–formaldehyde chemistry at high pH (*85*).

The first research on the kinetics of melamine chemistry was reported by Okano and Ogata (*131*) in 1952. These authors studied the reaction rate of melamine with formaldehyde over a wide range of conditions. Consistent with formaldehyde equilibria, the addition reaction, in the initial stages of reaction of formaldehyde with melamine, can be considered as proceeding according to Eq. (98), which illustrates monomethylolation:



(98)

As the reaction proceeds, condensation occurs as in Eq. (99) to form methylene bridges.



(99)

The consumption of formaldehyde was followed by the sulfite method. The total formaldehyde present as unreacted formaldehyde and as methylol was determined by iodometry. Thus the formaldehyde present as methylene bridges could be estimated by difference to establish the degree of condensation, as the reaction of formaldehyde with melamine proceeded.

The rate of reaction of melamine with formaldehyde to form methylol-substitution products was determined at 35° and 40°C. The reaction was studied over a pH range of 3.0 to 10.6 and was found to be reversible and very similar to the reaction of urea with formaldehyde.

A product to which the authors (*131*) assigned the structure of trimethylolmelamine was very easily formed and it was implied that there was little difference between the rates of formation of mono-, di-, and trimethylol melamines. In the reaction of formaldehyde with melamine the reaction mixtures reached an equilibrium value of unreacted formaldehyde. A marked dependence on pH was shown for the rate constant; the consumption of formaldehyde was increased significantly by increasing pH. Rate constants were calculated using conventional equilibrium formulas and are shown in Tables 26 and 27.

Table 26
THE RATE CONSTANTS OF HYDROXYMETHYLATION; THE EFFECT OF THE MOLE RATIO OF REACTANTS[a] (*131*)

Temp., °C	Initial concentration, M Melamine [Me]	Initial concentration, M Formaldehyde [F]	pH	$k_{av} \times 10^4$ liter/mole-sec	$k'_{av} \times 10^4$ liter/mole-sec
40.0 ± 0.1	0.100	0.050–0.300	7.7	2.14 ± 0.03	0.43
40.0 ± 0.1	0.050–0.125	0.100	7.7	2.11 ± 0.04	0.46
40.0 ± 0.1	0.050–0.150	0.100	3.8	0.72 ± 0.01	0.76
35.0 ± 0.1	0.035–0.065	0.100	10.2	6.2 ± 0.1	0.56

[a] [ ] denotes concentration in moles/liter; k, rate constant for reaction for formaldehyde with melamine; k', rate constant for dissociation of methylol melamine.

Table 27
THE RATE CONSTANTS[a] OF HYDROXYMETHYLATION OF MELAMINE: THE EFFECT OF pH (*131*)

pH	$k \times 10^4$ liter/mole-sec	pH	$k \times 10^4$ liter/mole-sec
(a) 35.0°C; Initial molar concentration: [Me] = 0.5; [F] = 0.10		(b) 40.0°C; Initial molar concentration: [Me] = 0.10; [F] = 0.10	
7.6	1.62 ± 0.01	7.7	2.14 ± 0.03
9.5	2.54 ± 0.03	5.3	1.94 ± 0.03
10.0	3.76 ± 0.04	3.8	0.72 ± 0.01
10.6	14.1 ± 0.2	3.0	0.74 ± 0.01

[a] Symbol k is the rate constant for methylolation.

It was found that at both 40° and 70° C and pH 7 even a value of $N_F/N_{Me} = 20/1$ could not drive the reaction beyond the trimethylol stage. Based on the data at hand, they concluded that perhaps the trimethylol derivative might be the most highly methylolated species attainable. Further research has since indicated that the hexamethylol derivative can be synthesized. In fact, hexamethylol melamine derivatives are now available on a commercial scale.

The condensation reaction of methylol melamines to form compounds with methylene bridges was studied to some degree. The rate constant for this reaction was estimated at 70°C and a pH 4.9 and some additional rate data were obtained over a pH range of 3.8 to 5.8.

A mechanism similar to the urea–formaldehyde reaction was proposed for methylolation under basic conditions. The reactions are shown in Eqs. (100)–(102) in which Me represents melamine.

$$\mathrm{Me + OH^- \rightleftharpoons Me^- + H_2O} \quad \text{(fast)} \tag{100}$$

$$\mathrm{Me^- + HCHO \rightleftharpoons MeCH_2O^-} \quad \text{(slow)} \tag{101}$$

$$\mathrm{MeCH_2O^- + H_2O \rightleftharpoons MeCH_2OH + OH^-} \quad \text{(fast).} \tag{102}$$

In an acidic medium, a mechanism involving reaction of protonated formaldehyde with melamine was postulated as the rate-determining step. A mechanism for methylene-bridge formation was also proposed:

$$\mathrm{MeCH_2OH + H_3O^+ \rightleftharpoons MeCH_2{}^+ + 2H_2O} \quad \text{(fast)} \tag{103}$$

$$\mathrm{MeCH_2{}^+ + Me \rightleftharpoons MeCH_2Me + H^+} \quad \text{(slow).} \tag{104}$$

The reaction in Eq. (104) was proposed as rate determining.

The methylolation of melamine was investigated further by Koeda (*132*). A more complete characterization of the products of reaction was obtained, in addition to convenient techniques, by the use of paper chromatographic analyses. It was shown that the trimethylol melamine previously prepared by other researchers was probably not a pure trisubstitution product but a mixture of methylolated species.

Melamine and 2.0–8.0 moles of formaldehyde were allowed to react at a pH 9.0 at 70°C. The reaction products were isolated by precipitation and were analyzed. When $N_F/N_{Me} = 8/1$, the product isolated had an average methylol content of 5.9. The products were separated chromatographically and evidence for the presence of up to seven compounds was obtained. Preparative conditions and analytical results for the various samples obtained are shown in Table 28.

Thus under these conditions it appears that a wide variety of methylolated melamines could be prepared and evidence for formation of the hexasubstituted melamine in substantial quantities was presented. By paper chromatography, all products obtained were shown to be mixtures of methylolated species.

Koeda (*132*), in additional research using paper chromatographic analysis, continued to study the methylolation reaction of melamine. Products up to hexamethylol melamine were formed even in the early stages of reaction in both dilute and concentrated reaction solutions. Additional evidence for reversibility of the reaction was obtained by placing methylolated melamines in solution and noting the development of lower methylolated melamines by chromatography. About 60% of the methylol melamines was dissociated.

Koeda (*132*) also followed the acid-catalyzed reaction of melamine with formaldehyde by paper chromatography. At a pH 5.0 and 70°C, both

Table 28

Preparative Conditions and Analyses of Methylol Melamines (*132*)

Reacting mixture	Amount (grams)			Time to precipitation of crystals[a]	Melting point, °C	*N*, %	Combined CH_2O, %	Combined moles CH_2O as $-CH_2OH$
	Me	$F_{aq.}$ 37.5%	H_2O					
Me + 2F	63	80	43	(a) 2 h	151–153	41.9	36.1	2.4
				(b) 6 days		49.8	29.8	1.7
Me + 3F	63	120	33	(a) 1 h	155–158	39.0	40.8	2.9
				(b) 6 days		40.2	38.7	2.7
Me + 4F	63	160	23	(a) 20 min	152–154	35.5	46.8	3.7
				(b) 24 h		38.0	41.3	3.0
Me + 5F	31.5	100	60	(a) 20 min	158–162	29.7	55.3	5.2
				(b) 24 h		35.6	46.4	3.6
Me + 6F	31.5	120	78	(a) 1 h	168–170	28.2	55.8	5.3
				(b) 4 days		32.6	53.3	4.8
Me + 6F	15.7	80	40	(a) 1 h	163–164	27.9	58.2	5.9
				(b) 24 h		28.1	57.0	5.6

[a] Reaction mixtures were allowed to react 10 min, were poured into 2–3 volumes of methanol, and were filtered after standing the indicated time. Analyses shown were performed on dried samples.

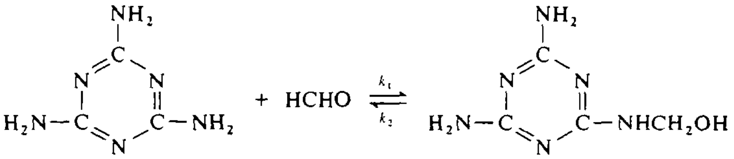
methylolated and methylene-bridged products were formed. The latter were confirmed chromatographically by the appearance of bandlike images. These increased with time while the methylolated products diminished in concentration. Noteworthy was the fact that under these weakly acidic conditions, even penta- and hexamethylol melamines were observed by paper chromatography in the initial stages of reaction.

Although Koeda's research did not include obtaining reaction rate constants, it provided considerable knowledge toward a better understanding of the reaction of melamine with formaldehyde. Further efforts to elucidate the kinetics have been aided by this research.

Gordon et al. (*133*) utilized Koeda's method to conduct additional methylolation studies with melamine. They confirmed that seven chromatographic spots could be resolved from the product obtained at 45°C and a pH 9.5. Utilizing C_{14}-labeled formaldehyde, they were able to estimate the concentrations of the nine possible methylol melamine compounds. Standard counting techniques were performed on the chromatographic spots. In this manner they arrived at a rather complete distribution of methylolated species in equilibrium mixtures at N_F/N_{Me} of 1, 3, 6, and 10.

The structural distribution of methylol groups was compared with that attainable, assuming random methylolation. They found some deviation with their model and attributed this to the lower reactivity of secondary as compared with primary amino sites and to a general substitution effect. By introducing two modifying factors to the kinetic equations they were then able to improve agreement with the distribution of methylol groups determined experimentally.

Gordon et al. (*134*) further elucidated the reaction kinetics of melamine with formaldehyde. Assuming the random reaction scheme in Fig. 15 for the formation of the possible methylolated melamines, several kinetic and thermodynamic constants were determined. It was assumed that formaldehyde reacts with melamine randomly with rate constants of k_1 and k_2:



(105)

The rate constant k_1 was for the second-order methylolation reaction and k_2 for the first-order demethylolation reverse reaction. The equilibrium constant K was then equal to k_2/k_1.

The reaction was studied at 25°–55°C, a pH 5.7–10.2, and N_F/N_{Me} of 0.5/1 to 15/1. Thus a wide variation of conditions was utilized. The reaction

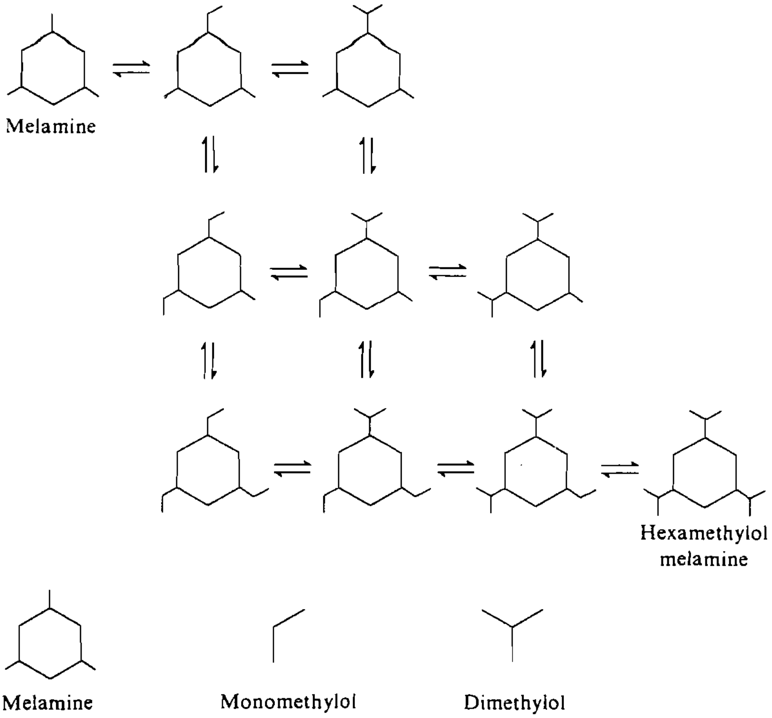


Fig. 15. Equilibria during the addition reaction of formaldehyde with melamine (*134*, *135*). Formaldehyde is involved in each equilibrium. Schematic of possible methylolation and demethylolation reactions.

rate was measured by formaldehyde consumption as a function of time and the course of the reaction was followed to equilibrium.

At equilibrium conditions it was found that K varied over a range of about 1.65 as [F] was increased 30-fold. This variation in K was attributed to deviations from randomness. From K values as a function of temperature the heat of reaction was calculated as 2.94 kcal/mole for $N_F/N_{Me} = 3.0$ and as 2.80 kcal/mole for $N_F/\mathrm{N}_{Me} = 7.0$. In studies at various pH's it was found that the equilibrium constant was somewhat independent of pH, particularly in the range of 7.5–10.2. At lower pH some dependence was apparent. Some equilibrium constants obtained are shown in Table 29.

Rate constants for methylolation (k_1) were also obtained as a function of [F], temperature, and pH. The rate constant varied over a fourfold range with a 30-fold [F] variation. From rate constant data obtained as a function of temperature the activation energy was calculated as 23.6 kcal/mole for the

Table 29

DEMETHYLOLATION EQUILIBRIUM CONSTANTS (*134*)

N_F/N_{Me}	T, °C	pH	K, mole/liter
0.5	45	9.5	0.235
5.0	45	9.5	0.280
15.0	45	9.5	0.393
3.0	25	9.5	0.192
3.0	35	9.5	0.248
2.916	45	9.5	0.257
3.0	55	9.5	0.324
7.0	25	9.5	0.210
7.0	45	9.5	0.329
7.0	55	9.5	0.327
3.0	45	5.7	0.193
3.0	45	8.6	0.273
3.0	45	10.2	0.281

methylolation reaction. Some methylolation rate constants obtained are shown in Table 30.

Based on the data obtained, Gordon et al. (*134*) concluded that the random theoretical model does not adequately describe the system. Deviations in the rate constant k_1 with [F] were particularly important in reaching this conclusion. The increase in the equilibrium constant K with increasing [F] clearly indicated that methylolation proceeds with increasing difficulty.

Table 30

METHYLOLATION RATE CONSTANTS (*134*)

N_F/N_{Me}	T, °C	pH	$k_1 \times 10^4$ liter/mole-sec
3.0	25	9.5	0.25
3.0	35	9.5	2.30
3.0	55	9.5	7.10
7.0	35	9.5	0.22
7.0	35	9.5	2.30
7.0	55	9.5	6.80
3.0	45	5.7	1.59
3.0	45	7.5	1.44
3.0	45	8.6	1.78
2.916	45	9.5	6.25
3.0	45	10.2	28.00

This was explained by noting that addition of the second methylol to the nitrogen might be more difficult than the first addition. This hypothesis was tested by assigning a parameter to the rate equation, which accounted for reduced reactivity of three hydrogen atoms. Equilibrium constants were then recalculated and much improved constancy was noted over a wide range of N_F/N_{Me}.

Aldersley et al. (*135*) continued the study of the addition reaction of formaldehyde to melamine at 45°C and a pH 9.5. Under these conditions, the condensation reaction of methylol groups is negligible. Simultaneous differential equations were set up to describe the rate of formation of all methylolated species. The forward rate constant (k_1) was assigned for the formation of all species, while the reverse rate constant (k_2) was assigned for the demethylolation of each product. Two parameters were included to account for the deviations from randomness previously found. One was postulated to account for a change in rate of methylolation owing to a general substitution effect. Another was assigned to account for the difference in reactivity of unsubstituted amine groups compared to those with a methylol group.

Experimental data on the rate of consumption of formaldehyde were obtained and confirmed the increasing deactivation of amino groups with successive substitution on melamine. Computer simulations were also conducted with the mathematical model described, and optimum values of K and the two parameters were established. The general substitution parameter was found to be close to unity so that it could probably be ignored. However, the parameter accounting for localized substitution was found to be about 0.61. Utilizing the values determined as well as 0.221 mole/liter for the equilibrium constant K, kinetic data were tested over a wide range of N_F/N_{Me}. Good agreement of calculated values with experimental values was observed.

Similarly, using computer simulation techniques, optimum values for k_1, the methylolation rate constant, and k_2, the demethylolation rate constant, were obtained. These rate constants were shown to hold over a wide range of N_F/N_{Me}, again utilizing the adjustment parameters discussed previously.

D. CONCLUSION

The latter part of this chapter has been concerned with the kinetics and mechanisms of the formation of low molecular weight reaction products from the reaction of formaldehyde with amines and amides. The more recent publications regarding the reactions of formaldehyde with urea, aniline, and melamine have been emphasized. The systems are dynamic and complex.

Analysis of the reactants and products is difficult. Nevertheless, by studying the consumption of formaldehyde in the early stages of reaction and by employing chromatographic methods of analysis, progress has been made toward understanding these reactions of formaldehyde. The addition reaction has been studied to a considerable degree. As new analytical instruments and techniques become available, further elucidation of this chemistry continues.

Much research remains to be done. The existence of hemiformals in phenolic chemistry has been shown and it may well be important in amino chemistry. There is no doubt of this when alcoholic formaldehyde solutions are used. Application of thin-layer chromatography as well as gel-permeation chromatography may provide more quantitative characterization of formaldehyde addition compounds and low molecular weight condensation products. Some studies of model compounds have been accomplished but further research is indicated. Additional effort in the conversion to more stable derivatives for analysis may prove fruitful. Analysis of etherified products or other more stable derivatives may assist our understanding of these product mixtures.

Greatly neglected is the chemistry of reactions of melamine and urea with formaldehyde in the presence of considerable amounts of alcohol(s). In fact, the hemiformals of methanol and butanol are used as sources of formaldehyde in some cases. More often, aqueous alcoholic reaction media are used. In these cases, the initial reaction can involve condensations to form methyl and butyl ethers of methylol melamines and ureas. The complexity of the kinetics and mechanisms of these systems offers substantial challenge.

The condensation reaction of methylol derivatives has been studied; however, more information needs to be obtained. Little has been reported about the role of ether formation during condensation. In highly methylolated urea and melamine addition products, ether formation during condensation and branching may be very significant.

With the rapid development of computer technology, solution of simultaneous and consecutive competitive reactions has become almost commonplace. The application of computers has provided more accurate kinetic parameters in melamine/formaldehyde reaction products. Further research should provide a more profound understanding as data obtained by improved analytical instruments are combined with computer developments.

Thus the technology of the reactions of formaldehyde is changing constantly. While more sophisticated commercial requirements of these products forming the subject of this chapter are being developed, more fundamental knowledge on their chemistry is being gained. The complexity of the systems has slowed understanding of the kinetics and mechanisms of the reactions.

However, considerable progress is being made by the application of modern research tools to these old but still challenging fields of chemistry.

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REFERENCES

1. J. F. Walker, *Formaldehyde, American Chemical Society Monograph No. 159, 3rd ed.*, Reinhold, New York (Chapman & Hall, London), 1964.
2. M. Trantz and E. Ufer, *J. Prakt. Chem.*, **113**, 105 (1926); cf. (*1*), p. 37.
3. F. Auerbach and H. Barschall. *Studien Uber Formaldehyde—Die Festern Polymeren der Formaldehyde*, Springer, Berlin, 1907; cf. (*1*), p. 150.
4. A. Iliceto and S. Bezzi, *Chim. Ind.* (*Milan*), **42**, 728–735 (1960); *Chem. Abstr.*, **55**, 21772f (1961).
5. S. A. Schou, *J. Chim. Phys.*, **26**, 72–76 (1929); cf. (*1*), p. 55.
6. H. H. Nielson and E. S. Ebers, *J. Chem. Phys.*, **5**, 823 (1937); cf. (*1*), p. 56.
7. R. P. Bell and P. G. Evans, *Proc. Roy. Soc.* (*London*), *Ser. A.*, 297–323 (1966).
8. P. Le Hénaff, *Compt. Rend.*, **256**, 1752–1754 (1963).
9. R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1–29 (1966).
10. R. J. L. Martin, *Australian J. Chem.*, **7**, 335–347 (1954).
11. C. Cupit, Ph.D. Thesis, Univ. of Illinois, University Microfilms, Ann Arbor, Mich., 1958.
12. A. Iliceto and S. Bezzi, *Ric. Sci.*, **19**, 999–1001 (1949); cf., (*1*), p. 71.
13. E. L. Piret and M. W. Hall, *Ind. Eng. Chem.*, **40**, 661–672 (1948).
14. A. Iliceto, S. Bezzi, N. Dallaporta, and G. Giacommetti, *Gazz. Chim. Ital.*, **81**, 915–932 (1951); cf. (*1*), p. 64.
15. K. Moedritzer and J. R. Van Wazer, *J. Phys. Chem.*, **70**, 2025–2029 (1966).
16. C. Russo, *Gazz. Chim. Ital.*, **44**, I, 18 (1914); cf. (*1*), p. 524.
17. E. Philippi and J. Lobering, *Biochem. Z.*, **277**, 365–375 (1935); *Chem. Abstr.*, **29**, 4655 (1935).
18. N. J. L. Megson, *Phenolic Resin Chemistry*, Academic Press, New York, 1958.
19. J. H. Freeman, *Anal. Chem.*, **24**, 955–959, 2001–2 (1952).
20. K. Hultzsch, *Chemie der Phenolharze*, Springer-Verlag, Berlin 1950.
21. R. W. Martin, *The Chemistry of Phenolic Resins*, Wiley, New York, 1956.

22. A. A. K. Whitehouse, E. G. K. Pritchett, and G. Barnett, *Phenolic Resins*, American Elsevier, New York, 1968.

22a. W. A. Keutgen, *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 15, Wiley-Interscience, New York, 1968, pp. 176–209.

22b. W. A. Keutgen, *Encyclopedia of Polymer Science and Technology*, Vol. 10, Wiley-Interscience, New York, 1969, pp. 1–73.

23. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithica, New York, 1953.

24. N. J. L. Megson, *J. Soc. Chem. Ind.* (*London*), **52**, 420 (1933).

25. S. H. Hollingdale and N. J. L. Megson, *J. Appl. Chem.* (*London*), **5**, 616–624 (1955).

26. H. G. Peer, Ph.D. Thesis, University of Leiden (1956).

27. T. T. Jones, *J. Soc. Chem. Ind.* (*London*), **65**, 264–275 (1946).

28. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **72**, 497–509 (1953).

29. L. M. Yeddanapalli and A. K. Kuriakose, *J. Sci. Ind. Res.* (*India*), **18B**, 467–475 (1959).

30. A. A. Zavitsas, *J. Polymer Sci., Part A-1*, **6**, 2533–2540 (1968); A. A. Zavitsas, R. D. Beaulieu, and J. R. LeBlanc, *J. Polymer Sci.*, 2541–2559 (1968).

31. H. S. Lilley, *J. Soc. Chem. Ind.* (*London*), **67**, 196–199 (1948).

32. J. S. Rodia and J. H. Freeman, *J. Org. Chem.*, **24**, 21–26 (1959).

33. S. R. Finn and J. W. James, *J. Appl. Chem.* (*London*), **6**, 466–476 (1956).

33a. W. H. Moss and E. Moss, *Brit. Polym. J.*, 1969, **1**(1), 29–33.

34. H. Kakiuchi and T. Otsu, *Chem. High Polymers* (*Japan*), **9**, 305–315 (1952); *Chem. Abstr.*, **48**, 4247i (1954).

34a. R. M. Secor, *AIChE Journal*, **15**(6), 861–865 (1969).

35. J. J. Gardikes and F. M. Konrad, *Amer. Chem. Soc., Div. Organic Coatings and Plas. Chem., Preprints*, **26**(1), 131–133 (1966).

36. M. Imoto, I. Ijichi, C. Tanaka, and M. Kinoshita, *Makromol. Chem.*, **113**, 117–130 (1968).

37. E. L. Humberger, *Paint and Varn. Prod.*, June 1968, 49–51.

38. A. N. MacDonald and M. F. Drumm, unpublished results, this laboratory, 1969.

39. W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45–55 (1943).

40. P. J. Flory, *Frontiers in Chemistry*, Vol. VI, Wiley-Interscience, New York, 1949, pp. 211–280.

40a. M. Jonason, *J. Appl. Polymer Sci.*, **4**, 129–140 (1960).

41. R. Dijkstra and J. de Jonge, Presented before Am. Chem. Soc., Div. Organic Coatings and Plas. Chem., April 1967.

42. M. F. Drumm, C. W. H. Dodge, and L. E. Nielsen, *Ind. Eng. Chem.*, **48**, 76–81 (1956).

43. N. J. L. Megson, *Brit. Plastics*, **20**, 27–31 (1948).

44. H. P. Higginbottom, unpublished results, this laboratory, 1969.

45. W. J. Burke, G. A. Short, and H. P. Higginbottom, *J. Polymer Sci.*, **43**, 49–58 (1960).

46. M. Imoto and S. Nakade, *Bull. Chem. Soc. Japan*, **36**, 580–585 (1963).

47. W. J. Burke, W. E. Craven, A. Rosenthal, S. H. Ruetman, C. W. Stephens, and C. Weatherbee, *J. Polymer Sci.*, **20**, 75–88 (1956).

48. W. J. Burke, S. H. Ruetman, C. W. Stephens, and A. Rosenthal, *J. Polymer Sci.*, **22**, 477–483 (1956).

49. W. J. Burke, S. H. Ruetman, and H. P. Higginbottom, *J. Polymer Sci.*, **38**, 513–520 (1959).

50. W. J. Burke and S. H. Ruetman, *J. Polymer Sci.*, **32**, 221–228 (1958).

51. A. Rosenthal, F. Lederer, and K. Gilson, *Can. J. Chem.*, **34**, 679–688 (1956).

52. V. A. Popov, I. S. Druyan, and B. G. Vershal, *Soviet Plastics*, **5**, 15–19 (1964).

52a. G. S. Learmonth and D. P. Searle, *J. Appl. Sci.*, **13**, 437–443 (1969).

53. H. Hosada, *Kogyo Kagaku Zasshi*, **63**, 1651–1654 (1960); *Chem. Abstr.*, **56**, 15662e (1962).

54. A. M. Raskina and I. N. Kogan, *Plast. Massy*, **1966**(3), 44–45; *Soviet Plastics*, **1966**(3), 49–50.
55. B. T. Hayes and R. F. Hunter, *J. Appl. Chem.* (*London*), **8**, 743–748 (1958).
56. K. Hultzsch, *Kunstoffe*, **39**, 57–63 (1949).
57. P. D. Bartlett and H. J. Dauben, *J. Am. Chem. Soc.*, **62**, 1339–1344 (1940).
58. G. R. Sprengling and C. W. Lewis, *J. Am. Chem. Soc.*, **75**, 5709–5711 (1953).
59. G. R. Sprengling, *J. Am. Chem. Soc.*, **76**, 1190–1193 (1954).
60. R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1947**, 1260–1269.
61. J. J. Keane, Ph.D. Thesis, Univ. of Utah, Ann Arbor, Michigan, L. C. Card No. Mic. 59-2984 (1959).
62. N. D. Coggeshall, *J. Am. Chem. Soc.*, **72**, 2836–2844 (1950).
63. T. Cairns and G. Eglinton, *J. Chem. Soc.*, **1965**, 5906–5913.
64. R. F. Goddu, *Anal. Chem.*, **30**, 2009–2013 (1958).
65. T. Cairns and G. Eglinton, *Nature*, **196**, 535–537 (1962).
66. V. P. Pshenitsyna, A. N. Shabadash, and T. V. Fremel, *Dokl. Akad. Nauk SSSR*, **153**(3), 650–652 (1963).
67. T. T. Jones, *J. Appl. Chem.* (*London*), **2**, 134–149 (1952).
68. H. L. Bender, A. G. Farnham, and T. W. Guyer, Bakelite Corp., U.S. Pats. 2,464,207 and 2,475,587 (1949); *Mod. Plastics*, **30**(6), 136–138, 220–222 (1953).
69. D. A. Fraser, R. W. Hall, and A. L. J. Raum, *J. Appl. Chem.* (*London*), **7**, 676–688 (1957).
70. D. A. Fraser, R. W. Hall, P. A. Jenkins, and A. L. J. Raum, *J. Appl. Chem.* (*London*), **7**, 689–700 (1957).
70a. R. Dijkstra, N.V. Philips' Gloeilampenfabrieken, personal communication, 1969.
71. H. G. Peer, *Rev. Trav. Chim.*, **79**, 825–835 (1960).
72. S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.* (*London*), **69**, S49–S51 (1950).
73. M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, **71**, 2907–2913 (1949).
74. A. M. Partansky, *Am. Chem. Soc., Div. Org. Coatings Plast. Chem., Preprints*, **27**(1), 115–124 (1967).
75. R. M. Huck, Monsanto Co., U.S. Pat. 3,332,911 (1967).
76. S. Murayama, *Bull. Chem. Soc. Japan*, **39**, 1019–1035 (1966).
77. L. H. Baekeland, *Ind. Eng. Chem.*, **17**, 225 (1925).
78. J. Reese, *Angew. Chem.*, **66**, 170–173 (1954).
79. H. P. Higginbottom, H. M. Culbertson, and J. C. Woodbrey, *Anal. Chem.*, **37**, 1021–1026 (1965).
80. J. C. Woodbrey, H. P. Higginbottom, and H. M. Culbertson, *J. Polymer Sci.*, Part A, 3, 1079–1106 (1965).
81. R. C. Hirst, D. M. Grant, R. E. Hoff, and W. J. Burke, *J. Polymer Sci.*, **3**, 2091–2105 (1965).
82. L. M. Debing, G. E. Murray, and R. J. Schatz, *Ind. Eng. Chem.*, **44**, 356–359 (1952).
83. J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080–2087 (1954).
84. R. Dijkstra and J. de Jonge, *Rec. Trav. Chim.*, **76**, 92–100 (1957).
85. R. Dijkstra, J. de Jonge, and M. F. Lammers, *Rec. Trav. Chim.*, **81**, 285–296 (1962).
86. H. G. Peer, *Rec. Trav. Chim.*, **78**, 851–863 (1959).
87. I. I. Paul and I. V. Bochkareva, *Chem. Abstr.*, **61**, 13160b (1964).
88. A. A. Zavitsas and R. D. Beaulieu, unpublished data, this laboratory, 1967.
89. J. H. Freeman, *Amer. Chem. Soc., Div. Organic Coatings and Plas. Chem., Preprints*, **27**(1), 84–99 (1967).
89a. D. J. Francis and L. M. Yeddanapalli, *Makromol. Chem.*, **125**, 119–125 (1969).
90. A. A. Zavitsas, *J. Chem. Eng. Data*, **12**(1), 94–97 (1967).
91. D. J. Francis and L. M. Yeddanapalli, *Indian J. Chem.*, **2**(4), 166–167 (1964); *Chem. Abstr.*, **12**, 196–200 (1962).

92. G. E. Little, *J. Appl. Chem.*, **12**, 196–200 (1962).
93. T. Minami and T. Ando (Osaka Ind. Research Inst.), *Osaka Kogyo Gijyutsu Shinkenjyo Kiho*, **8**, 51–54 (1957); *Chem. Abstr.*, **53**, 13649g (1959).
94. T. Minami and T. Ando, *Kogyo Kagaku Zasshi*, **59**, 668–672 (1956); *Chem. Abstr.*, **52**, 5946a (1958).
95. L. M. Yeddanapalli and V. V. Gopalakrishna, *Makromol. Chem.*, **32**, 112–123 (1959).
96. V. V. Gopalakrishna and L. M. Yeddanapalli, *Makromol. Chem.*, **32**, 124–129 (1959).
97. V. V. Gopalakrishna and L. M. Yeddanapalli, *Makromol. Chem.*, **32**, 130–138 (1959).
98. L. M. Yeddanapalli and D. J. Francis, *Makromol. Chem.*, **55**, 74–86 (1962).
99. C. P. Eapen and L. M. Yeddanapalli, *Makromol. Chem.*, **119**, 4–16 (1968).
100. D. J. Francis and L. M. Yeddanapalli, *Makromol. Chem.*, **119**, 17–22 (1968).
101. R. Dijkstra and J. de Jonge, *Amer. Chem. Soc., Div. Organic Coatings and Plas. Chem., Preprints*, **26**(1), 107–111 (1966).
101a. N. I. Basov, U. V. Kazankov, A. I. Peonov, V. A. Pubartovich, and V. A. Mironov, *Izo. Vyssh. Ucheb. Zaved., Khim. Khim. Tekknol.*, **12**(11), 1578–1582 (1969).
102. I. V. Kamenskii and V. N. Tsvetkov, *Trudy Maskov Chim.—Tekknol. Inst.* im. D. I. Mendeleeva No. 25 (**1957**), 86–93.
102a. E. W. Orrell and R. Burns, *Plast. Poly.*, **1968**, 36 (125), 469–477.
103. E. J. Quinn, H. W. Osterhoudt, J. S. Heckles, and D. C. Ziegler, *Anal. Chem.*, **40**, 547–551 (1968).
103a. J. E. Armonas, *Forest Prod. J.*, **20**(7), 22–28 (1970).
103b. R. C. Vasishth, F. E. Schwarz, and S. Y. Leong, *Spectrovision*, **1968**, No. 20, 4–7.
104. B. Tollens, *Ber.*, **17**, 659 (1884).
105. A. Einhorn and A. Hamberger, *Chem. Ber.*, **41**, 24–28 (1908).
106. H. John, U.S. Pat. 1,355,834 (1920).
107. F. Pollak, British Pat. 171,094 (1920).
108. C. Ellis, *Chemistry of Synthetic Resins*, Reinhold, New York, 1935.
109. G. Walter, *Trans. Faraday Soc.*, **32**, 377–395 (1936).
110. A. E. Dixon, *J. Chem. Soc.*, **113**, 238–239 (1918).
111. Henkel and Cie, G.N.B.H., British Pat. 455,008 (1935).
112. C. Vale and W. Taylor, *Aminoplastics*, Iliffe Books, London, 1964.
113. J. Blais, *Amino Resins*, Reinhold, New York, 1959.
114. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **71**, 643–660 (1952).
115. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **71**, 661–667 (1952)
116. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **71**, 890–898 (1952).
117. J. I. de Jong, J. de Jonge, and H. Eden, *Rec. Trav. Chim.*, **72**, 88–90 (1953).
118. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **72**, 139–156 (1953).
119. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **72**, 169–172 (1953).
120. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **72**, 202–206 (1953).
121. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **72**, 1027–1036 (1953).
122. N. Landquist, *Acta Chem. Scand.*, **11**, 776–779 (1957).
123. N. Landquist, *Acta Chem. Scand.*, **11**, 780–785 (1957).
124. N. Landquist, *Acta Chem. Scand.*, **11**, 786–791 (1957).
125. N. Landquist, *Acta Chem. Scand.*, **11**, 792–803 (1957).
126. Y. Ito, *Kogyo Kaguku Zasshi*, **64**, 382–785, 385–389 (1961).
127. A. Iliceto, *Ann. Chim. (Rome)*, **43**, 625 (1953).
128. E. Wagner, *J. Org. Chem.*, **19**, 1862–1881 (1954).
129. Y. Ogato, M. Okano, and M. Sugaware, *J. Am. Chem. Soc.*, **73**, 1715–1717 (1951).
130. F. Erikson and D. Sharp, Monsanto Co., U.S. Pat. 2,818,433 (1957).
130a. R. A. Lapina and F. B. Zhurina, *J. Appl. Chem. USSR*, **42**, 2028–2029 (1969).
131. M. Okano and Y. Ogata, *J. Am. Chem. Soc.*, **74**, 5728–5731 (1952).

132. I. Koeda, *J. Chem. Soc. (Japan) Pure Chem. Section*, 75, 571–578 (1954).

133. M. Gordon, A. Halliwell, and T. Wilson, *Chemistry of Polymerization Processes Monograph No. 20*, Society of Chemical Industry, London, 1966.

134. M. Gordon, A. Halliwell, and T. Wilson, *J. Appl. Polymer Sci.*, **10**, 1153–1170 (1966).

135. J. Aldersley, M. Gordon, A. Halliwell, and T. Wilson, *Polymer*, 9(7), 345–358 (1968).

136. A. Frost and R. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1953.

Chapter 6

DIELS-ALDER POLYMERIZATION

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I. Introduction

The Diels–Alder reaction is probably one of the most prolific and versatile of the reactions at the disposal of the synthetic organic chemist. In its most general form it can be depicted as