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The Reaction between Phenol and Formaldehyde in Non-Aqueous Media. I. The Kinetics of the Reaction Catalyzed by Boron Trifluoride-Etherate

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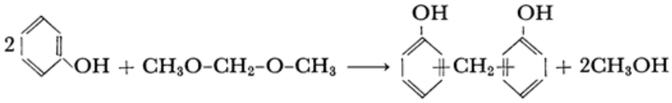
The papers of this series are kinetic studies of the reaction between phenol and formaldehyde in non-aqueous media; this reaction has, however, not been investigated as thoroughly as the reactions in aqueous media. During the course of the reaction, the reactants and products have been determined by gas chromatography. Within the range of low conversion, the overall reaction between phenol and methylal may be represented by:



Moreover, the kinetic equation and the apparent activation energy have been estimated as follows :

$$\frac{d[\text{methyl alcohol}]}{dt} = -\frac{d[\text{phenol}]}{dt} = \frac{k[\text{phenol}]^2[\text{methylal}]^0[\text{catalyst}]^1}{[\text{methyl alcohol}]^3}$$

$$E \fallingdotseq 18.6 \text{ kcal./mol.}$$

At the same time, methyl phenyl formal is detected as an intermediate in the reaction system. Judging from these experimental results, it seems that the acetal exchange reaction, and the substitution on aromatics proceed concurrently and consecutively in the complex system.

The reaction between phenol and aldehydes has been investigated intensively over the past fifty years, and the mechanisms of the reaction in aqueous media have been almost established.[1,2] However, very little is known concerning the reaction in non-aqueous media.

Since formaldehyde in aqueous media exists as a mixture of methylene glycol, polymethylene glycol, their hemiacetals and acetals (when an alcohol is present),[3] the reactions in aqueous media may be very complicated, especially when such a solvent as alcohol or dioxane is present in the system.[4]

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[1] M. Imoto, H. Kakiuchi and M. Oiwa, *Kobunshi Kagaku*, **6**, 67, 385, 398 (1949); ibid., **8**, 29, 33 (1951); *Kobunshi Tenbo*, **4**, 60 (1951); ibid., **8**, 30 (1952); *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **61**, 1646 (1958); K. Oshima and E. Imoto, *Kobunshi Kagaku*, **3-4**, 51, 57, 60, 65 (1946—47); K. Manaka, ibid., **8**, 276 (1951); ibid., **10**, 346 (1953); ibid., **11**, 34, 421 (1954); R. Inoue and T. Minami, ibid., **9**, 179, 191 (1952); *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **61**, 1340 (1958); K. Hultzch, *Ang. Chem.*, **A60**, 179 (1948).

[2] S. Seto and H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **57**, 842 (1954); ibid., **58**, 378 (1955); ibid., **61**, 1387 (1958); ibid., **66**, 139 (1963).

[3] M. Tsuge, 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

[4] T. Tanigaki and M. Imoto, *J. Chem. Soc. Japan. Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **59**, 712 (1956); ibid., **61**, 144 (1958); K. Manaka, ibid., **59**, 1436 (1956); ibid., **60**, 346 (1957); H. Horiuchi, ibid., **66**, 155 (1963).

$$\begin{tikzcd} CH_2{=}O \arrow[r, shift left, "H_2O"] & HO\text{-}CH_2\text{-}OH \arrow[l, shift left] \arrow[r, shift left, "CH_2{=}O"] \arrow[d, shift left, "CH_3OH"] & HO\text{-}(\text{-}CH_2\text{-}O\text{-})_n\text{-}H \arrow[l, shift left] \arrow[d, shift left, "CH_3OH"] \\ & CH_3OCH_2OH \arrow[u, shift left] \arrow[r, shift left] & CH_3O\text{-}(\text{-}CH_2\text{-}O\text{-})_n\text{-}H \arrow[l, shift left, "CH_2{=}O"] \arrow[u, shift left] \end{tikzcd} \qquad (1)$$

Several years ago, Uenaka, Naokawa and Yoshino⁵⁾ developed a new technique of producing phenol resins; this was one of the earliest examples of the reaction in non-aqueous media. They used paraformaldehyde as the source of formaldehyde, butyl alcohol as the solvent, and calcium hydroxide as the catalyst; then the water produced was removed from the reaction system by azeotropic distillation during the course of the reaction. It was shown by their results that both the rates and the products of the reaction in the non-aqueous media differed remarkably from those of the reaction in the aqueous media. It was also found that the presence of butyl phenyl formal in the reaction system had a significant effect on the rate of reaction.⁶⁾

Recently, Horiuchi⁷⁾ found, by means of gas chromatography, that a small amount of methyl phenyl formal was present only at the early stage of the reaction between phenol and the formaldehyde solution containing water and methyl alcohol. However, the alkyl phenyl formal produced at an earlier phase of the reaction was subsequently decomposed by hydrolysis and the rate of the overall reaction may not be appreciably influenced by this intermediate in aqueous media.

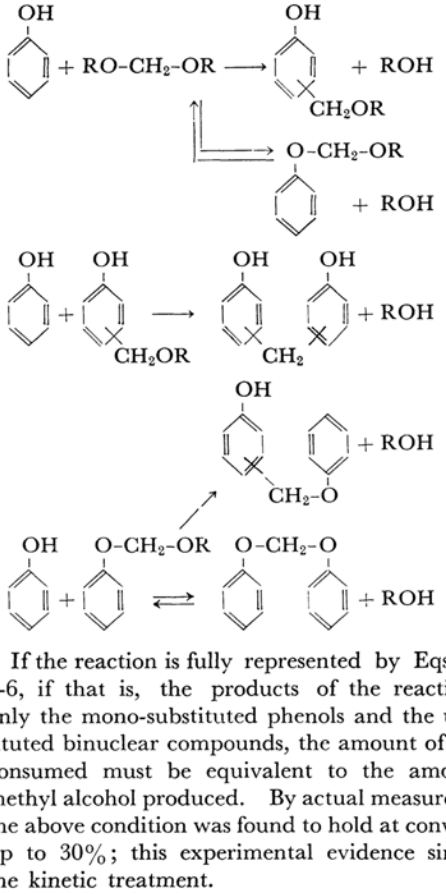
More recently, Heslinga and Schors⁸⁾ developed a new type of phenolic resin, one prepared by curing novolac with cyclic formals in the presence of an acid as the catalyst at room temperature and under atmospheric pressure. Although the preparation,⁸⁾ the processing and the physical properties⁹⁾ of the phenol formal resins were studied extensively, however, the mechanism of the reaction between phenol (or novolac) and cyclic formals was not fully investigated.

Meerwein¹⁰⁾ has reviewed recent research on the reactions of acetals including the syntheses, the decomposition, the acetal exchange, the hydrolyses, and the alcoholyses. In this review, some aspects of the behavior of alkyl aryl formals are described, especially those of methyl phenyl formal.

Since acetals are relatively stable in alkaline media, but not in acidic media, almost all the reactions of acetals can be catalyzed by a small amount of an acid, for example, hydrochloric acid, sulfuric acid, phosphoric acid, ferric chloride, calcium chloride, ammonium chloride, boron trifluoride, hydrogen sodium sulfate, monochloroacetic acid, *p*-touenesulfonic acid or the acidic forms of ion exchange resins.

It seems probable that the principal reactions between phenol and formals in non-aqueous media are the acetal exchange¹⁰,¹¹⁾ and the substitution on the aromatic ring; the former is reversible, while the latter is irreversible.

If formaldehyde is added to the system as a formal, the acid-catalyzed phenol-formaldehyde reactions in non-aqueous media may be simpler than those in aqueous media.



(2-1)
(2-2)
(2-3)
(2-4)
(2-5)
(2-6)

If the reaction is fully represented by Eqs. 2-1—2-6, if that is, the products of the reaction are only the mono-substituted phenols and the unsubstituted binuclear compounds, the amount of phenol consumed must be equivalent to the amount of methyl alcohol produced. By actual measurements, the above condition was found to hold at conversions up to 30%; this experimental evidence simplifies the kinetic treatment.

Even though the phenol-formaldehyde reaction in non-aqueous media is one of the most important problems in the field of phenol resins, no kinetic studies have been done on this reaction, as has been mentioned earlier. From this point of view, this investigation has been undertaken, therefore, first to deduce the kinetic equation for the reaction between phenol and methylal in non-aqueous media; second, to elucidate the reaction mechanism,

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5) M. Uenaka, T. Naokawa and S. Yoshino, Japanese Pat. 232910 (1957); ibid., 236930 (1957); ibid., 242652 (1958).

6) K. Ishikawa, T. Naokawa and Y. Okada, ibid., 275695 (1960).

7) H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 150 (1963).

8) A. Heslinga and A. Schors, *J. Appl. Polym. Sci.*, **8**, 1921 (1964).

9) L. K. H. Von Beek, ibid., **8**, 2843 (1964).

10) H. Meerwein, "Methoden der Organischen Chemie," Ed. by E. Müller, Georg Thieme Verlag, Stuttgart, **VI/3**, (1965), pp. 204—207, 272—278.

11) W. J. Croxall, *J. Am. Chem. Soc.*, **71**, 2736, 2741 (1949).

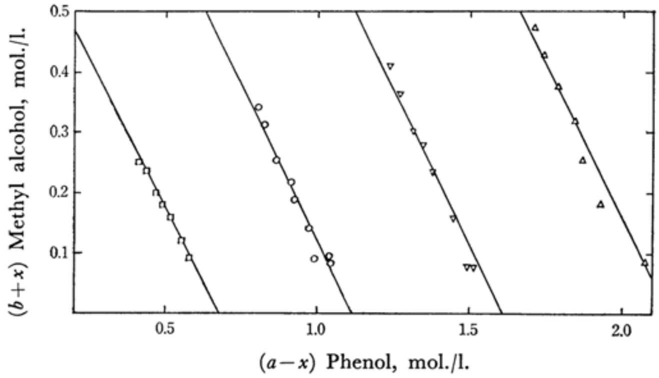

Fig. 1. The rate of production of methyl alcohol and the rate of consumption of phenol.
Methylal 1.0 mol./l., Methyl alcohol 0.1 mol./l., BF_3OEt_2 0.01 mol./l. at 30°C in nitromethane.
Phenol △ : 2.07 mol./l. ▽ : 1.50 mol./l. ○ : 1.00 mol./l. □ : 0.57 mol./l.

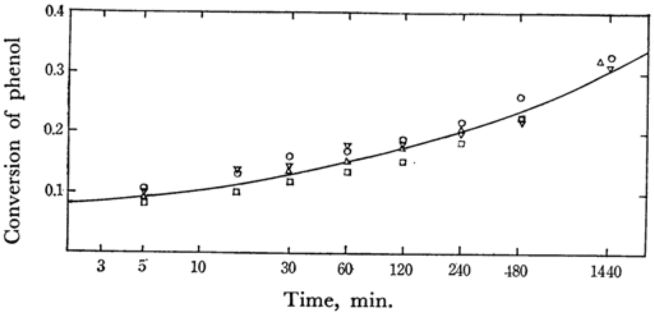

Fig. 2. The effect of methylal on rate.
Phenol 2.0 mol./l., $BF_3 \cdot OEt_2$ 0.02 mol./l. at 30°C in nitromethane.
Methylal □ : 0.5 mol./l. ○ : 1.0 mol./l. △ : 2.0 mol./l. ▽ : 3.0 mol./l.

and third, to point out several interesting problems incident to these results.

Investigations of the mechanism of the reaction in non-aqueous media should be based on exact and detailed experimental results with many kinds of reactants, catalysts and solvents over a wide range of reaction conditions; consequently, the present work should be considered as a mere attempt in this direction.

Experimental

Materials.—The reactants, solvents and catalysts used are purified by conventional methods and, their purity is checked by gas chromatography.[12] Methyl phenyl formal, an important intermediate, is prepared from monochloromethyl methyl ether and potassium phenolate in dioxane,[13] and checked by gas chromatography.[7] Diphenyl formal is prepared from diiodomethane and potassium phenolate in xylene,[14] and checked by gas chromatography.[15]

The Determination of the Concentration of Reactants by Gas Chromatography.—*Apparatus.*—A Kotaki Model GU-21 vapor fractiometer was used with a hot wire detector. The column used for methylal and methyl alcohol was 3 meters long, formed of 4.5 mm.ϕ copper tubing packed with 30% of polyethylene glycol 1500 on diabase A, and the gas chromatography was carried out at 100°C with a helium flow of 40 ml. per minute as measured at the column exit.[12] The column used for phenol and methyl phenyl formal was 1.5 m. long, formed of 4.5 mm.ϕ copper tubing packed with 20% of dilauryl phthalate on diabase A, and the gas chromatography was carried out at 155°C with a helium flow of 40 ml. per minute as measured at the column exit.[7] The correction for the differences in the amounts of samples injected was made by using carbon tetrachloride, toluene and *p*-chlorotoluene as internal markers for methylal, methyl alcohol and phenol (methyl phenyl formal) respectively.

Procedure.—The reactants, the catalyst ($BF_3 \cdot OEt_2$) and the solvent (nitromethane) were mixed, and then the mixture was placed, without stirring, in a water bath regulated at a constant temperature (usually

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[12] M. Tsuge, private communication.

[13] S. Seto and K. Ozaki, *J. Chem. Soc Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **56**, 936 (1953).

[14] H. Meerwein, "Methoden der Organischen Chemie," Ed. by E. Müller, Georg Thieme Verlag, Stuttgart, **VI/3**, (1965), p. 240.

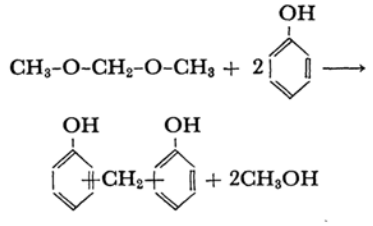
[15] F. Fujiwara, 12th Annual Meeting on Thermosetting Resin, Osaka, 1962; H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 146 (1964).

30±0.1°C). During the course of the reaction, two milliliters of the solution were withdrawn, and these samples were added to a dioxane solution (0.5 ml.) containing the internal markers (CCl_4, CH_3–C_6H_5, and *p*-CH_3–C_6H_4–Cl) and the reaction stopper (tribenzyl amine). Then they were subjected to gas chromatographic analysis in order to determine the amounts of methylal, methyl alcohol and sometimes phenol.

The Detection of the Intermediates by Paper Chromatography.—The following intermediates in the reaction system are examples of the intermediates detected by the two-dimensional paper chromatography developed by Seto and Ozaki:[16] mononuclear compounds (*o*-, or *p*-methoxymethyl phenol), dinuclear compounds (*o*-*o*′ *o*-*p*′ and *p*-*p*′ dioxydiphenyl methane, and their derivatives containing methoxymethyl group), and trinuclear compounds. On the other band, intermediates such as methyl phenyl formal are detected by gas chromatography.[7,15]

Results and Discussion

Before a detailed discussion of the experimental results is undertaken, it is advantageous to consider the overall processes of the reaction in non-aqueous media, as determined by gas chromatography. The overall reaction between phenol and methylal may be represented as follows:



(3)

This equation shows a stoichiometric relationship in which the rate of consumption of phenol is equal to the rate of the production of methyl alcohol, or twice the rate of the consumption of methylal. In the actual reactions these relationships were examined as is shown in Fig. 1. When the conversion is low (up to 30%), these quantitative relationships hold among the reactants and the products. This equation does not, however, show the details of the kinetics; they will be discussed later.

The characteristic features of the reaction are as follows: 1) The reaction rate is very fast at earlier stages, becomes considerably slower later, but does not reach an equilibrium even after 24 hr. or more (cf. Figs. 2 and 5).

2) As the initial concentration of phenol is increased, the rate of conversion is decreased. Accordingly, it seems clear that the overall reaction order is a minus value (cf. Figs. 10 and 15).

3) Because of the facts described in 1) and 2), the reaction order may not be determined by the use of only conventional methods, such as the half-lives, the initial rates or the integration.

4) The reaction products, such as methyl alcohol or methyl phenyl formal, have significant effects on the reaction order.

5) The above experimental results suggest that the reaction rate is very much contributed to by rapid reactions, such as acetal exchange, which are more probable in non-aqueous media than in aqueous media.

On the basis of these considerations, the experimental determination of kinetic equation of the reaction can be carried out. To start with, the following expression will represent the kinetic equation:

$$\frac{dx}{dt} = \frac{d[\text{methyl alcohol}]}{dt} = -\frac{d[\text{phenol}]}{dt}$$
$$= k[\text{phenol}]^{\alpha}[\text{methylal}]^{\beta}\cdot$$
$$[\text{methyl alcohol}]^{\gamma}[\text{catalyst}]^{\delta} \tag{4}$$

The Effect of Methylal.—As is shown in Fig. 2, the reaction rates do not depend upon the initial concentration of methylal over the range of 0.5—3.0 mol./l., when the initial concentrations of phenol and the catalyst are kept constant. Accordingly, the order with respect to methylal, β, can be estimated to be about zero; this implies the presence of a very fast opposing reaction involving methylal. Because of this experimental fact, the further kinetic examination was considerably simplified.

The Effect of Phenol.—In this experiment, a small amount of methyl alcohol is added into each reaction system in order to retard the initial reaction

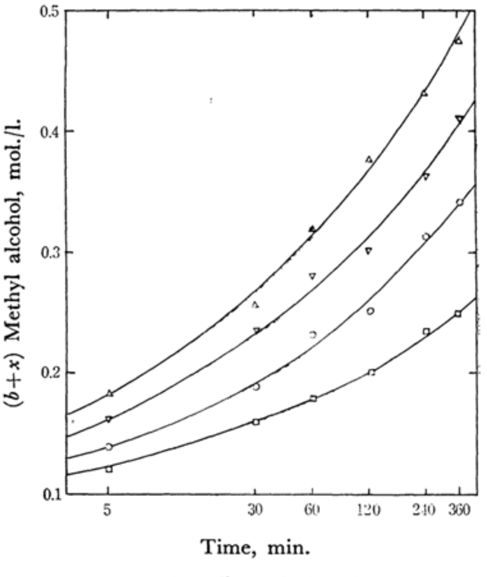


Fig. 3. The effect of phenol on rate.

Methylal 0.5 mol./l., methyl alcohol 0.1 mol./l.
$BF_3\cdot OEt_2$ 0.01 mol./l. at 30°C in nitromethane
Phenol ▽ : 2.07 mol./l. ▽ : 1.50 mol./l.
○ : 1.00 mol./l. □ : 0.57 mol./l.

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[16] G. A. Olah and M. W. Meyer, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience Publishers, New York (1963), pp. 230—235, pp. 686—688.

rate. The effect of the initial concentrations of phenol is shown in Fig. 3, at constant initial concentrations of methyl alcohol, methylal and catalyst. As is shown in Fig. 3, the higher the initial concentration of phenol, the lower the rate of conversion becomes. The reaction rates at various phenol concentrations were compared after negating the influence of methyl alcohol. When $\beta=0$, and the concentrations of methyl alcohol and the catalyst are kept constant, Eq. 4 will be simplified to:

$$\Delta x/\Delta t = K_1[\text{phenol}]^{\alpha} \qquad (4')$$

$$\log \Delta t = (\log \Delta x - \log K_1) - \alpha \log[\text{phenol}] \qquad (5)$$

The values of Δx are kept constant as 0.0125 mol./l. and the values of Δt are calculated from the curves of Fig. 3. Then, $\log \Delta t$ is plotted against log-[phenol] to be as is shown in Fig. 4.

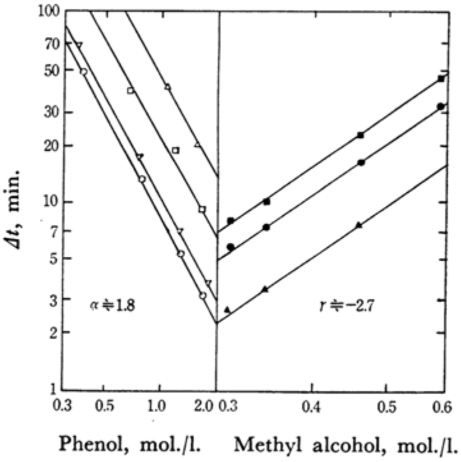


Fig. 4 Fig. 5

Fig. 4. Reaction order of phenol.
$\Delta x/\Delta t = k_1[\text{phenol}]^{\alpha}$

Fig. 5. Reaction order of methyl alcohol.
$\Delta x/\Delta t = k_2[\text{methyl alcohol}]^{\gamma}$
$\Delta x = 0.0125$ mol./l.
Methyl alcohol
△ : 0.389 mol./l. □ : 0.306 mol./l.
▽ : 0.231 mol./l. ○ : 0.206 mol./l.
Phenol
■ : 1.0 mol./l. ● : 1.2 mol./l.
▲ : 1.8 mol./.l

If Eq. 5 is applicable to this system, the relationship between $\log \Delta t$ and log[phenol] should be linear, and the slope of the straight line must correspond to the reaction order of phenol. From the slopes of straight lines in Fig. 4, the order of phenol, α, is estimated to be about two for the period of low conversion (up to about 30%).

The Effect of Methyl Alcohol.—The effect of methyl alcohol can be deduced by negating the influence of the phenol remaining according to a method similar to the one used in the earlier section. The time intervals, Δt, which elapsed for the production of methyl alcohol, Δx, at the same concentrations of phenol are calculated from the results of Fig. 4. As is shown in Fig. 5, parallel straight lines are obtained. From the slopes of these lines, the order of methyl alcohol is estimated by the relation of Eq. 5′ to be about minus three;

$$\log \Delta t \fallingdotseq (\log \Delta x - \log K_2) - \gamma[\text{methyl alcohol}] \qquad (5')$$

Thus, the reaction order with respect to methyl alcohol, γ, can be determined experimentally by considering the effect of methyl alcohol on the reaction rates.

Thus, the kinetic equation obtained over the range of low conversion is as follows:

$$\frac{d[\text{methyl alcohol}]}{dt} = k\frac{[\text{methylal}]^0[\text{phenol}]^2}{[\text{methyl alcohol}]^3} \qquad (6)$$

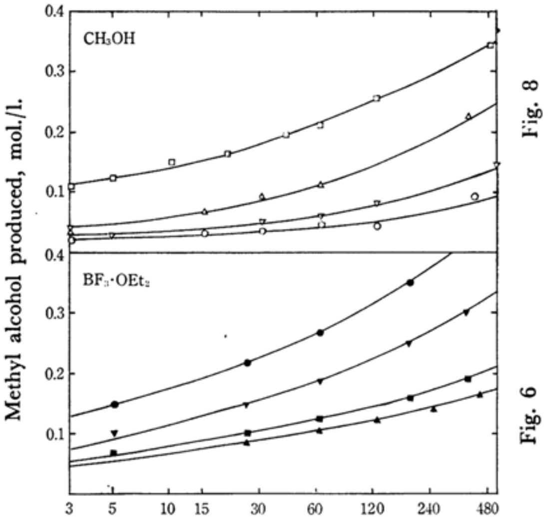


Fig. 6. Effect of methyl alcohol added on rate.
Phenol 1 mol./l., Methylal 0.6 mol./l., $BF_3 \cdot OEt_2$ 0.02 mol./l. in nitromethane at 30°C.
Methyl alcohol
□ : 0 mol./l. △ : 0.14 mol./l.
▽ : 0.30 mol./l. ○ : 0.50 mol./l.

Fig. 8. The effect of catalyst on rate.
Phenol 0.5 mol./l., methylal 0.5 mol./l. in nitromethane at 30°C
$BF_3 \cdot OEt_2$
● : 0.02 mol./l. ▼ : 0.05 mol./l.
■ : 0.001 mol./l. ▲ : 0.005 mol./l.

The Effect of the Methyl Alcohol Added.—In order to confirm the appropriateness of the kinetic equation obtained in the earlier section, the following supplementary experiments were undertaken. Figure 6 shows the relationship between the reaction rates and the initial concentrations of methyl alcohol over the range of 0.15—0.5 mol./l., when the initial concentrations of phenol, methylal and catalyst are kept constant.

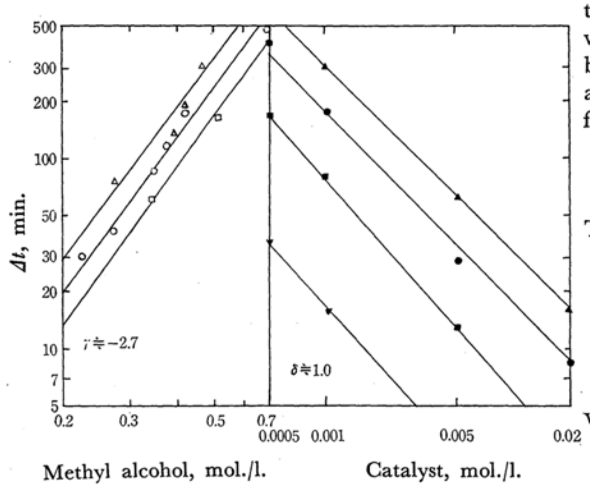


Fig. 7 Fig. 9

Fig. 7. Reaction order of methyl alcohol.
$\Delta x/\Delta t = k_3[\text{methyl alcohol}]^\gamma$
Methyl alcohol
△ : 0.175 mol./l. □ : 0.05 mol./l.
○ : 0.125 mol./l.

Fig. 9. Reaction order of catalyst
$\Delta x/\Delta t = k_4[\text{catalyst}]^\delta$
Methyl alcohol
▲ : 0.250 mol./l. ■ : 0.150 mol./l.
● : 0.200 mol./l. ▼ : 0.100 mol./l.

As was expected, the order of methyl alcohol is about minus three (Fig. 7). This confirms the reaction order of methyl alcohol determined in the earlier section.

The Effect of the Catalyst.—The effect of the concentration of the catalyst on the reaction rate is shown in Fig. 8. In a similar way, the concentration of the catalyst is plotted against the time intervals in Fig. 9. From the slopes of the straight lines in Fig. 9, the order of the catalyst is estimated to be about one. The catalyst used is $BF_3 \cdot OEt_2$, which easily reacts with one or two moles of water or alcohol to produce complex compounds. If a large amount of methyl alcohol is present in the reaction system, the activity of the catalyst is considerably decreased as a result of the formation of a relatively inactive complex compound, such as $BF_3 \cdot [CH_2OH]_2$.[17] The interaction between the catalyst and methyl alcohol may be one of the reasons why the reaction order of methyl alcohol has a minus value in this reaction system:

$$\begin{aligned}&[BF_3 \cdot \text{solvent}] + 2CH_3OH \rightleftarrows \\ &\quad [BF_3 \cdot CH_3OH] + CH_3OH + \text{solvent} \rightleftarrows \\ &\quad [BF_3 \cdot 2CH_3OH] + \text{solvent} \qquad (7)\end{aligned}$$

The Integral Form of Kinetic Equation.—In general, kinetic studies should be conducted in two or more ways, for example, differential or integration methods. After a number of attempts, the following integral form of the kinetic equation, with certain initial conditions, has been found to be most satisfactory for the reaction between phenol and methylal in nitromethane. The differential form;

$$\frac{dx}{dt} = \frac{k(a-x)^2}{(b+x)^3}$$

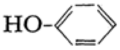
The integral form:

$$kt = \frac{(a+b)^2}{2}[(1-p)^2 - 6(1-p) + 6\ln(1-p) + 6\ln(a+b) + 2/(1-p)] - C_0 \qquad (9)$$

where

x : the concentration of CH_3OH produced
b : the initial concentration of CH_3OH
a : the initial concentration of HO-ϕ
p : a variable depending upon the conversion that is:

$$p = (b+x)/(a+b) \qquad (10)$$

C_0: integral constant
x/a: the conversion of phenol
$(b+x)$: the concentration of CH_3OH present
$(a-x)$: the concentration of HO- remaining

The initial conditions:

at $t=0$,

$$x = 0.035a,\ p = (b + 0.035a)/(a+b) \qquad (11)$$

Therefore,

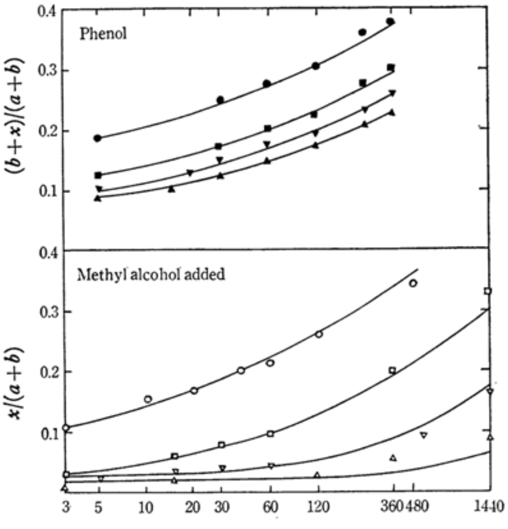
$$C_0 = \frac{(a+b)^2}{2}\left[\left(\frac{0.965a}{a+b}\right)^2 - 6\left(\frac{0.965a}{a+b}\right) + 6\ln(0.965a) + 2\frac{(a+b)}{0.965a}\right] \qquad (12)$$

In Figs. 10 and 11, the solid lines are the calculated values, while the points plotted are the measured values. There is a good agreement between them within the range of low conversion up to 30%. If x is assumed to be zero at $t=0$ as the initial condition of Eq. 9, the calculated values differ significantly from the measured values, especially in Fig. 11, which corresponds to a system containing a relatively high concentration of methyl alcohol. Careful examination shows that the kinetic equation obtained above is good enough to explain any experimental results over a wide range of conditions.

The Reaction Rate over the Range of High Conversion.—When no methyl alcohol is added to the system, the overall reaction rate is remarkably fast at an early stage of the reaction, and the conversion often reaches 30% or more within a few minutes, especially in the case of a low initial concentration of phenol, as is shown in Fig. 12. Over the range of high conversion, the estimated values of the reaction orders of phenol and methyl alcohol are about 1 and −2.5 respectively; these values differ significantly from the values in a low conversion, as Figs. 13—15 show.

The differential form:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k(a-x)^1}{(b+x)^{2.5}}$$

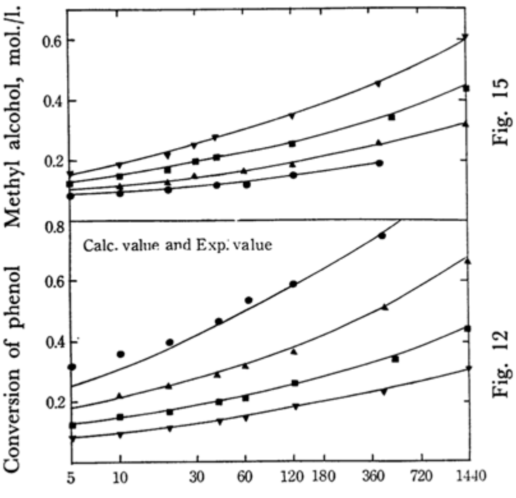


Time, min.

Fig. 10, 11 Comparison of calculated values and experimental values.
$kt=((a+b)^2/2)\{(1-p)^2-6(5p)+6\ln(1-p)+2/(1-p)+6\ln(a+b)\}+C_0$
at $t=0$, $x=0.035a$, $p=(b+x/a+b)$

Phenol
● : 0.57 mol./l. ■ : 1.0 mol./l.
▼ : 1.5 mol./l. ▲ : 2.0 mol./l.

Methyl alcohol
○ : 0.0 mol./l. □ : 0.14 mol./l.
▽ : 0.30 mol./l. △ : 0.02 mol./l.

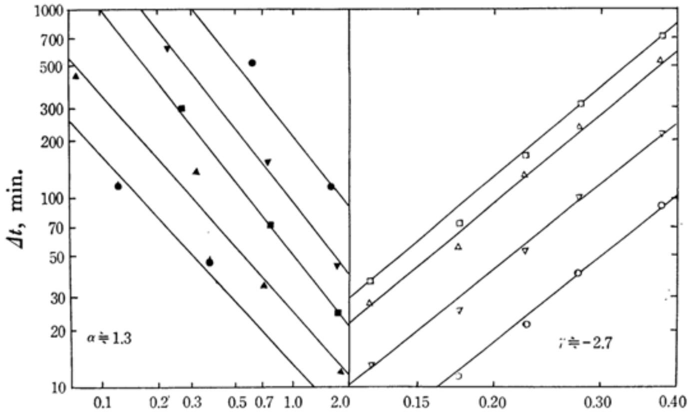


Time, min.

Fig. 12. The effect of phenol on rate (high conversion).

Fig. 15. Comparison of calculated values and experimental values.
Methylal 0.6 mol./l., catalyst 0.02 mol./l. in nitromethane at 30°C.

Phenol
● : 0.25 mol./l. ▲ : 0.50 mol./l.
■ : 1.00 mol./l. ▼ : 2.00 mol./l.



Phenol, mol./l. Methyl alcohol, mol./l.

Fig. 13 Fig. 14

Fig. 13. Reaction order of phenol (high conversion).
$\Delta x/\Delta t = k'[\text{phenol}]^{\alpha'}$, $\Delta x = 0.05$ mol./l.
Methyl alcohol ● : 0.40 mol./l. ■ : 0.25 mol./l. ◆ : 0.15 mol./l.
▼ : 0.30 mol./l. ▲ : 0.20 mol./l.

Fig. 14. Reaction order of methyl alcohol (high conversion).
$\Delta x/\Delta t=k'[\text{methyl alcohol}]^{r'}$, $\Delta x'=0.05$ mol./l.
Phenol ○ : 0.4 mol./l. △ : 0.5 mol./l. ▽ : 1.0 mol./l. ○ : 2.0 mol./l.

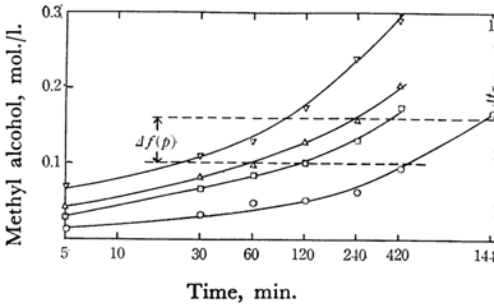


Fig. 16

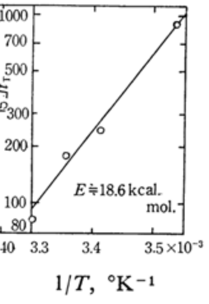


Fig. 17

Fig. 16. Rates of production of methyl alcohol at various temperatures.
Phenol 10 mol./l., methylal 0.5 mol./l., methyl alcohol 0.1 mol./l., $BF_3 \cdot OEt_2$ 0.01 mol./l. in nitromethane at 30°C.
Temperature ▽ : 30°C △ : 25°C □ : 20°C ○ : 10°C

Fig. 17. Activation energy of the reaction.
$k_T t_T = f(p)_T$ if $\Delta f(p)_T = \text{const.}$, $\log k_T = -K'_T \log \Delta t_T$

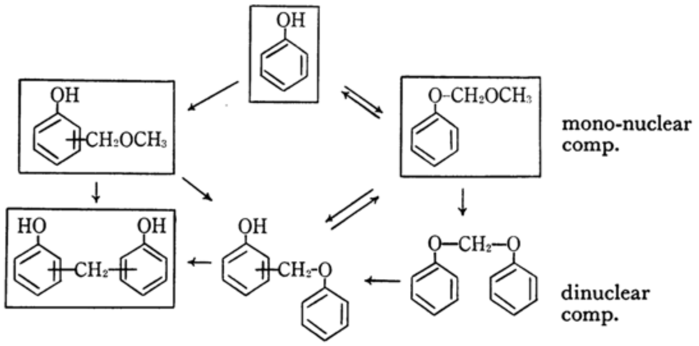


Fig. 18. Probable scheme of the reaction between phenol and methylal.

The integral form:

$$kt = 2(a+b)^{2.5}\{\ln|\tan(1/2\cdot\sin^{-1}p^{1/2}+\pi/4)| - p^{1/2} - 1/3\cdot p^{3/2} - 1/5\cdot p^{5/2} - C_0\} \tag{14}$$

where

x: the concentration of CH_3OH produced

a: the initial concentration of phenol

b: the initial concentration of CH_3OH added

p: a variable depending upon the conversion, that is,

$$p = (b+x-0.035a)/(a+b) \tag{15}$$

The initial conditions:

$$x = 0$$

$$x = 0.035a,\ p = \frac{b}{a+b}$$

C_0: integral constant

As is shown in Fig. 15, although there is a fair agreement between the experimental and the calculated values over the range of high conversion, still the stoichiometric relation in Eq. 3 does not hold in this system. Consequently, it seems probable that the reaction mechanism changes gradually, depending upon the degree of conversion, particularly in the range of conversion beyond 30%.

The Temperature Dependence of the Reaction Rate.—A comparison of reaction rates at various temperature (30, 25, 20, 10°C) is shown in Fig. 16. The time intervals, Δt, which elapse for the production of a certain amount of methanol at each temperature are measured from Fig. 16. The relation between a logarithm of the time interval and a reciprocal temperature is a straight line, as Fig. 17 shows. From the slope of Fig. 17, the apparent activation energy in this non-aqueous medium can be said to be about 18.6 kcal./mol., which is comparable to that in aqueous media.[1] Nevertheless, the overall rate of the reaction in non-aqueous media is faster than that in aqueous media. The kinetic system is too complicated for the entropy of activation to be discussed. However, the difference in overall reaction rate between non-aqueous and aqueous media may be ascribed to the entropy of activation rather than to the energy of activation.

The Estimation of the Reaction Scheme.—

The reaction in non-aqueous media is very complex; it involves substitution on aromatics, acetal exchange by methyl alcohol or phenol, and interaction between methyl alcohol and $BF_3 \cdot OEt_2$, etc.. A probable reaction scheme is shown in Fig. 18.

Phenol and methyl phenyl formal can be identified by gas chromatography, while *p*-methoxymethylphenol and dioxydiphenylmethane (*pp'* and *op'*) can be identified by paper chromatography; however, the other intermediate can not be detected so definitely. Therefore, it seems probable that the process passing through methyl phenyl formal is important in non-aqueous media. A detailed discussion of the reaction mechanism will be given in the following reports.

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