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The Reaction between Phenol and Formaldehyde in Non-Aqueous Media. II.
The Behavior of Methyl Phenyl Formal in the Reaction Catalyzed by Boron Trifluoride - Etherate

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Methyl phenyl formal (MPF) is one of the most important intermediates in the acid-catalyzed reaction between phenol and methylal in non-aqueous media. On the acidic decomposition of MPF itself, phenol and methylal are mainly produced, along with a small amount of methyl alcohol at the first step; at the same time, there exists an equilibrium state between the reactants and the products. At the second step, the phenol produced is gradually consumed, and the reaction eventually yields methyl alcohol and such condensation products of phenol as methoxymethylphenol and dioxydiphenylmethane. Thus, the acetal exchange proceeds faster than the substitution on aromatics. On the other hand, the acidic decomposition of MPF is retarded remarkably by methyl alcohol, considerably by methylal, and fairly much by phenol. This behavior of MPF can be explained by its interaction with the catalyst and the opposing reactions with it. As a result, the reaction of MPF can better be understood.

The previous paper reported on the kinetics of the phenol-formaldehyde reaction in non-aqueous media, but it was confined to the experimental characterization of the complex system.[1] This paper will deal with several intermediates of the reaction, such as methyl phenyl formal, methoxymethylphenols and dioxydiphenylmethanes, which were detected in the reaction system. It seems probable that methyl phenyl formal is one of the most important intermediates in the reaction of non-aqueous media; an understanding of its behavior is the key to an elucidation of the reaction mechanism.

Therefore, the objects of this investigation are: (1) to examine the reaction of methyl phenyl formal with and without other reactants, and then (2) to establish a reaction scheme for these reactions.

There have been only a few reports on the reaction of alkyl aryl formal, especially in non-aqueous media. In the presence of a trace of an acid, alkyl aryl formal may change at once partly to symmetric formals, and probably also to nuclear-substituted compounds.[2] Though a small amount of methyl phenyl formal has been obtained in the acid-catalyzed phenol-formaldehyde reaction in aqueous media by Horiuchi,[3] the role of the formal as an active intermediate has been not thoroughly studied in aqueous media, because

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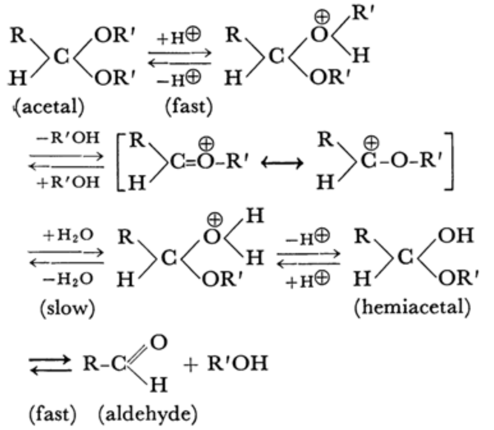
[1] Part I of this Series: S. Murayama, This Bulletin, **39**, 1019 (1966).

[2] H. Meerwein, "Methoden der Organishen Chemie," **VI/3**, Ed. by E. Müller, Georg Thieme Verlag, Stuttgrart pp. 237—238 (1965); P. Hoering and F. Baum, German Pat. 209, 608 (1907); *Chem. Zentr.*, **1909** I, 1681.

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

the formal is easily hydrolyzed in acidic aqueous media. The extensive studies of the kinetics and the mechanisms of the reactions of acetals have been performed with regard only to the hydrolysis[4] or the alcoholysis.[5]



According to this mechanism, the rate of the acid-catalyzed hydrolysis of an acetal depends mainly on either the stability of the carbonium ion produced or on the electron density on the oxygen atom, while the rate of the hydrolysis of a hemiacetal is very rapid, even in the absence of an acid catalyst.[4]

On the other hand, the acetal-exchange reaction with an alcohol or an aldehyde also proceeds in the presence of an acid catalyst, such as HCl, H_2SO_4, $FeCl_3$ or BF_3.[5,6]

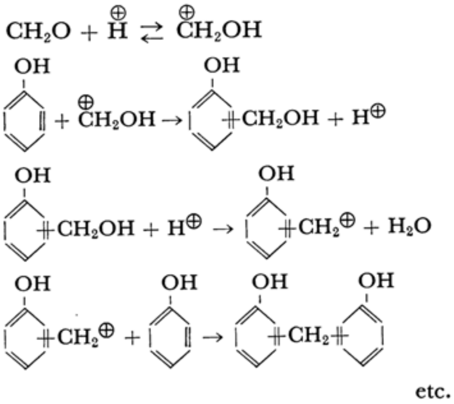
$$RCH(OR')_2 + R''(OH) \rightleftarrows RCH(OR')(OR'') + R'(OH)$$
$$RCH(OR')(OR'') + R''(OH) \rightleftarrows RCH(OR'')_2 + R'(OH)$$
$$RCH(OR')_2 + R'''CHO \rightleftarrows R'''CH(OR')_2 + RCHO$$

The rates and the equilibrium constants of the hydrolyses of acetals have been studied systematically. Dimethyl formal is one of the most stable acetals, while alkyl aryl formals are unstable; diaryl formals are stable.[6]

The catalytic action of boron trifluoride-etherate is very complex, but it may be regarded as the action of hydrogen ions produced by the reaction between the catalyst and a trace of water present in the reaction system. It is known that boron trifluoride-etherate easily forms complex compounds with alcohols, ether, nitromethane or phenol.[7]

$$[BF_3\cdot OEt_2] + H_2O \rightleftarrows [BF_3\cdot H_2O] + OEt_2 \overset{+H_2O}{\rightleftarrows}$$
$$[BE_3\cdot 2H_2O] \rightleftarrows [BF_3\cdot OH]^{\ominus} + H_3O^{\oplus}$$
$$[BF_3\cdot H_2O] \rightleftarrows [BF_3\cdot OH]^{\ominus} + H^{\oplus}$$

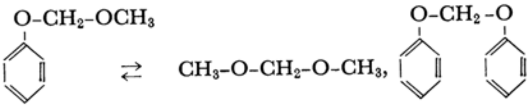
As for the acid-catalyzed phenol-formaldehyde reaction in aqueous media, the reaction mechanism has been established by Imoto et al.[8] to be:



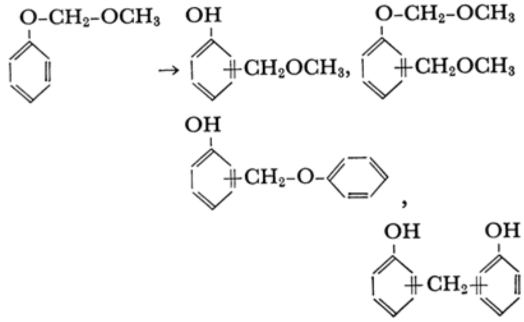
The ratio of the amounts of *o*- and *p*-derivatives produced mainly depends upon the reaction temperature and upon the catalyst (or pH) in an aqueous media.[9]

Therefore, it seems that the main reactions of methyl phenyl formal in the presence of boron trifluoride-etherate include the following two types of reactions:

(A) Acetal exchange



(B) Substitution on aromatics



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[4] M. M. Kreevoy and R. W. Taft, *J. Am. Chem. Soc.*, **77**, 3146, 5590 (1955).

[5] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960); W. J. Croxall, *J. Am. Chem. Soc.*, **71**, 2736, 2741 (1949).

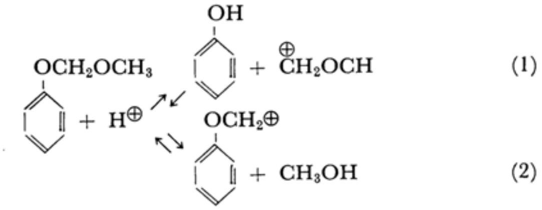
[6] H. Meerwein, "Methoden der Organishen Chemie," **VI/3**, Ed. by E. Müller, Georg Thieme Verlag, Stuttgart, (1965), pp. 272—276.

[7] N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, **1953**, 1427.

[8] M. Imoto, *Kobunshi Tenbo*, **4**, 60 (1951); ibid., **8**, 29, 33 (1952).

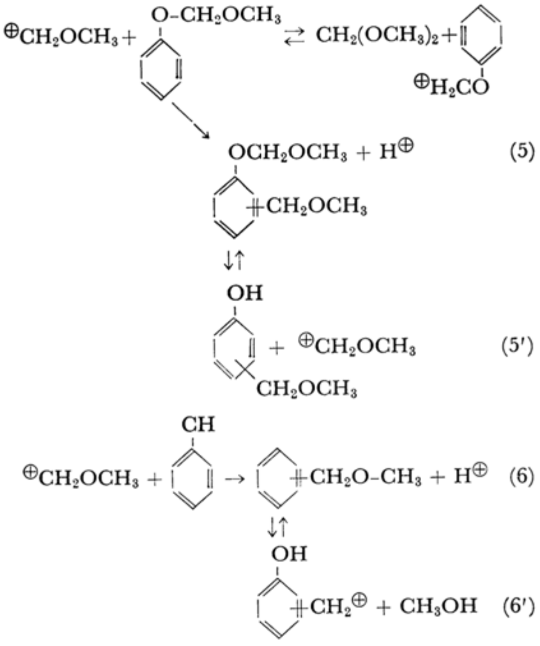
[9] H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 1379 (1963); H. L. Bender *Modern Plastics*, **30**, 136 (Feb. 1953); ibid., **31**, 115 (Mar. 1954); S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, **69**, S49 (1950); H. L. Bender, A. G. Farnham, J. W. Guyer, F. N. Apel and T. B. Gibb, Jr., *Ind. Eng. Chem.*, **44**, 1619 (1952); D. A. Flaser, R. W. Hall and A. J. Raum, *J. Appl. Chem.* (*London*), **7**, 676, 689 (1957), R. Inoue and T. Minami, *J. Chem. Scc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **61**, 1340 (1958).

By analogy with the reaction in aqueous media, the following reaction scheme may be postulated.
(1) The Activation of MPF by $H^{\oplus}$ (MPF= methyl phenyl formal):

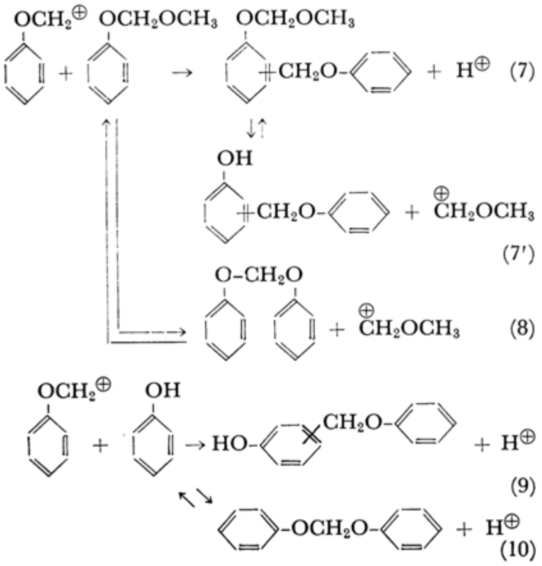

(1)
(2)

(2) The Reactions of the methoxymethyl cation:

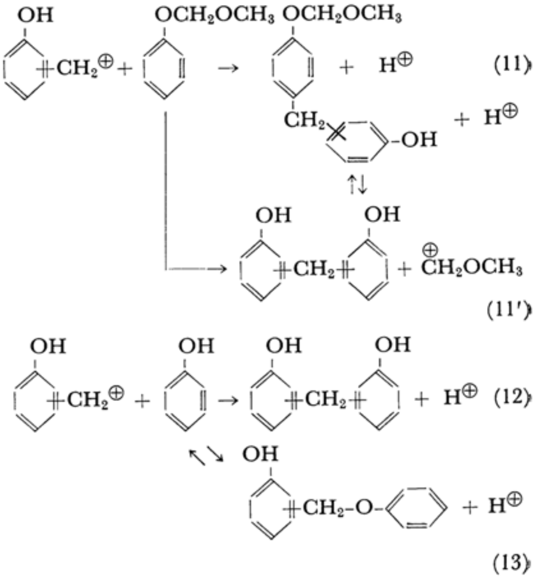
$$^{\oplus}CH_2OCH_3 + CH_3OH \rightleftarrows CH_2(OCH_3)_2 + H^{\oplus} \quad (3)$$


(5)
(5′)
(6)
(6′)

(3) The Reactions of the phenoxymethyl cation:


(7)
(7′)
(8)
(9)
(10)

(4) The Reactions of the oxybenzyl cation:


(11)
(11′)
(12)
(13)

The scheme postulated above will now be examined through experiments on the reactions of the intermediates. It is expected that the effects of the other reactants, catalysts and solvents can be understood better through these experiments.

Experimental

Materials.—The reagents, the solvent and the catalyst used were purified by the conventional methods and were checked by gas chromatography.[1]

Analytical Method.—The amounts of methyl phenyl formal, phenol, methyl alcohol and methylal were measured quantitatively by gas chromatography.[1]

Procedure.—Conventional techniques were used throughout this study. In every experiment, nitromethane was used as the solvent and boron trifluoride - etherate was used as the catalyst.

Results and Discussion

The Decomposition of Methyl Phenyl Formal (MPF).—In order to investigate the decomposition of MPF (1 mol./l.) in the presence of the boron trifluoride - etherate catalyst (0.001—0.00025 mol./l.), the amounts of MPF, phenol, methylal and methyl alcohol were determined during the course of the reaction, as is shown in Fig. 1.

At the first step of the acidic decomposition of MPF, the amount of phenol produced is almost equal to that of the methylal produced, while only a small amount of methyl alcohol is produced.

It follows from this fact that the two reactions activating MPF by proton (Eqs. 1 and 2) are very fast and of almost equal rates. This means that the methoxy-methyl cation, methyl alcohol, phenol and the phenoxymethyl cation are produced

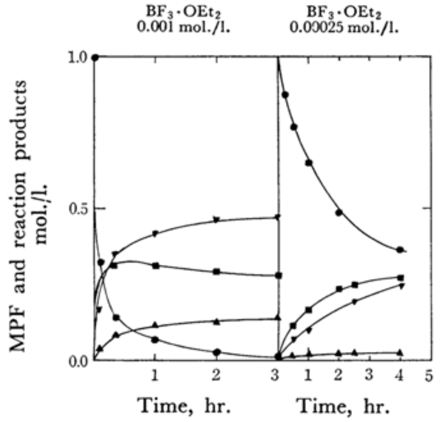


Fig. 1. The effect of the catalyst on the reaction of M.P.F.

M.P.F. 1 mol./l. in nitromethane at 30°C
●: MPF; ■: Phenol; ▼: Methylal;
▲: Methyl alcohol

in amounts almost equivalent to one another. Then, the methoxymethyl cation reacts with methyl alcohol at once to produce methylal, while the phenoxymethyl cation reacts with MPF to form various condensation products by Eqs. 7, 7′, 8, etc.

After the reaction has proceeded to some extent, the amount of phenol in the system becomes so great that the reactions of phenol, such as Eqs. 6 and 6′, take place significantly. Then the amounts of methyl alcohol and methylal remarkably increase, while the amount of phenol decreases gradually after passing through a maximum; at the same time, the amount of MPF decreases rapidly toward zero.

The reactions of the earlier stage (such as Eqs. 1, 2 and 3) proceed rapidly in the presence of a very low concentration of the catalyst, but the rates of the reactions of the later stage (such as 6 and 6′) depend markedly upon the concentration of the catalyst, as is shown in Fig. 1.

It seems probable that the unstable assymmetric acetal (MPF) is changed to the stable symmetric acetal (methylal) by the acetal exchange in the presence of a trace of an acidic catalyst, until an equilibrium is established between them.

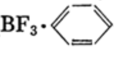
Diphenyl formal was not detected in the reaction mixture under these conditions, contrary to our expectation; this fact may have something to do with the stability or the rate of formation of the diaryl formal.

The substitution reactions on aromatics may easily accompany the acetal exchange reactions at relatively high concentrations of the catalyst, and the amounts of methyl alcohol produced may indicate the amounts of the di- or polynuclear compounds produced.

The Reaction of MPF with Phenol.—The reaction between MPF (1 mol./l.) and phenol (1 mol./l.) in the presence of BF$_3$·OEt$_2$ (0.00025 mol./l.) was also investigated. Figure 2 shows the amounts of the reactants and the products produced during the course of the reaction.

The reaction of MPF with phenol is very similar to the decomposition of MPF alone, but it has the following distinctive characteristics : 1) The amount of phenol produced is certainly smaller than that of methylal.

2) The overall reaction rate is slightly decreased by the addition of phenol to the reaction system.

The condensation reactions of phenol, such as Eqs. 6, 9, 10, 12, and 13, will proceed markedly to consume phenol in the presence of a considerable amount of phenol, and thus, the overall reaction rate might be increased by these reactions. On the other hand, phenol may form relatively stable complexes with catalysts such as [BF$_3$·-OH]

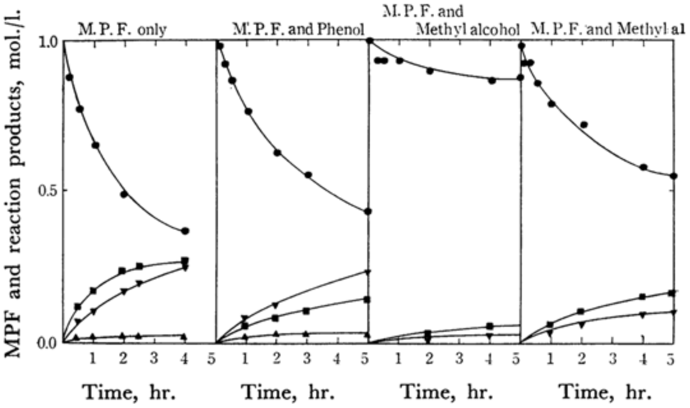
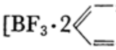


Fig. 2. The effect of reactants on the reaction of MPF
MPF 1 mol./l., BF$_3$·OEt$_2$ 0.00025 mol./l. in nitro methane at 30°C other reactant 1 mol./l. (if present)
●: MPF., ■: Phenol; ▼: Methylal; ▲: Methylalcohol

or [$BF_3\cdot 2$-OH]; the formation of these complexes should result in the decrease of the overall reaction rate. These two effects of phenol on the reaction rate compensate each other, and the net effect of the addition of phenol was a slight decrease in the overall reaction rate, while a relatively large amount of the nuclear-substituted compounds are produced.

The Reaction of MPF with Methylal.—The reaction between MPF (1 mol./l.) and methylal (1 mol./l.) in the presence of $BF_3\cdot OEt_2$ (0.00025 mol./l.) was investigated by measuring the amounts of the reactants and products during the course of the reaction; the results are shown in Fig. 2. In this case, the overall reaction rate is considerably lower than that of MPF by itself, and methyl alcohol is not produced at all, while phenol and methylal are produced as in the case of MPF alone. These results indicate that, in the presence of a considerable amount of methylal, the reaction of methylal with the phenoxymethyl cation (the back reaction of Eq. 4) is very fast and produces the methoxymethyl cation, which then consumes methyl alcohol (by Eq. 3) and probably phenol (by the back reaction of Eq. 1). Thus, the presence of methylal inhibits the overall rate of the reaction by promoting various opposing reactions, though the interaction of methylal with the catalyst may be negligibly small.

The Reaction of MPF with Methyl Alcohol.—In the presence of methyl alcohol (1 mol./l.), the reaction of MPF (1 mol./l.) with $BF_3\cdot OEt_2$ (0.00025 mol./l.) as a catalyst is significantly inhibited, and both MPF and methyl alcohol are consumed very gradually; this fact shows that methyl alcohol may promote the opposing reaction. The catalyst readily changes to a stable complex by reacting with methyl alcohol. Since the two types of effects in the presence of methyl alcohol are additional, methyl alcohol decreases the overall reaction rate remarkably.

Summary

The acidic decomposition of MPF in nitromethane has been studied, and the reaction mechanism has been investigated. 1) There must exist an equilibrium between MPF, methylal, phenol and methyl alcohol through acetal exchange reactions, but the actual equilibrium state is changed successively by substitution reactions on aromatics.

2) The acetal exchange reactions proceed very fast, even in the presence of a very low concentration of the catalyst, while the substitution reactions on aromatics proceed more slowly under the same conditions.

3) The formation of complex compounds between the catalyst and such reactants as phenol, methylal and methyl alcohol results in various decreases in the overall reaction rate according to the stabilities of the various complexes.

4) The acidic decomposition of MPF may be significantly inhibited by methylal and methyl alcohol as a result of the opposing reactions, but not inhibited by phenol, if the effects of complex formations on reaction rates are eliminated. The reaction using sulfuric acid as the catalyst may prove this fact more clearly.[10]

5) The behavior of MPF can be explained by supposing that the reaction proceeds through some reactive intermediates, such as the methoxymethyl cation, the phenoxymethyl cation and the oxybenzyl cation.

6) Diphenyl formal is not formed during the disproportionation reactions of MPF, contrary to our expectation. This experimental evidence suggests a difference in reactivity between the methoxymethyl cation and the phenoxymethyl cation.

7) From the results of this experiments, the mechanism of the reaction between phenol and methylal in non-aqueous media can be better understood.

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[10] S. Murayama, M. Niwa and R. Nakatsuka, 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.