BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1032—1035 (1966)

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

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(Received October 16, 1965)

In the previous papers of this series, the reaction between phenol and methylal in non-aqueous media has been investigated by means of the experimental characterization of the kinetic system; a plausible reaction scheme has thus been presented. The object of the present paper is to make a mathematical characterization of the kinetic system, a kinetic equation has been obtained by calculation based on the probable reaction scheme; it has been found to be in good agreement with the kinetic equation obtained experimentally.

There are only few reactions which lend themselves to a simple kinetic description in terms of the reaction order in the field of the resin-forming condensation reactions. Since there are many processes by which the reaction proceeds, the author has expected to find a concomitant difficulty in expressing the rates of phenol-formaldehyde reactions in simple terms. Since the phenol-formaldehyde reactions involve the opposing, concurrent and consecutive reactions, their kinetic studies have been established only in aqueous media.[1] Unfortunately, the mechanism of the reactions in aqueous media is not suitable for explaining the behavior of the reactions in non-aqueous media. The series of works conducted at this laboratory have aimed at clarifying the differences between the reactions in non-aqueous media and those in aqueous media.

The previous papers of this series have dealt with the kinetics of the reaction between phenol and formaldehyde in nitromethane catalyzed by boron trifluorideetherate. The course of the reaction was followed by the quantitative gas chromatographic analysis of the reactants and products.

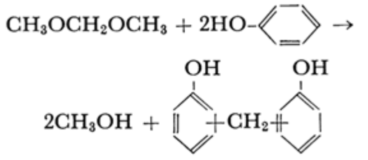
After the experimental characterization of this reaction system, the following kinetic equation was obtained:[2]

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

Methyl phenyl formal was detected as one of the reactive intermediates in this reaction system; the behavior of methyl phenyl formal was therefore studied as a means of estimating the reaction scheme.[3] The objects of the present paper are: (1) to perform a mathematical characterization of the kinetic system, and (2) to gain detailed information about the mechanism of the phenol-formaldehyde reaction in non-aqueous media.

Results and Discussion

Reaction Scheme.—The reaction between phenol and methylal in nitromethane catalyzed by boron trifluoride-etherate may be represented in the following simplified form:



(1)

The stoichiometric relations of Eq. 1 are in accordance with the experimental findings[2] that the rate of phenol consumed is almost equal to the rate of methyl alcohol produced, and that the ratio of the rates of the consumption of methylal and phenol is 1 : 2, when the conversion is low (up to 30%).

On the other hand, the acidic decomposition of methyl phenyl formal can be explained by using an ionic mechanism, which involves the formation of such active intermediates as the methoxymethyl cation, the phenoxymethyl cation and the oxybenzyl cation.

From the experimental evidence, it seems that the reaction between phenol and methylal in non-aqueous media should be regarded as a complex kinetic system consisting of two series of consecutive reactions passing through methoxymethylphenols or methyl phenyl formal, and that each of the two series involves such concurrent

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

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

[3] Part II of This Series: S. Murayama, ibid., **39**, 1027 (1966).

reactions as the acetal exchange and the substitution on aromatics. Nevertheless, from the analogy of acidic reactions in aqueous media, the formation of di- or tri-methoxymethylphenols may also be neglected in non-aqueous media so as to simplify the mathematical calculation. The differences in the reactivities of the ortho- and para-positions of phenol is not taken into consideration.

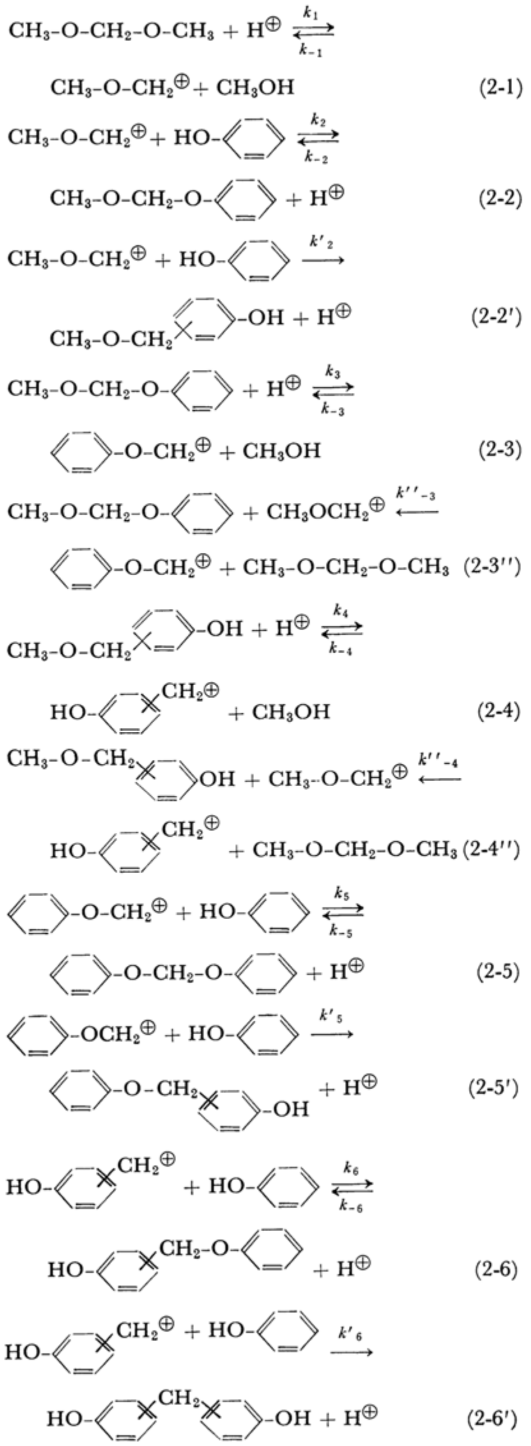

Fig. 1. Reaction scheme.

The following reaction scheme may, then, be presented for the phenol-formaldehyde reaction in non-aqueous media:

The Mathematical Calculation of the Reaction Rate.—On the basis of the reaction scheme shown in Fig. 1, the rate of the methyl alcohol produced is calculated by using the stoichiometric relations and the stationary-state hypothesis.

First, the terms and the rate of production (or consumption) of reactants and intermediates are represented as follows:

m: methylal
p: phenol
a: methyl alcohol
c^*: the effective concentration of catalyst
α: the methoxymethyl cation
β: methylphenyl formal
γ: methoxymethylphenol
δ: the phenoxymethyl cation
ε: the oxybenzyl cation
ρ: phenoxymethylphenol
φ: diphenyl formal

$$\frac{d\alpha}{dt} = -(k_{-1}a + k_2p + k'_2p)\alpha + k_{-2}c^*\beta + k''_{-3}m\delta + k''_{-4}m\varepsilon + k_1mc^* \quad (3\text{-}1)$$

$$\frac{d\beta}{dt} = k_2p\alpha + (k_{-3}a + k''_{-3}m)\delta - (k_3c^* + k_{-2}c^*)\beta \quad (3\text{-}2)$$

$$\frac{d\gamma}{dt} = k'_2p\alpha + (k_{-4}a + k''_{-4}m)\delta - k_4c^*\gamma \quad (3\text{-}3)$$

$$\frac{d\delta}{dt} = k_3c^*\beta + k_{-5}c^*\varphi - (k_{-3}a + k''_{-3}m + k_5p + k'_5p)\delta \quad (3\text{-}4)$$

$$\frac{d\varepsilon}{dt} = k_4c^*\gamma + k_{-6}c^*\rho - (k_{-4}a + k''_{-4}m + k_6p + k'_6p)\varepsilon \quad (3\text{-}5)$$

$$\frac{d\varphi}{dt} = k_5p\delta - k_{-5}c^*\varphi \quad (3\text{-}6)$$

$$\frac{d\rho}{dt} = k'_5p\delta + k_6p\varepsilon - k_{-6}c^*\rho \quad (3\text{-}7)$$

$$-\frac{dp}{dt} = (k_2 + k'_2)p\alpha - k_{-2}c^*\beta + (k_5 + k'_5)p\delta + (k_6 + k'_6)p\varepsilon - k_{-5}c^*\varphi - k_{-6}c^*\rho \quad (3\text{-}8)$$

$$\frac{da}{dt} = k_1c^*m - k_{-1}a\alpha + k_3c^*\beta - k_{-3}a\delta + k_4c^*\gamma - k_{-4}a\varepsilon \quad (3\text{-}9)$$

$$\frac{dm}{dt} = -k_1a\alpha + k''_{-3}m\delta + k''_{-4}m\varepsilon + k_1mc^* \quad (3\text{-}10)$$

Second, we have two conditions:

Conditions (A):

(i) Stoichiometric relations:

$$-\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\mathrm{d}a}{\mathrm{d}t} = -2\frac{\mathrm{d}m}{\mathrm{d}t} \tag{4}$$

(ii) Stationary-state hypothesis:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\mathrm{d}\beta}{\mathrm{d}t}=\frac{\mathrm{d}\gamma}{\mathrm{d}t}=\frac{\mathrm{d}\delta}{\mathrm{d}t}=\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}=\frac{\mathrm{d}\varphi}{\mathrm{d}t}=\frac{\mathrm{d}\rho}{\mathrm{d}t}=0 \tag{5}$$

From these conditions, we can obtain the solution of each variable as follows:

$$\alpha = k_1k'_6Fmc^*/\varDelta_0 \tag{6-1}$$

$$\beta = k_1k_2k'_6m[k''_{-3}m + k_{-3}a + k'_5p]/\varDelta_0 \tag{6-2}$$

$$\gamma = k_1[k_2k_3k'_5D + k'_2(D+k'_6)F]mp/k_4\varDelta_0 \tag{6-3}$$

$$\delta = k_1k_2k_3k'_6mc^*/\varDelta_0 \tag{6-4}$$

$$\varepsilon = k_1(k_2k_3k'_5+k'_2F)mc^*/\varDelta_0 \tag{6-5}$$

$$\rho = k_1k_2k_3k_5k'_6mp/k_{-5}\varDelta_0 \tag{6-6}$$

$$\varphi = k_1\{k_2k_3k'_5(k_6+k'_6) + k'_2k_6F\}mp/k_{-6}\varDelta_0 \tag{6-7}$$

where:

$$\left\{\begin{aligned} \varDelta_0 &= k_{-1}k'_6Fa + \{k_2k_3k''_{-3}k'_6-k''_{-4}(k_2k_3k'_5 \\ &\quad +k'_2F)\}m+(k_2k_3k'_5+k'_2F)k'_6p && (6'\text{-}1)\\ F &= k_3k'_5 + k_{-2}k'_5 + k_{-2}(k_{-3}a/p + k''_{-}m/p) && (6'\text{-}2)\\ D &= k_{-4}a/o + k''_{-4}m/p && (6'\text{-}3)\end{aligned}\right.$$

Lastly, the general equation for the rate of the production of methyl alcohol is obtained as follows:

$$\begin{aligned}\frac{\mathrm{d}a}{\mathrm{d}t} &= 2[k_2k_3k'_5 + k'_2F]k_1k'_6mpc^*[k_{-1}k'_6Fa \\ &\quad + (k''_{-3}k_2k_3k'_6 - k_2k_3k''_{-4}k'_5 - k'_2k''_{-4}F)m \\ &\quad + (k_2k_3k'_5 + k'_2F)k_6'p]^{-1}\end{aligned} \tag{7}$$

When further plausible assumptions are added to Eq. 7, a simple form of the kinetic equation is deduced.

Assumptions (B):

$$\begin{aligned} &k''_{-3} \gg k_{-3}\\ &k''_{-3} \gg k'_5\\ &k_{-2}k''_{-3} \gg k_3k'_5\\ &k_2k_3k'_5 \gg k_2'k_{-2}k''_{-3} \quad (\text{or } k_2 \rangle\rangle\rangle\, k_2')\\ &k_{-1}k_{-2} \gg k_2k_3\\ &k_{-1}k_{-2}k''_{-3}k'_6 \gg k_2k_3k''_{-4}k'_5\\ &\qquad (\text{or } k''_{-3}k'_6 \geq k''_{-4}k'_5)\end{aligned} \tag{8'}$$

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{2k_1k_2k_3k'_5}{k_{-1}k_{-2}k''_{-3}}\,\frac{p^2c^*}{a} \tag{8}$$

On the other hand, we assume that the effective concentration of the catalyst, c^*, can be estimated from the consideration of the equilibrium of the reaction forming the complex with methyl alcohol:

$$\begin{aligned}&[\mathrm{BF_3\cdot solvent}] + 2\mathrm{CH_3OH} \overset{K}{\rightleftarrows} \\ &\qquad [\mathrm{BF_3\cdot 2CH_3OH}] + \mathrm{solvent}\end{aligned} \tag{9}$$

where the equilibrium constant, K, is very large,

$$[\mathrm{BF_3\cdot solvent}] = \frac{[\mathrm{BF_3\cdot 2CH_3OH}][\mathrm{solvent}]}{K[\mathrm{CH_3OH}]^2} \tag{10}$$

$$\therefore \quad c^* = \frac{k_0\cdot c}{a^2} \tag{11}$$

From Eqs. 8 and 11, the kinetic equation 12 is deduced.

The calculated equation:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{2k_0k_1k_2k_3k'_5}{k_{-1}k_{-2}k''_{-3}}\,\frac{m^0p^2c^1}{a^3} \tag{12}$$

The experimental equation:

$$\frac{\mathrm{d[methyl\ alcohol]}}{\mathrm{d}t} = \frac{k[\mathrm{methylal}]^0[\mathrm{phenol}]^2[\mathrm{catalyst}]^1}{[\mathrm{methyl\ alcohol}]^3} \tag{12'}$$

Thus, the kinetic equation obtained by calculations based on the reaction scheme of Fig. 1 is in good agreement with the kinetic equation obtained experimentally. This fact indicates that the reaction scheme of Fig. 1 represents the reactions actually taking place. Therefore, our attempt to elucidate the mechanism of the reaction may be regarded as satisfactory.

The Probable Reaction Paths.—The probable paths of the reaction between phenol and methylal in non-aqueous media are shown in Fig. 2. In Fig. 2, the assumptions used for the deduction of Eq. 8 from Eq. 7 are presented in relation to the behavior of intermediates.[3)]

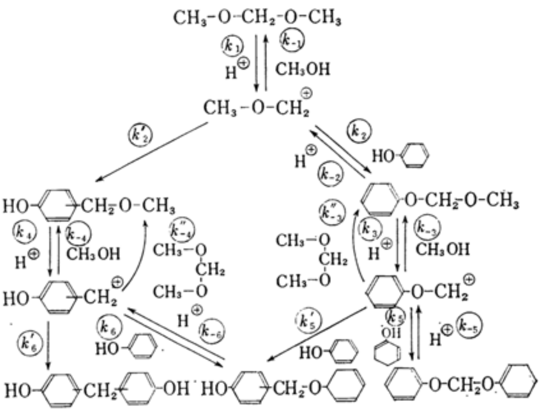

Fig. 2. Reaction scheme.

The assumption, that $k_2 \gg k'_2$ means that the reaction passes mainly through methyl phenyl formal instead of methoxymethylphenol, that is, that the methoxymethyl cation reacts more easily with the phenolic OH group than with the aromatic nuclei of phenol. The assumption that $k''_{-3} \gg k_{-3}$ or that $k_3{}''_{-} \gg k'_5$ means that the phenoxymethyl cation reacts more easily with methylal than with methyl alcohol or phenol

The assumptions that $k_{-1}/k_2 \gg k_3/k_{-2}$, that $k''_{-3}/k'_5 \geq k''_{-4}/k'_6$ and that $k''_{-3}/k'_5 \gg k_3/k_{-2}$ are connected with the reactivities of the methoxymethyl cation, the phenoxymethyl cation, the oxybenzyl cation and methyl phenyl formal.

The assumptions used in the calculation are plausible and are not contradictory to the actual behavior of the reactants and the intermediates.[3]

The probable reaction path from methylal to dioxydiphenylmethane in this system is estimated to be as follows:

The Activation of Methylal.—In the first step of the reaction, methylal is activated by the proton to produce methyl alcohol and the methoxymethyl cation in a reversible manner.

The proton is produced by the reaction of the $BF_3 \cdot$ solvent with a trace of water in the reaction system; therefore, the affinities of BF_3 toward the solvent, the reactants, and the products have a remarkable effect on the activity of the catalyst. Particularly, the activity of the catalyst depends upon the concentration of methyl alcohol because of the formation of stable complexes from the catalyst and methyl alcohol.

The Reaction of the Methoxymethyl Cation with Phenol.—The methoxymethyl cation readily attacks the oxygen atom of phenol, instead of the benzene ring, to produce methyl phenyl formal in a reversible manner. Consequently, the main path passes through methyl phenyl formal, instead of methoxymethylphenols. The reaction of the methoxymethyl cation with phenol is considerably inhibited by the competing reactions with methyl alcohol.

The Activation of Methyl Phenyl Formal by Proton.—The acidic decomposition of methyl phenyl formal yields the methoxymethyl cation and the phenoxymethyl cation in a reversible manner.

The Reaction of the Phenoxymethyl Cation with Phenol.—Phenoxymethylphenols are produced slowly in the irreversible reaction of phenoxymethyl cations with the nuclei of phenol; this reaction may be the rate-determining step of this reaction system.

At the same time, the phenoxymethyl cation easily attacks the oxygen atom of methylal to reproduce the methoxymethyl cation and methyl phenyl formal; accordingly, methylal inhibits the reaction rate in this reaction step. Though it was expected that the phenoxymethyl cation would rapidly attack the oxygen atom of phenol, not even a trace of diphenyl formal was detected in the reaction system.

Phenoxymethylphenols change in the presence of proton to dioxydiphenylmethane, passing through the oxybenzyl cation in a similar manner; at the same time, methoxymethylphenols are formed as by-products.

The Reaction Rate at Higher Conversions.——As has been mentioned above, the reaction mechanism can be explained when the conversion is low (up to 30%). If the B asumptions and Eq. 8′ are changed slightly, then the calculated equation, Eq. 8, is modified as follows:

Modified assumptions C:

$$\begin{aligned} &k''_{-3} \gg k_{-3} \\ &k''_{3-} \gg k_6' \\ &k_{-2}k''_{-3} \gg k_3k'_5 \\ &k_2k_3k'_5 \gg k'_2k_{-2}k''_{-3} \quad (\text{or } k_2 \rangle\rangle\rangle\, k'_2) \qquad (13') \\ &k''_{-3}k'_6 \gg k''_{-4}k'_5 \\ &k_{-1}k_{-2} \geq k_2k_3 \end{aligned}$$

Modified calculated equation:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{2k_1k_2k_3k'_5 \cdot pc}{(k_{-1}k_{-2}k''_{-3} \cdot a/p + k_2k_3k''_{-3})a^2} \qquad (13)$$

Experimental equation at higher conversions[2]:

$$-\frac{\mathrm{d}[\text{methyl alcohol}]}{\mathrm{d}t} = \frac{k[\text{phenol}]^1[\text{methylal}]^0[\text{catalyst}]^1}{[\text{methyl alcohol}]^{2.5}} \qquad (14)$$

The calculated equation, Eq. 13, may be almost equal to the experimental equation, Eq. 14. Equations 13 and 14 are applicable only for the systems of a high conversion.

It seems probable that there are few differences between Eqs. 12 and 13 with respect to the mathematical characterization of the kinetic system, while the stoichiometric relations, Eq. 4, and the stationary state hypothesis, Eq. 5, may not be used so exactly in systems of a higher conversion.

Summary

By the mathematical calculation of the reaction system, a kinetic equation has been deduced, and it has been found to represent satisfactorily the experimental findings of the phenol-formaldehyde reaction in non-aqueous media.

The reaction mechanism has then been elucidated from both the experimental and the mathematical points of view.

The most important difference between the aqueous and non-aqueous media is the contribution of formals as reactive intermediates.

Moreover, several interesting information regarding the effects of the solvent or the catalyst on the reaction mechanism have been obtained.

The author is indebted to Professor Hiromu Murata of the Faculty of Science of Hiroshima University for his helpful discussions and encouragement throughout the work. He also wishes to express his gratitude to Dr. Keiji Oshima, Managing Director of the Sumitomo Bakelite Co., Ltd., and Director of the Central Research Laboratory of the same company, for permission to publish this paper, and to Dr. Ryuzo Nakatsuka and Mr. Mitsuo Niwa of this Laboratory for their valuable assistance.