ORIGINAL ARTICLE

Mitsuo Higuchi · Sho-ichi Nohno · Shin-ichiro Tohmura

Kinetics of the hydroxymethylation of phenol I: Rate equation and method of analysis*

Abstract Seven reactions take place consecutively and competitively during the hydroxymethylation of phenol in aqueous alkaline media. This hydroxymethylation is the first step in the formation of phenolic resins and has long been studied. However, the rate equation, which can describe the seven reactions in those reaction systems where the alkali/phenol molar ratios are <1.0, has not yet been obtained. The authors present a rate equation (in a differential form) for a computer simulation. This equation involves the concentration of hydroxide ion, [OH⁻], which changes with the change in the composition of the reaction system and cannot be expressed as a function of reaction time. However, the value of [OH⁻] can be obtained by numerical calculation. In the computer simulation the reactions occur for an infinitesimal unit of time, and the changes in the concentrations of formaldehyde, phenols, and hydroxide ion are calculated. The next step of the reaction takes place according to the reaction conditions that result from the previous step. In this manner the reactions progress step by step in a computer. Using this method we can describe the reaction time course, (i.e., the changes in the concentrations of phenol, formaldehyde, and five species of hydroxymethylphenols with the reaction time).

Key words Chemical kinetics · Hydroxymethylation of phenol · Computer simulation

M. Higuchi (✉) · S. Nohno
Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan
Tel. +81-92-642-2996; Fax +81-92-642-3078
e-mail: mhiguchi@agr.kyushu-u.ac.jp

S. Tohmura
Forestry and Forest Products Research Institute, Tsukuba Norin Kenkyu Danchi, Ibaraki 305-8687, Japan

Introduction

Alkaline phenolic adhesives usually used in the wood industry are formed by the reaction of phenol with formaldehyde with sodium hydroxide as a catalyst. The hydroxymethylation of phenol is the first reaction step of resin formation. In this hydroxymethylation process, as Fig. 1 shows, five species of hydroxymethylphenols (2-hydroxymethylphenol; 4-hydroxymethylphenol; 2,4-dihydroxymethylphenol; 2,6-dihydroxymethylphenol; 2,4,6-trihydroxymethylphenol) form by seven reactions that occur consecutively and competitively. The kinetics of this hydroxymethylation has attracted the attention of many researchers. Knop and Pilato overviewed the papers on this subject published before 1984.[1] There are considerable discrepancies among the kinetic data obtained, as seen in Table 1.

We are studying the impregnation of wood with phenolic resin and seeking a reasonable synthetic procedure for an ideal resin. The resin we have in mind is a mixture of hydroxymethylphenol monomers free from phenol and formaldehyde. The design of a reasonable synthetic procedure requires an analytical method that can describe the reaction time course. Thus we investigated the rate equation for a computer simulation.

Theory and results

Hydroxymethylation in reaction systems with alkali/phenol molar ratios <1.0

In reaction systems with the alkali/phenol molar ratios <1.0, the degrees of dissociation of phenolic compounds change as the reaction progresses because there are differences in the acid strength among the phenolic compounds.[5] These changes complicate the kinetic analysis. Researchers in the past conducted their experiments with a sodium hydroxide/phenol (NaOH/P) molar ratio of 1.0 to avoid the problem; those who carried out their experiments with

Table 1. Relative values of the rate constants of the seven reactions hitherto reported

Reaction	Relative values of rate constants			
	Freeman & Lewis[2] (30°C)	Minami & Ando[3] (40°C)	Zsavitsas & Beaulieu[4] (30°C)	Eapen & Yeddanapalli[5] (30°C)
P + F →2-HMP	1.00	1.00	1.00	1.00
P + F →4-HMP	1.18	2.08	1.09	1.46
2-HMP + F →2,6-DHMP	1.66	1.08	1.98	1.70
2-HMP + F →2,4-DHMP	1.39	2.58	1.80	3.80
4-HMP + F →2,4-DHMP	0.71	0.83	0.79	1.02
2,6-DHMP + F →THMP	7.94	3.25	3.33	4.54
2,4-DHMP + F →THMP	1.73	1.25	1.67	1.76
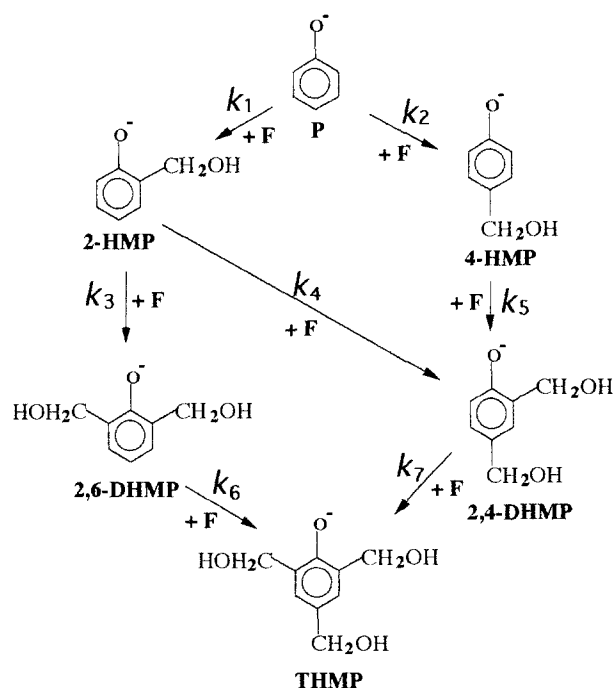
Fig. 1. Seven reactions that occur consecutively and competitively for hydroxymethylation of phenol in aqueous alkaline medium

NaOH/P molar ratios <1.0 neglected the problem. Thus a rate equation that takes the changes in the degrees of dissociation of phenols into consideration has not been established until now.

The hydroxymethylation of phenol is considered to go through an S_N2 mechanism where a quinoidal anion attacks the carbon of formaldehyde; it has been confirmed that the reaction is of second order (i.e., first order with respect to each of the concentrations of formaldehyde and ionized phenolic body) in the reactions of 2,4-dihydroxymethylphenol and 2,6-dihydroxymethylphenol.[2,3] Moreover, the second-order rate plots for the hydroxymethylation of 2,4-dihydroxymethylphenol and 2,6-dihydroxymethyl-phenol obtained by Freeman and Lewis[2] gave straight lines throughout the reaction courses where the maxima of the

degrees of reaction exceeded 0.75, indicating that the reverse (dehydroxymethylation) reactions can be neglected. Therefore, in cases where the Cannizaro reaction can be neglected, the rate of formaldehyde consumption can be expressed by the following equation:

$$-d[F]/dt = (2k_1 + k_2)[F][P^-] + (k_3 + k_4)[F][2\text{-}HMP^-]$$
$$+ 2k_5[F][4\text{-}HMP^-] + k_6[F][2,6\text{-}DHMP^-]$$
$$+ k_7[F][2,4\text{-}DHMP^-] \qquad (1)$$

where [F], [P⁻], [2-HMP⁻], [4-HMP⁻], [2,6-DHMP⁻], and [2,4-DHMP⁻] represent the concentrations of formaldehyde, dissociated phenol, dissociated 2-hydroxymethylphenol, dissociated 4-hydroxymethylphenol, dissociated 2,6-dihydroxymethylphenol, and dissociated 2,4-di hydroxymethylphenol, respectively; and $k_1 \ldots k_7$ denote the rate constants of the corresponding reactions.

We do not have any analytical means to determine the concentrations of dissociated phenols in the reaction system. We can determine only the sums of the amounts of dissociated and undissociated phenols. Hence we need to express the concentrations of dissociated phenols in terms of the sums of the concentrations of dissociated and undissociated phenols. The following equilibria hold in aqueous media.

$$[H^+][P^-] = K_{a1}[PH] \qquad (2)$$

$$[H^+][2\text{-}HMP^-] = K_{a2}[2\text{-}HMPH] \qquad (3)$$

$$[H^+][4\text{-}HMP^-] = K_{a3}[4\text{-}HMPH] \qquad (4)$$

$$[H^+][2,6\text{-}DHMP^-] = K_{a4}[2,6\text{-}DHMPH] \qquad (5)$$

$$[H^+][2,4\text{-}DHMP^-] = K_{a5}[2,4\text{-}DHMPH] \qquad (6)$$

$$[H^+][THMP^-] = K_{a6}[THMPH] \qquad (7)$$

where [PH] ... [THMPH] represent the concentrations of corresponding undissociated phenols, and $K_{a1} ... K_{a6}$ are the dissociation constants. When the sum of the concentrations of dissociated and undissociated phenol is expressed as $[P^-] + [PH] = [P]$ and the concentration of hydrogen ion as $[H^+] = K_w/[OH^-]$, Eq. (2) can be converted to the following form:

$$[P^-] = (K_{a1}[OH^-]/K_w)/(1 + K_{a1}[OH^-]/K_w)[P] \qquad (8)$$

where [OH$^-$] and K_w represent the concentration of hydroxide ion and the ion product of water, respectively. The same can be adapted to the other phenols. Thus we obtain the following equation instead of Eq. (1):

$$-d[F]/dt = (2k_1 + k_2)[F](K_{a1}[OH^-]/K_w)/$$
$$(1 + K_{a1}[OH^-]/K_w)[P]$$
$$+ (k_3 + k_4)[F](K_{a2}[OH^-]/K_w)/$$
$$(1 + K_{a2}[OH^-]/K_w)[2 - HMP]$$
$$+ 2k_5[F](K_{a3}[OH^-]/K_w)/$$
$$(1 + K_{a3}[OH^-]/K_w)[4 - HMP]$$
$$+ k_6[F](K_{a4}[OH^-]/K_w)/$$
$$(1 + K_{a4}[OH^-]/K_w)[2,6 - DHMP]$$
$$+ k_7[F](K_{a5}[OH^-]/K_w)/$$
$$(1 + K_{a5}[OH^-]/K_w)[2,4 - DHMP] \qquad (9)$$

where [2-HMP] ... [2,4-DHMP] denote the sums of the concentrations of corresponding dissociated and undissociated phenols. This equation involves the concentration of hydroxide ion, which decreases as the reaction proceeds because of the increase of polyhydroxymethyl phenols of stronger acidity. [OH$^-$] cannot be expressed as a function of time, but we can obtain the values for [OH$^-$] by numerical calculations. In the reaction systems the following equation holds at any time:

$$[OH^-] + [P^-] + [2-HMP^-] + [4-HMP^-]$$
$$+ [2,6-DHMP^-] + [2,4-DHMP^-] + [THMP^-]$$
$$= [H^+] + [Na^+] \qquad (10)$$

Here [H$^+$] is small and can be neglected. By expressing the concentrations of dissociated phenols in the forms represented by Eq. (8), we obtain the following equation:

$$[OH^-] + (K_{a1}[OH^-]/K_w)/(1 + K_{a1}[OH^-]/K_w)[P]$$
$$+ (K_{a2}[OH^-]/K_w)/(1 + K_{a2}[OH^-]/K_w)[2 - HMP]$$
$$+ (K_{a3}[OH^-]/K_w)/(1 + K_{a3}[OH^-]/K_w)[4 - HMP]$$
$$+ (K_{a4}[OH^-]/K_w)/(1 + K_{a4}[OH^-]/K_w)$$
$$[2,6 - DHMP] + (K_{a5}[OH^-]/K_w)/$$
$$(1 + K_{a5}[OH^-]/K_w)[2,4 - DHMP]$$
$$+ (K_{a6}[OH^-]/K_w)/(1 + K_{a6}[OH^-]/K_w)[THMP]$$
$$= [Na^+] \qquad (11)$$

This equation cannot be solved arithmetically, but it can be solved easily by a trial-and-error method using a computer. Incidentally, the value of [Na$^+$] is calculated from the amount of sodium hydroxide added to the reaction system.

Thus we have obtained the basis for a computer simulation of hydroxymethylation.

Computer simulation

In a computer the reactions proceed step by step according to the reaction conditions given. At first the initial concentrations of phenols, formaldehyde, and sodium hydroxide, the rate constants of the seven reactions, the dissociation constants of phenols, and the ion product of water are given. The computer calculates the initial concentration of hydroxide ion according to Eq. (11). The first step of reaction then takes place for an infinitesimal unit of time according to Eq. (9). The computer calculates the changes in the concentrations of formaldehyde, phenols, and hydroxide ion. The next step of reaction takes place for an infinitesimal unit of time in accordance with the reaction conditions resulted from the former step of the reaction.

The concentrations of formaldehyde and phenols existing after the nth step of reaction are expressed by the following equations:

$$[F]_n = [F]_{n-1} - (2k_1 + k_2)[F]_{n-1} (K_{a1}[OH^-]_{n-1}/K_w)/$$
$$(1 + K_{a1}[OH^-]_{n-1}/K_w)[P]_{n-1}$$
$$- (k_3 + k_4)[F]_{n-1} (K_{a2}[OH^-]_{n-1}/K_w)/$$
$$(1 + K_{a2}[OH^-]_{n-1}/K_w)[2 - HMP]_{n-1}$$
$$- 2k_5[F]_{n-1} (K_{a3}[OH^-]_{n-1}/K_w)/$$
$$(1 + K_{a3}[OH^-]_{n-1}/K_w)[4 - HMP]_{n-1}$$
$$- k_6[F]_{n-1} (K_{a4}[OH^-]_{n-1}/K_w)/$$
$$(1 + K_{a4}[OH^-]_{n-1}/K_w)[2,6 - DHMP]_{n-1}$$
$$- k_7[F]_{n-1} (K_{a5}[OH^-]_{n-1}/K_w)/$$
$$(1 + K_{a5}[OH^-]_{n-1}/K_w)[2,4 - DHMP]_{n-1} \qquad (12)$$

$$[P]_n = [P]_{n-1} - (2k_1 + k_2)[F]_{n-1} \left(K_{a1}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a1}[OH^-]_{n-1}/K_w\right)[P]_{n-1} \tag{13}$$

$$[2\text{-}HMP]_n = [2\text{-}HMP]_{n-1} + 2k_1[F]_{n-1}$$
$$\left(K_{a1}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a1}[OH^-]_{n-1}/K_w\right)[P]_{n-1}$$
$$- (k_3 + k_4)[F]_{n-1} \left(K_{a2}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a2}[OH^-]_{n-1}/K_w\right)[2\text{-}HMP]_{n-1} \tag{14}$$

$$[4\text{-}HMP]_n = [4\text{-}HMP]_{n-1} + k_2[F]_{n-1}$$
$$\left(K_{a1}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a1}[OH^-]_{n-1}/K_w\right)[P]_{n-1}$$
$$- 2k_5[F]_{n-1} \left(K_{a3}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a3}[OH^-]_{n-1}/K_w\right)[4\text{-}HMP]_{n-1} \tag{15}$$

$$[2,6\text{-}DHMP]_n = [2,6\text{-}DHMP]_{n-1} + k_3[F]_{n-1}$$
$$\left(K_{a2}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a2}[OH^-]_{n-1}/K_w\right)[2\text{-}HMP]_{n-1}$$
$$- k_6[F]_{n-1} \left(K_{a4}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a4}[OH^-]_{n-1}/K_w\right)$$
$$[2,6\text{-}DHMP]_{n-1} \tag{16}$$

$$[2,4\text{-}DHMP]_n = [2,4\text{-}DHMP]_{n-1} + k_4[F]_{n-1}$$
$$\left(K_{a2}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a2}[OH^-]_{n-1}/K_w\right)[2\text{-}HMP]_{n-1}$$
$$+ 2k_5[F]_{n-1} \left(K_{a3}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a3}[OH^-]_{n-1}/K_w\right)[4\text{-}HMP]_{n-1}$$
$$- k_7[F]_{n-1} \left(K_{a5}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a5}[OH^-]_{n-1}/K_w\right)$$
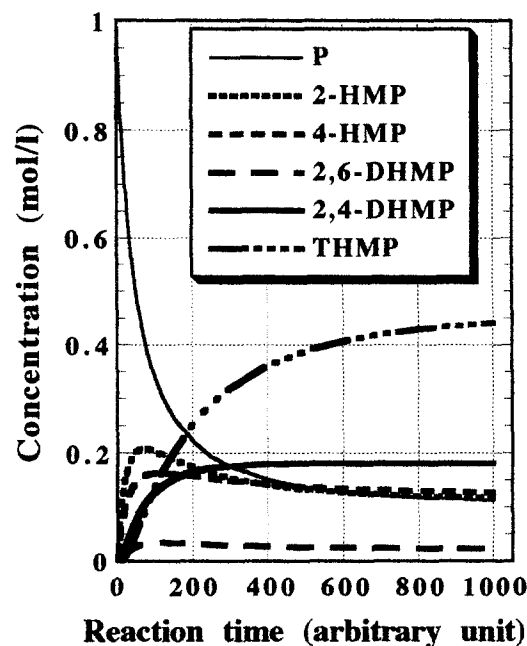$$[2,4\text{-}DHMP]_{n-1} \tag{17}$$

Fig. 2. Reaction time course drawn with the use of the kinetic data reported by Freeman and Lewis.[2] Reaction conditions: $[P]_0 = 1.0$; $[F]_0 = 2.0$; NaOH/P molar ratio 0.3

$$[THMP]_n = [THMP]_{n-1} + k_6[F]_{n-1}$$
$$\left(K_{a4}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a4}[OH^-]_{n-1}/K_w\right)[2,6\text{-}DHMP]_{n-1}$$
$$+ k_7[F]_{n-1} \left(K_{a5}[OH^-]_{n-1}/K_w\right)/$$
$$\left(1 + K_{a5}[OH^-]_{n-1}/K_w\right)[2,4\text{-}DHMP]_{n-1} \tag{18}$$

The computer calculates the concentrations of formaldehyde and phenols according to Eqs. (12)–(18) step by step and memorizes the values obtained.

Reaction time courses obtained with the kinetic data reported

Figures 2, 3, 4, and 5 show the reaction time courses obtained using our method with the kinetic data reported by Freeman and Lewis,[2] Minami and Ando,[3] Zsavitsas and Beaulieu,[4] and Eapen and Yeddanapalli[5] respectively. As there are considerable differences in the absolute values of the rate constants reported by the four groups of researchers, relative values of the seven rate constants were used, k_1 being put at 0.001 (liters mol^{-1} unit $time^{-1}$) in each case. It was assumed that the temperature dependence of the dissociation constants of the phenols is the same as that of the ion product of water; that is, the $K_{a1} K_{a2} K_{a3} K_{a4} K_{a5} K_{a6} K_w$ ratio does not change with temperature. If this assumption holds,
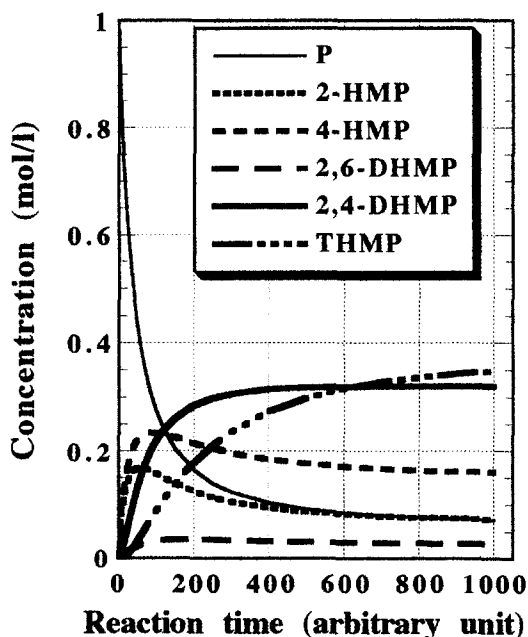
Fig. 3. Reaction time course drawn with the use of the kinetic data reported by Minami and Ando.[3] The reaction conditions are the same as those in Fig. 2
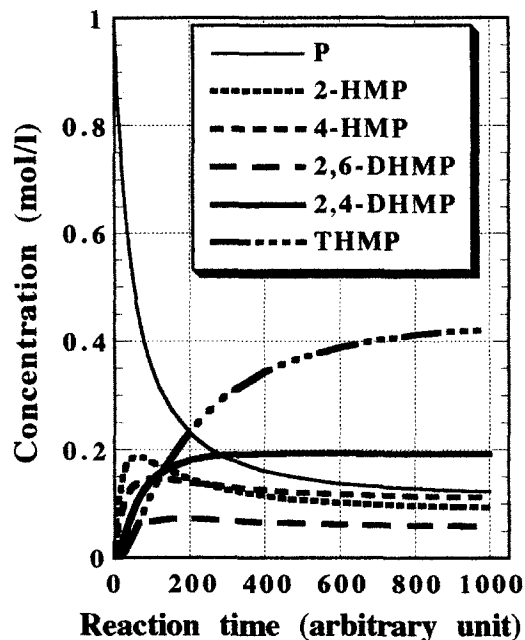

Fig. 4. Reaction time course drawn with the use of the kinetic data reported by Zsavitsas and Beaulieu.[4] The reaction conditions are the same as those in Fig. 2

we can use the known values of dissociation constants of phenols and the ion product of water at 25°C. The values used are as follows:[6]

$$K_{a1} = 1.0 \times 10^{-10}$$

$$K_{a2} = 1.445 \times 10^{-10}$$

$$K_{a3} = 1.862 \times 10^{-10}$$

$$K_{a4} = 1.995 \times 10^{-10}$$

$$K_{a5} = 2.042 \times 10^{-10}$$

$$K_{a6} = 3.548 \times 10^{-10}$$

$$K_{w} = 1.0 \times 10^{-14}$$

The initial concentrations of formaldehyde and phenol given are 2.0 and 1.0 mol/l, respectively; and the NaOH/P molar ratio is 0.3.

We can see a considerable difference among the four reaction time courses.

Figure 6 shows the changes in concentration of hydroxide ion in the reaction system. The differences in the change of the concentration of hydroxide ion are not as large as the differences in the compositions of the reaction system.

Figure 7 shows the compositions of the reaction system at the point where 99.9% of formaldehyde has been consumed. This figure clearly shows the large differences in the results of the reaction caused by the differences among the kinetic data.
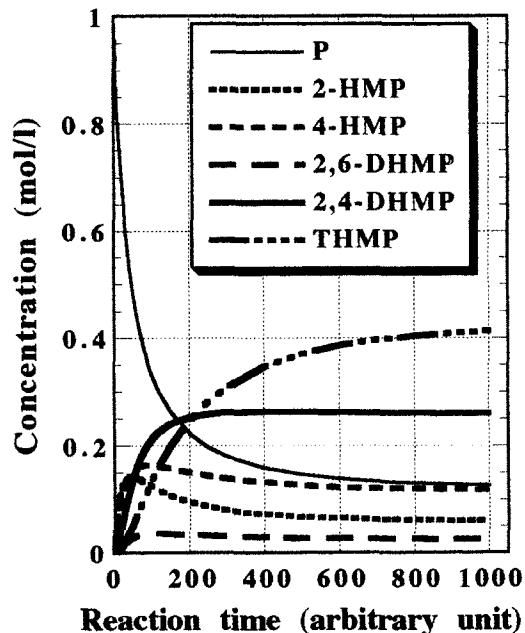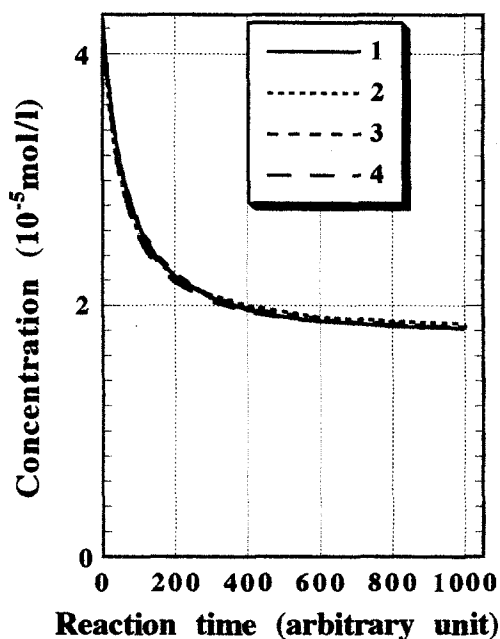

Fig. 5. Reaction time course drawn with the use of the kinetic data reported by Eapen and Yeddanapalli.[5] The reaction conditions are the same as those in Fig. 2

Discussion

As Figs. 2–7 show, there are significant differences in the results of the reaction calculated with the use of the kinetic data obtained by the four groups of researchers. Moreover, it cannot be determined which of the four data sets is cor-
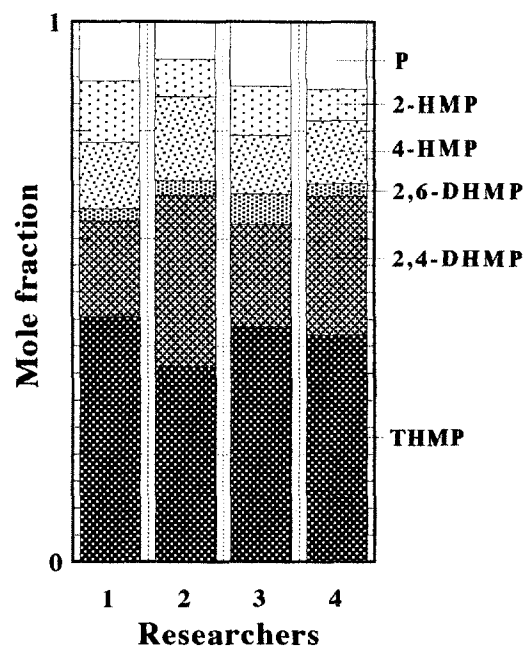
Fig. 6. Changes of the concentration of hydroxide ion in the reaction system drawn with the use of the kinetic data reported. 1, Freeman and Lewis[2]; 2, Minami and Ando[3]; 3, Zsavitsas and Beaulieu[4]; 4, Eapen and Yeddanapalli.[5] The reaction conditions are the same as those in Fig. 2

Fig. 7. Final compositions of the reaction system calculated with the use of the kinetic data reported. 1, Freeman and Lewis[2]; 2, Minami and Ando[3]; 3, Zsavitsas and Beaulieu[4]; 4, Eapen and Yeddanapalli.[5] The reaction conditions are the same as those in Fig. 2

rect. Therefore more experiments are needed to obtain accurate kinetic parameters.

Conclusion

As described above we have obtained a rate equation for the hydroxymethylation of phenol in reaction systems where the alkali/phenol molar ratios are <1.0. This equation involves the concentration of hydroxide ion, which changes with the progress of the reaction but cannot be expressed as a function of reaction time. However, the concentration of hydroxide ion can be obtained by numerical calculations. In the computer simulation the first step of the reaction occurs for an infinitesimal unit of time according to the rate equation under the reaction conditions given. The changes in the concentrations of formaldehyde, phenols, and hydroxide ion are then calculated. The second step of the reaction then takes place according to the reaction conditions resulted from the previous step. In this manner the reactions proceed step by step in a computer. Using this method we can describe the reaction time course. The examples of the reaction time course drawn with the use of the kinetic data reported by Freeman and Lewis, Minami

and Ando, Zsavitsas and Beaulieu, and Eapen and Yeddanapalli differ from each other, indicating that more experiments are needed to obtain accurate rate parameters.

References

1. Knop A, Pilato LA (eds) (1985) Phenolic resins: chemistry, applications and performance. Future directions. Springer, Berliin, pp 36–40
2. Freeman JH, Lewis CW (1954) Alkaline-catalyzed Reaction of Formaldehyde and the Methylols of Phenol; A Kinetic Study J Am Chem Soc 76:2080–2087
3. Minami T, Ando T (1956) J Chem Soc Jpn Indus Chem 59:668–672
4. Zsavitsas AA, Beaulieu RD (1985) Phenol-Formaldehyde Reaction under Alkaline Conditions. In: Knop A, Pilato LA (eds) Phenolic resins: chemistry, applications and performance. Future directions. Springer, Berlin, p 37
5. Eapen KC, Yeddanapalli LM (1968) Kinetics and Mechanism of the Alkali-Catalyzed Addition of Formaldehyde to Phenol and Substituted Phenols. Makromol Chem 119:4–16
6. Knop A, Pilato LA (eds) (1985) Phenolic resins: chemistry, applications and performance. Future directions. Springer-Verlag, Berlin, p 26