J Wood Sci (1999) 45:306–312

ORIGINAL ARTICLE

Mitsuo Higuchi · Shoichi Nohno · Mitsuhiro Morita
Shin-ichiro Tohmura

Kinetics of the hydroxymethylation of phenol II: values of rate parameters and results of simulation experiments

Received: October 13, 1998 / Accepted: November 30, 1998

Abstract The reaction course of the sodium hydroxide-catalyzed hydroxymethylation of phenol was analyzed by use of high-performance liquid chromatography (HPLC), and the rate constants for the seven reactions taking place consecutively and competitively were evaluated by means of a computer simulation technique. Calibration was done at the quantification of the six phenolic monomers from the peak areas in the HPLC chromatogram, taking the differences in molar ultraviolet absorption intensities of the six compounds into account. The values of the energies of activation for the seven reactions obtained differed greatly from those reported by Eapen and Yeddanapalli. Simulation experiments carried out by use of the newly obtained rate parameters showed that the amounts of phenol left unreacted and 2,4,6-trihydroxymethylphenol in the final reaction product increased as the reaction temperature was increased and the alkali/phenol molar ratio decreased. These phenomena can be attributed to the differences in the energies of activation for the seven reactions and differences in the acid strengths of the six phenolic monomers.

Key words Hydroxymethylation of phenol · Rate constants · Energies of activation · Computer simulation

M. Higuchi (✉) · S. Nohno · M. Morita
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 305-8691, Japan

Part of this paper was presented at the 48th annual meeting of the Japan Wood Research Society, Shizuoka, April 1998 and at the 1998 annual meeting of the Forest Products Society, Merida, Mexico, June 1998

Introduction

Hydroxymethylation is the first step in the formation of phenol-formaldehyde resins. In aqueous alkaline media, six hydroxymethylphenols are formed by seven reactions that occur consecutively and competitively, as shown in Fig. 1. As the rate parameters of the seven reactions together with the acid strengths of the phenolic compounds differ from each other, the molecular composition of the reaction product varies with reaction temperature and the alkali/phenol molar ratio even if the reaction is carried out with a fixed formaldehyde/phenol (F/P) molar ratio. However, there is little information on the relations between the molecular compositions of reaction products and the reaction conditions. In a previous paper[1] we proposed a computer simulation technique that can describe the reaction time course of hydroxymethylation under any given reaction conditions. However, there are considerable differences among the kinetic data hitherto reported[2] on the sodium hydroxide-catalyzed hydroxymethylation of phenol, and the computer simulation using those kinetic data gave significantly different results.[1] Moreover, there is no reliable report on the energies of activation for the seven reactions. Thus, we carried out hydroxymethylation experiments to obtain accurate values for the kinetic parameters and undertook simulation experiments using the computer simulation technique with the newly obtained kinetic parameters.

Experiments

Hydroxymethylation of phenol

The reactions were carried out under the following conditions: F/P molar ratio 3.0; sodium hydroxide/phenol (NaOH/P) molar ratios 0.3, 0.5, 0.75, 1.0; temperatures: 20°, 30°, 40°C; initial concentration of phenol ($[P]_0$) 1.0 mol/l. All reagents used were of analytical grade.

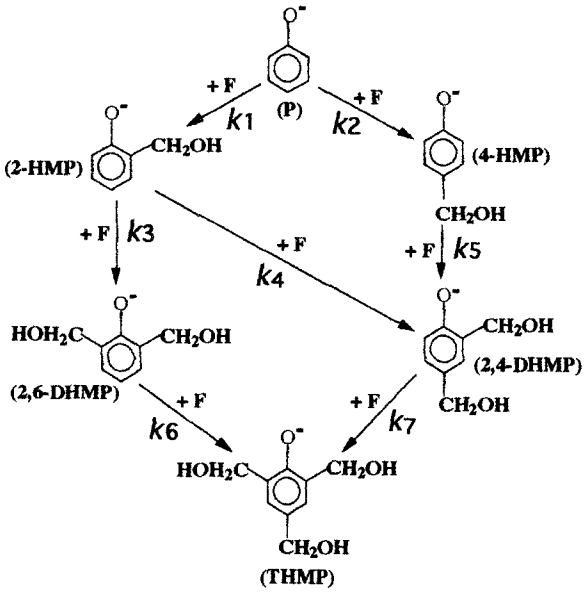

Fig. 1. Hydroxymethylation of phenol in an aqueous alkaline medium

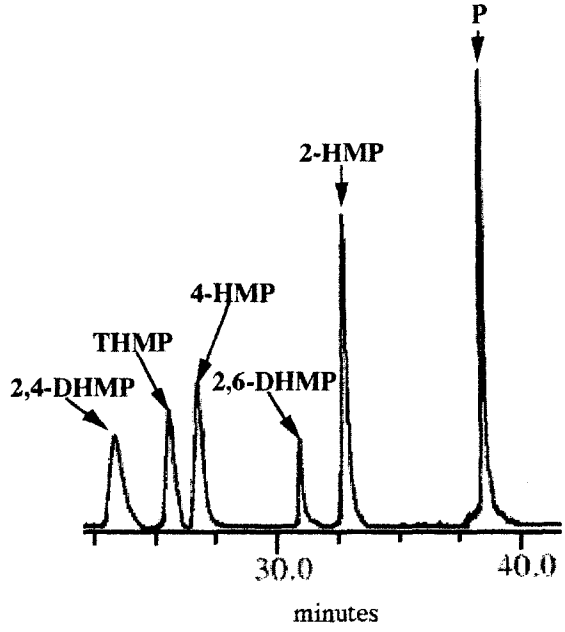

Fig. 2. Example of the high-performance liquid chromatography (HPLC) chromatogram. *HMP*, hydroxymethylphenol; *DHMP*, *THMP*, di- and trihydroxymethylphenol, respectively

Table 1. Gradient solvent ratios in the HPLC analysis

Time (min)	Solvent ratio (volume ratio)	
	Acetonitrile	Water
0	5	95
10	10	90
15	20	80
20	30	70
25	70	30
30+	100	0

HPLC, high-performance liquid chromatography

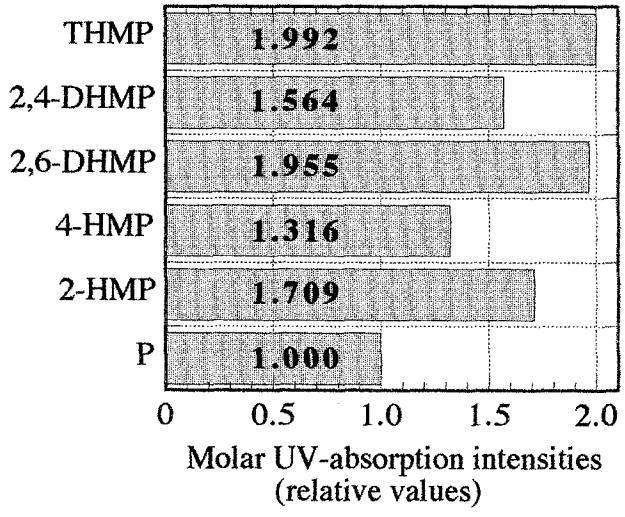

Fig. 3. Ultraviolet (UV)-absorption intensities of the six phenolic compounds in the HPLC system

Analysis of reaction systems

Aliquots of the reaction system were removed at the appropriate intervals, transferred to a volumetric flask containing acetic acid equivalent to the amount of NaOH in the reaction system sampled, and diluted 100 times with a water (95 vol%)–acetonitrile (5 vol%) mixture. The samples were analyzed using high-performance liquid chromatography (HPLC) under the following conditions: HPLC system: Waters (600 Controler-717); column: ODS-3 (GL Science); column temperature 25°C; mobile phase solvent: water (decreasing from 95 to 0 vol%)–acetonitrile (5–100 vol%) gradient system; flow rate 1 ml/min; detector: ultraviolet (UV) (280 nm). The solvent gradient pattern is shown in Table 1.

Figure 2 shows an example of the HPLC chromatogram. The six phenolic compounds were separated completely from each other under the HPLC conditions employed. Each phenolic compound was identified by liquid chromatography–mass spectometry (LC-MS) and proton nuclear magnetic resonance (H^1-NMR) spectrometry. The amount of each phenolic compound was determined from the corresponding peak area in the chromatogram.

Because the molar UV absorption intensities of the six phenolic compounds are not the same and a gradient solvent system was employed, calibration was done with the use of authentic samples. Figure 3 shows the relative values of the molar UV absorption intensities of the six phenolic compounds in the gradient solvent system. To obtain the molar fractions of the six phenolic compounds, each of the six peak areas was multiplied by the corresponding correction factor (the reciprocal of the relative value of UV absorption intensity in Fig. 3) and was divided by the total peak area corrected. The concentrations of the six phenols

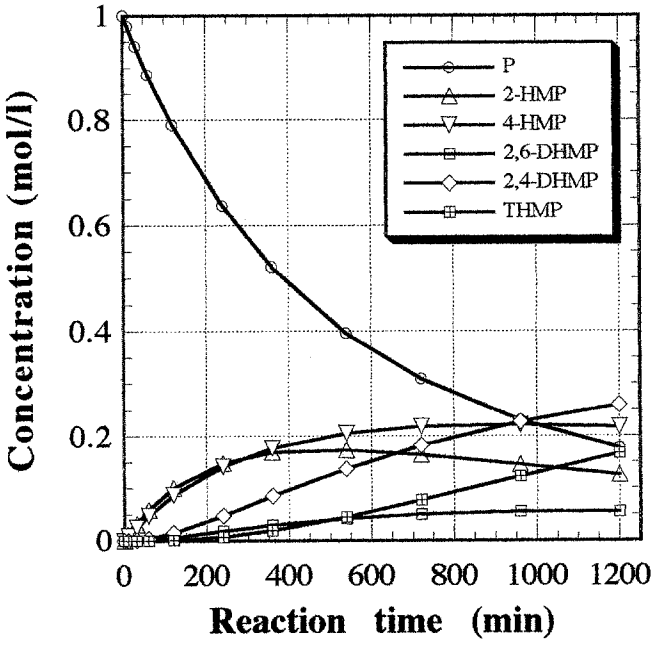

Fig. 4. Change of concentrations of phenols with time during hydroxymethylation of phenol at 20°C. $[P]_0 = 1.0$ mol/l; $[F]_0/[P]_0 = 3.0$; $[NaOH]/[P]_0 = 1.0$

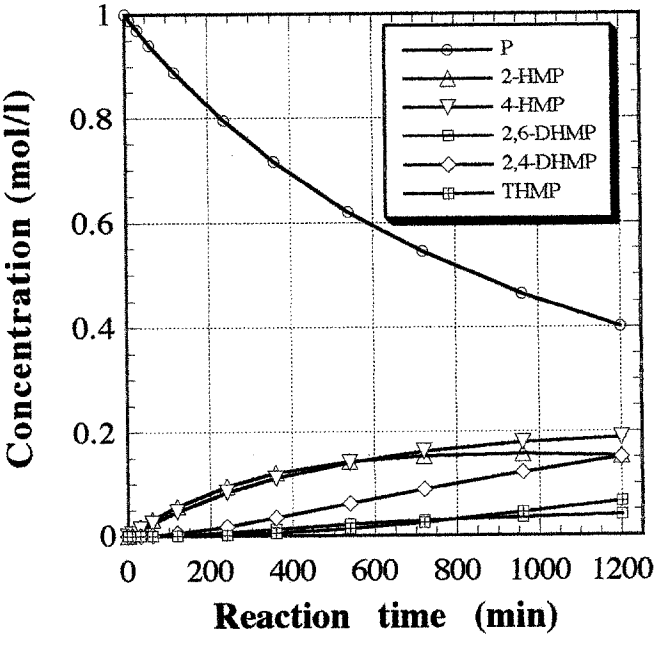

Fig. 5. Change of concentrations of phenols with time during hydroxymethylation of phenol at 20°C. $[P]_0 = 1.0$ mol/l; $[F]_0/[P]_0 = 3.0$; $[NaOH]/[P]_0 = 0.5$

in the reaction system were calculated from the initial concentration of phenol and the molar fractions of the phenols thus determined.

Incidentally, condensation reactions took place during the late stage of the hydroxymethylation. As the molar UV absorption intensities of the condensation products were not known, the analysis was done within the region where the condensation products were not detected or their amounts could be neglected. Furthermore, the analysis was made within the region where the consumption of formaldehyde by the Cannizzaro reaction could be neglected. The amount of formaldehyde was determined by a modified hydroxylamine method.[3]

Results and discussion

Determination of the rate parameters

Twelve reaction time courses (three levels of temperature × four levels of NaOH/P molar ratio) for hydroxymethylation were obtained by chemical experiments. Figures 4–7 show the examples. A computer simulation technique[1] was used to analyze the reaction time course. The values of the seven rate constants were determined as the values employed in the computer simulation that gave the reaction time course that exactly fit the experimental data. Under the conditions of a fixed temperature, there was no significant dependence of the values of rate constants on the NaOH/P molar ratios employed. Therefore, the average value was taken for each rate constant and examined in the Arrhenius relation. Figure 8 shows the

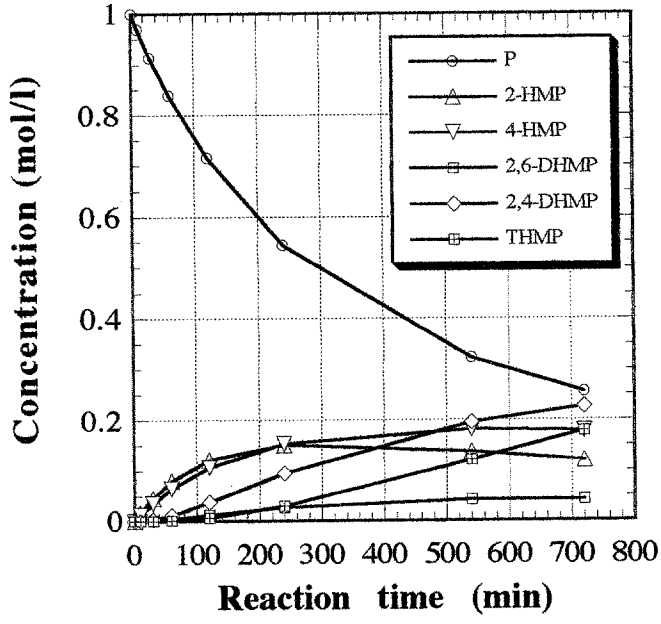

Fig. 6. Change of concentrations of phenols with time during hydroxymethylation of phenol at 30°C. $[P]_0 = 1.0$ mol/l; $[F]_0/[P]_0 = 3.0$; $[NaOH]/[P]_0 = 0.5$

Arrhenius plot of the rate constants. The values for the energies of activation were obtained from the gradients of the lines in Fig. 8.

Table 2 summarizes the values of the rate parameters obtained. It must be noted that the values of rate constants were calculated on the basis of the concentrations of phenols dissociated. That is, the rate constant of the reac-

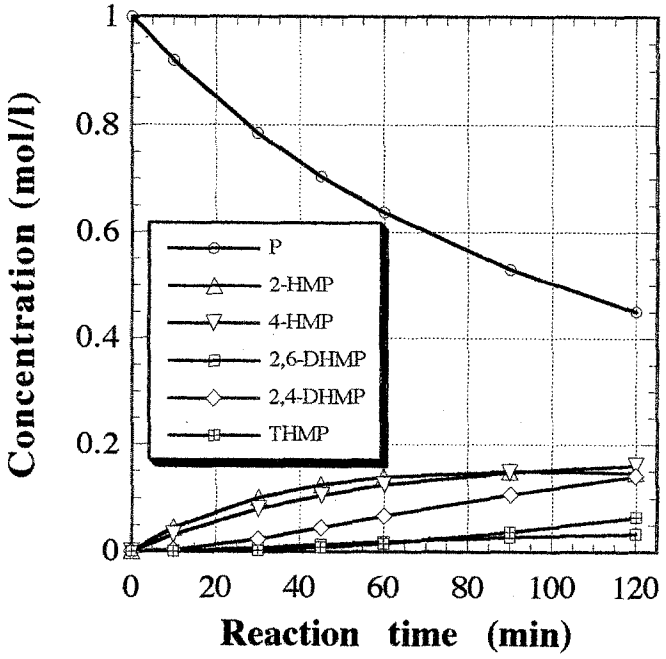

Fig. 7. Change of concentrations of phenols with time during hydroxymethylation of phenol at 40°C. $[P]_0 = 1.0$ mol/l; $[F]_0/[P]_0 = 3.0$; $[NaOH]/[P]_0 = 0.5$

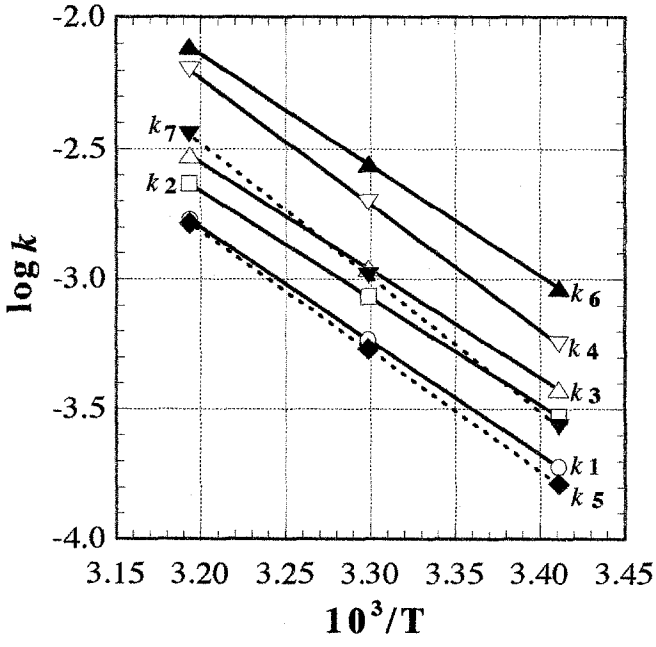

Fig. 8. Arrhenius plots of rate constants

Table 2. Kinetic parameters obtained

Reaction	Rate constants (30°C)[a]	Energies of activation[b]
	(10^{-4} l mol^{-1} min^{-1})	(kJ mol^{-1})
P + F → 2-HMP	k_1 5.88 ± 0.30	83.2 ± 2.0 (68.6)
P + F → 4-HMP	k_2 8.60 ± 0.30	78.7 ± 2.0 (65.3)
2-HMP + F → 2,6-DHMP	k_3 11.0 ± 0.3	79.0 ± 2.0 (67.8)
2-HMP + F → 2,4-DHMP	k_4 19.7 ± 0.5	92.3 ± 2.0 (60.7)
4-HMP + F → 2,4-DHMP	k_5 5.38 ± 0.30	88.0 ± 2.0 (77.4)
2,6-DHMP + F → THMP	k_6 27.8 ± 1.2	81.0 ± 2.0 (58.2)
2,4-DHMP + F → THMP	k_7 10.3 ± 0.3	98.7 ± 2.0 (60.2)

[a] On the basis of the concentrations of phenols dissociated
[b] Values in parentheses are those reported by Eapen and Yeddanapalli[4]

tion that forms 2-HMP from phenol, for example, is k_1 in the following rate equation:

$$d[2-HMP]/dt = 2k_1[F][P^-] \quad (1)$$

where [2-HMP], [F], [P^-] represent the concentrations of 2-hydroxymethylphenol, form aldehyde, and dissociated phenol, respectively. Incidentally, [P^-] was calculated according to the following equation:[1]

$$[P^-] = [P]\left(K_{a1}[OH^-]/K_w\right)\Big/\left(1 + K_{a1}[OH^-]/K_w\right) \quad (2)$$

where [P] and [OH^-] denote the concentrations of total phenol and hydroxide ion, respectively, and K_{a1} and K_w are the dissociation constants of phenol and the ion product of water, respectively.

The values of the energies of activation differ widely from those reported by Eapen and Yeddanapalli.[4]

Figure 9 shows the changes in the values of the rate constants with temperature estimated from the kinetic data in Table 1. It can be said that the reactivity of the *para*-position in phenol is higher than that of the *ortho*-position as reported by many researchers,[2] and this holds at any temperature below 100°C. The reactivity of the *para*-position in 2,6-dihydroxymethylphenol is high, and the rate constant k_6 is the largest among the seven rate constants at low temperatures as reported.[2] However, the reactivity of the *para*-position in 2-hydroxymethylphenol (k_4) becomes the highest at temperatures from 60° to 100°C, and the reactivity of the *ortho*-position in 2,4-dihydroxymethylphenol (k_7) exceeds that of the *para*-position in 2,6-dihydroxymethylphenol (k_6) at temperatures above 80°C and approaches that of the *para*-position in 2-hydroxymethylphenol (k_4).

Simulation experiments

Figure 10 is an example of the reaction time course obtained by the computer simulation technique with the use of

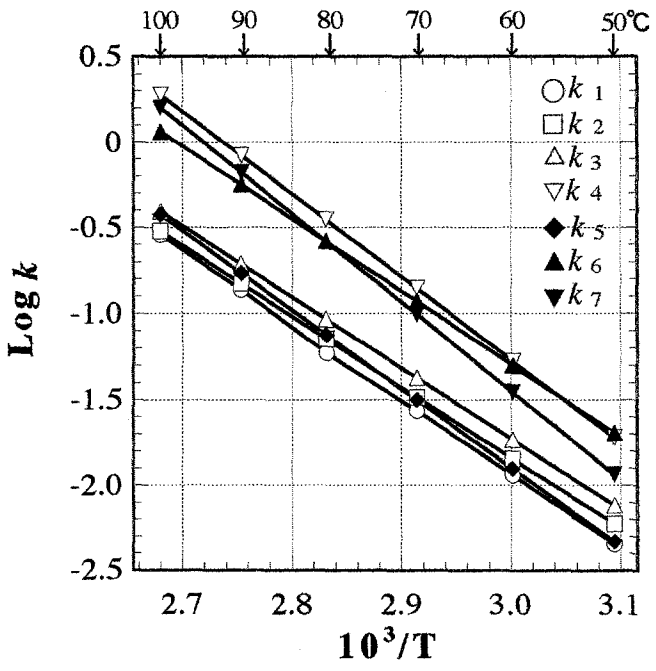

Fig. 9. Changes of rate constants with temperature estimated from the kinetic data

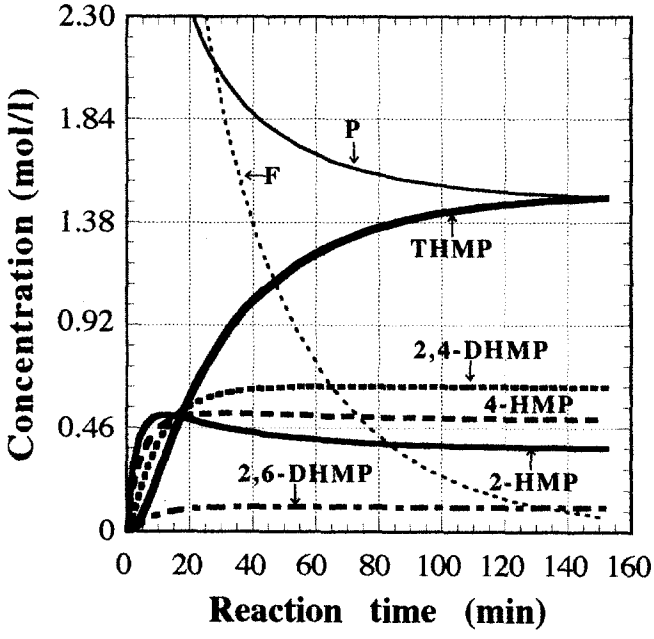

Fig. 11. Reaction time course obtained by the computer simulation for a reaction at 80°C. $[P]_0$ = 4.6 mol/l; $[F]_0/[P]_0$ = 1.5; $[NaOH]/[P]_0$ = 0.05

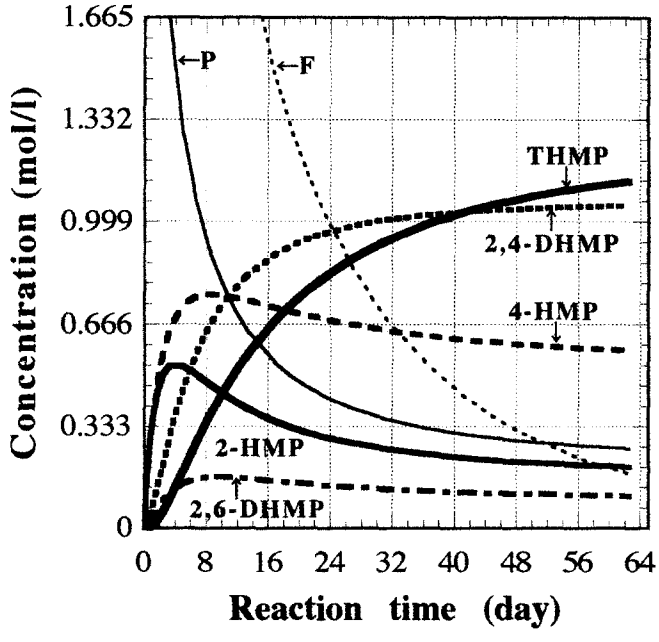

Fig. 10. Reaction time course obtained by the computer simulation for a reaction at 0°C. $[P]_0$ = 3.33 mol/l; $[F]_0/[P]_0$ = 2.0; $[NaOH]/[P]_0$ = 0.5

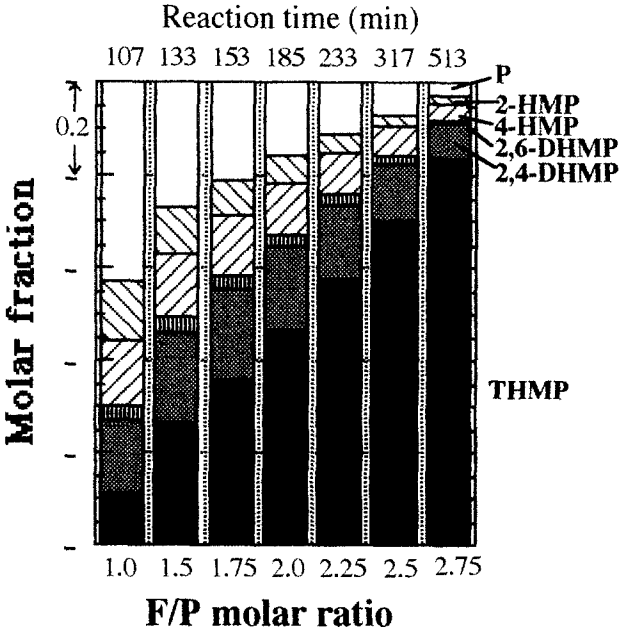

Fig. 12. Change in the molecular composition of reaction product with the F/P molar ratio. $[P]_0$ = 3.0 mol/l; $[NaOH]/[P]_0$ = 0.4; temperature: 60°C

the newly obtained rate parameters. This figure shows the changes of the concentrations of phenols and formaldehyde with time under the reaction conditions with the initial concentration of phenol at 3.33 mol/l, an F/P molar ratio of 2.0, an NaOH/P molar ratio of 0.5, and a temperature of 0°C. In Fig. 10 we can see, for example, that it takes about 48 days for the consumption of formaldehyde to reach 95%.

Figure 11 is another example of the reaction time course obtained by the computer simulation. Some resin makers conduct the hydroxymethylation reaction under the conditions of small NaOH/P molar ratios and high reaction temperatures to produce resins for the impregnation of wood and for the preparation of phenol-resorcinol adhesives. When the reaction is carried out under the conditions of an NaOH/P molar ratio of 0.05, F/P molar ratio of 1.5, initial concentration of phenol at 4.6 mol/l, and reaction temperature of 80°C, it takes about 90 min for the consumption of formaldehyde to reach

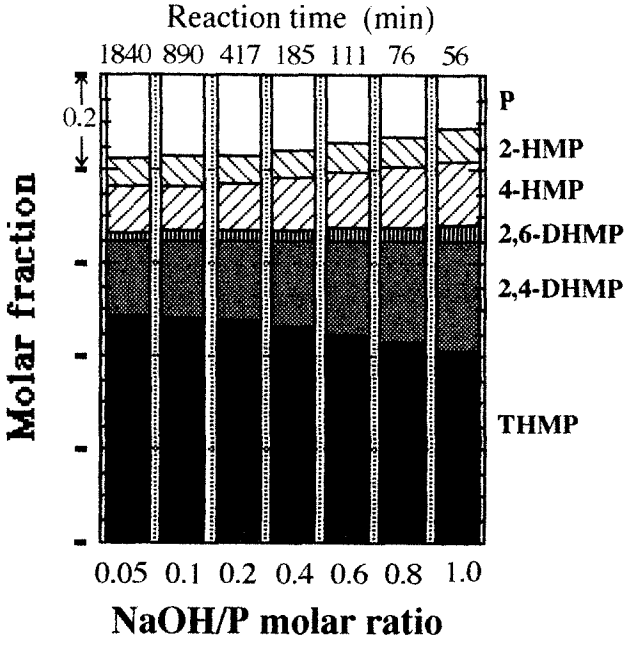

Fig. 13. Change in the molecular composition of reaction product with the NaOH/P molar ratio. $[P]_0$ = 3.0 mol/l; $[F]_0/[P]_0$ = 2.0; temperature 60°C

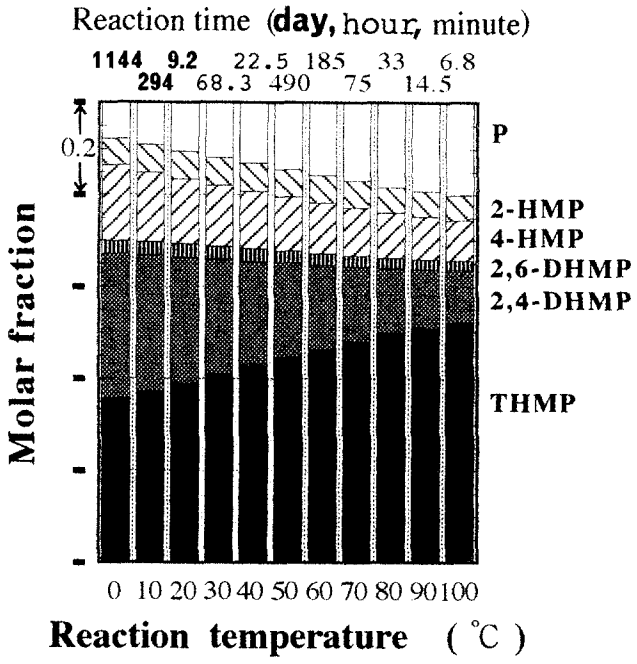

Fig. 14. Change in the molecular composition of reaction product with temperature. $[P]_0$ = 3.0 mol/l; $[F]_0/[P]_0$ = 2.0; $[NaOH]/[P]_0$ = 0.4

95%; at this point about 34% of phenol remains unreacted.

The actual figure of the reaction is considered to be somewhat different from that in Fig. 11 because of the occurrence of condensation reactions. However, it can be said that these reaction conditions are not suitable for producing resins of low contents of free phenol and of condensation products.

Figures 12, 13, and 14 show the effects of the F/P molar ratio, the NaOH/P molar ratio, and reaction temperature, respectively, on the final composition of reaction products. The point where 99% of formaldehyde had been consumed was chosen as the final state of the reaction. As Fig. 12 shows, the amount of unreacted phenol decreases as the F/P molar ratio increases and the trihydroxymethylphenol concentration and the reaction time required for the completion of the reaction increase.

As seen in Fig. 13, both unreacted phenol and trihydroxymethylphenol decrease as the NaOH/P molar ratio increases, and the reaction time becomes shorter than expected from the increase in the NaOH/P molar ratio. For example, it takes 185 min for the reaction with the NaOH/P molar ratio of 0.4 to come to an end. This time is shorter than the half-time of 417 minutes required for the reaction with the NaOH/P molar ratio of 0.2. These phenomena are considered to be due to the differences in the acid strengths of the six phenolic compounds. Because the acid strengths of the phenols[5] are in the order of phenol [pK_a (25°C) = 10.0], 2-hydroxymethylphenol [pK_a (25°C) = 9.84], 4-hydroxymethylphenol [pK_a (25°C) = 9.73], 2,6-dihydroxymethylphenol [pK_a (25°C) = 9.70], 2,4-dihydroxymethylphenol [pK_a (25°C) = 9.69], trihydroxymethylphenol [pK_a (25°C) = 9.45], the degrees of dissociation of phenol and monohydroxymethylphenol decrease as the reaction progresses; this tendency becomes more significant as the NaOH/P molar ratio decreases, resulting in the lower reaction rates of phenol and phenols of low substitution. Thus the low NaOH/P molar ratio leads to a large amount of phenol left unreacted and to the longer reaction time.

As Fig. 14 shows, the amounts of unreacted phenol and trihydroxymethylphenol increase as the reaction temperature is raised. This is due mainly to the large energy of activation for the two reactions by which 2,4-dihydroxymethylphenol is formed (2-HMP → 2,4-DHMP and 4-HMP → 2,4-DHMP) and the reaction that forms trihydroxymethylphenol from 2,4-dihydroxymethylphenol. The rates of these reactions increase much more than do those of the other reactions with the rise in temperature, leading to the larger amount of trihydroxy methylphenol in the reaction product. Moreover, the relative rates of the reactions of phenol (P → 2-DHMP and P → 4-DHMP) become smaller with the progress of the reaction, resulting in the larger amount of phenol left unreacted.

Conclusions

The rate constants and energies of activation for the seven reactions that take place during the sodium hydroxide-catalyzed hydroxymethylation of phenol were evaluated. The kinetic data newly obtained show that the reactivity of the *para*-position in phenol is higher than that of the *ortho*-position, as reported by many researchers,[2] and this holds at any temperature below 100°C. The reactivity of the

para-position in 2,6-dihydroxymethylphenol (2,6-DHMP) is high, and the rate constant (k_6) of the reaction between 2,6-DHMP and formaldehyde is the largest among the seven rate constants at low temperatures as reported.[2] However, the reactivity of the *para*-position in 2-hydroxymethylphenol (2-HMP, k_4) becomes highest at temperatures from 60° to 100°C, and the reactivity of the *ortho*-position in 2,4-dihydroxy-methylphenol (2,4-DHMP, k_7) exceeds that of the *para*-position in 2,6-DHMP (k_6) at temperatures above 80°C and approaches that of the *para*-position in 2-HMP (k_4).

Simulation experiments show that the amounts of phenol left unreacted and 2,4,6-trihydroxymethylphenol in the final reaction product increase as the reaction temperature is raised and as the alkali/phenol molar ratio decreases. These phenomena can be attributed to the differences in the energies of activation for the seven reactions and in the acid strengths of the six phenolic monomers.

Acknowledgment This study was supported by a Grant-in-Aid (06556031) for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

References

1. Higuchi M, Nohno S, Tohmura S (1998) Kinetics of the hydroxymethylation of phenol. I. Rate equation and method of analysis. J Wood Sci 44:198–203
2. Knop A, Pilato LA (eds) (1985) Phenolic resins: chemistry, applications and performance: future directions. Springer, Berlin, pp 36–40
3. Tohmura S, Higuchi M, Hattori Y, Sakata I (1994) Acceleration of the cure of phenolic resin adhesives. IV. Kinetics of the condensation reaction of 2,4,6-trimethylolphenol. Mokuzai Gakkaishi 40:390–398
4. Eapen KC, Yeddanapalli LM (1968) Kinetics and mechanism of the alkali-catalyzed addition of formaldehyde to phenol and substituted phenols. Mokromol Chem 119:4–16
5. Knop A, Pilato LA (eds) (1985) Phenolic resins: chemistry, applications and performance: future directions. Springer, Berlin, p 26