

## Kinetics and Mechanisms of the Condensation Reactions of Phenolic Resins II. Base-Catalyzed Self-Condensation of 4-Hydroxymethylphenol

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**ABSTRACT:** Kinetics of the base-catalyzed self-condensation of 4-hydroxymethylphenol (4-HMP) was investigated for the purpose of clarifying the mechanisms of the phenolic resin curing. In order to determine the order of reaction, the dependence of the initial rate of reaction on the initial concentration of the reactant was closely investigated under a wide range of reaction conditions. It was found that the order of reaction was around 1.3. An analysis revealed that unimolecular- and bimolecular reactions occur simultaneously as the rate-determining steps. This is different from the case of the self-condensation of 2-hydroxymethylphenol (2-HMP) where the order of reaction was found to be 1.0 that means only unimolecular reactions take place as the rate-determining step. The rate of reaction due to the unimolecular process could be explained quantitatively by the rate equation based on a quinone methide intermediate hypothesis. The rate of reaction due to the bimolecular process could be explained quantitatively by the rate equation that assumed the following three types of reactions: reactions occurring (1) between two undissociated 4-HMP molecules, (2) between an undissociated 4-HMP molecule and a dissociated 4-HMP molecule, and (3) between two dissociated 4-HMP molecules. As to the bimolecular reactions, the authors suggest that the  $S_N2$  type mechanism in which the negatively charged 2- or 4-position of the phenolate ion attacks the methylol carbon of the other molecule is insufficient to explain the kinetics.

**KEY WORDS** Phenolic Resin / 4-Hydroxymethylphenol / Self-Condensation / Kinetics / Reaction Mechanisms /

Alkaline phenol-formaldehyde (PF) resin is one of the most important adhesives for manufacturing wood-based materials. The major part of the curing (hardening) of the PF resin is ascribed to the condensation reactions of hydroxymethylphenols (HMPs). Although quite a few papers have been published on the condensation reactions of model compounds (HMP monomers)<sup>1</sup> the reaction mechanisms have not been clarified yet. There are many discrepant experimental results and interpretations. Yedanapalli proposed a  $S_N2$ -type mechanism in which the negatively charged 2- or 4-position of a phenolate ion attacks the methylol carbon of another molecule for the reactions of 2-hydroxymethylphenol (2-HMP), 4-hydroxymethylphenol (4-HMP), and 2,4-dihydroxymethylphenol (2,4-DHMP).<sup>2</sup> This mechanism has been cited in many textbooks<sup>3</sup> (bimolecular reaction theory). On the other hand, Jones reported that the self-condensation of 2,4,6-trihydroxymethylphenol (THMP) was first order with respect to the concentration of THMP, and proposed a quinone methide intermediate hypothesis<sup>4</sup> (unimolecular reaction theory). Which is true? Or, does the mechanism change with the species of reactant? Moreover, even in the case of the self-condensation of the same model compound, different results on the order of reaction have been ob-

tained among the experiments carried out with different initial concentrations of the reactant.<sup>5</sup> Does the reaction mechanism change with the reaction conditions, too? Incidentally, as any means for direct observation of the activated complexes or intermediates have not been found yet, kinetics is the last means to investigate the reaction mechanism. Here, we notice that almost all of the previous kinetic studies adopted only a graphing method that plots a function of the reactant concentration against the reaction time, *e.g.*,  $\log(a - x)$  vs.  $t$  or  $x/(a - x)$  vs.  $t$ , where  $a$  and  $x$  represent the initial reactant concentration and the decrease in the reactant concentration in time  $t$ , respectively, and concluded the reactions to be of the first-order or of the second-order. This graphing method, however, sometimes leads to misunderstanding. It gives correct results only in the case where reaction products have no effect on the reaction. In the base-catalyzed condensation of HMPs, reaction products take part in the reaction with the starting reactant. That is, the rate of reaction,  $-dx/dt$ , cannot be expressed by a simple equation composed of only one term of the reactant concentration. Therefore, there is a possibility of error being included in the previous findings. Thus, we consider that it needs close reexamination of each of the condensation reactions of HMPs. We previously have confirmed the order of reaction of the self-condensation of 2-HMP

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to be 1.0 from the linear relationship between the initial rate of reaction and the initial concentration of 2-HMP.<sup>6</sup> This paper deals with the self-condensation of 4-HMP, the other one of the two monohydroxymethylphenols. The difference between the two HMPs is the location of the hydroxymethyl group on the phenolic nucleus. Incidentally, Yeddanapalli and Francis observed the self-condensations of both the two HMPs to obey the first-order rate equation, though they considered the reactions to be of pseudo first-order<sup>7</sup> implying no difference in the mechanism of the formation of activated complex in the rate determining step.

## EXPERIMENTAL

### Materials

4-HMP (99%) was purchased from Aldrich Chemical Company Inc.

### Analysis of the Self-Condensation Reaction of 4-HMP

4-HMP was dissolved in an aqueous sodium hydroxide (NaOH) solution at room temperature, and then 1 mL portions of the solution were sealed in glass ampules. Each ampule was immersed in a constant-temperature bath for its allotted time to make the reaction progress. Then the ampule was cooled in an ice-containing bath and thereafter it was diluted with acetonitrile-water solution containing acetic acid of a required amount for neutralizing the reaction system. After being made a known volume with the use of a volumetric flask, the reaction system was subjected to high performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC/MS) analyses. The self-condensation reactions were carried out with various initial concentrations of 4-HMP and NaOH/4-HMP molar ratios. A carbonate-free aqueous NaOH solution and degassed deionized-water were used. For the identification of reaction products, fractions collected by a preparative HPLC system were subjected to nuclear magnetic resonance (NMR) analyses. The changes in the concentration of 4-HMP during the reaction were calculated from the corresponding peak areas of the HPLC chromatograms. The rate of reaction at an arbitrary time was determined as  $([4\text{-HMP}]_{t_1} - [4\text{-HMP}]_{t_2}) / (t_2 - t_1)$ , and it was plotted against time,  $(t_2 - t_1)/2$ , and the value at time zero obtained by extrapolation was taken as the initial rate of reaction ( $R_i$ ), where  $[4\text{-HMP}]_{t_1}$  and  $[4\text{-HMP}]_{t_2}$  denote the concentrations of 4-HMP at time  $t_1$  and  $t_2$ , respectively. The dependence of  $R_i$  on the initial concentration of 4-HMP ( $[4\text{-HMP}]_i$ ) was investigated with fixed NaOH/4-HMP molar ratios.

### HPLC Analysis

A SHIMADZU 10AD liquid chromatograph was used. The following conditions were adopted: column: Intersil ODS-3 (5 $\mu$ m, 4.6  $\times$  250 mm) (GL SCIENCE); solvent: water-acetonitrile gradient system (starting with the water/acetonitrile volume ratio of 5/95, 50/50 at 10 min, 0/100 after 25 min); flow rate: 1.0 mL min<sup>-1</sup>; column temperature: 25°C; detection: UV 280 nm.

### LC/MS Analysis

A HITACHI M-1200 AP/ES Mass spectrometer was used. The following conditions were used: column, solvents, gradient ratios, column temperature, flow rate, and detection in the LC part: the same as those in the HPLC analysis; ionization: APCI (negative); nebulizer temperature: 300°C; desolvator temperature: 400°C; drift: 60 V.

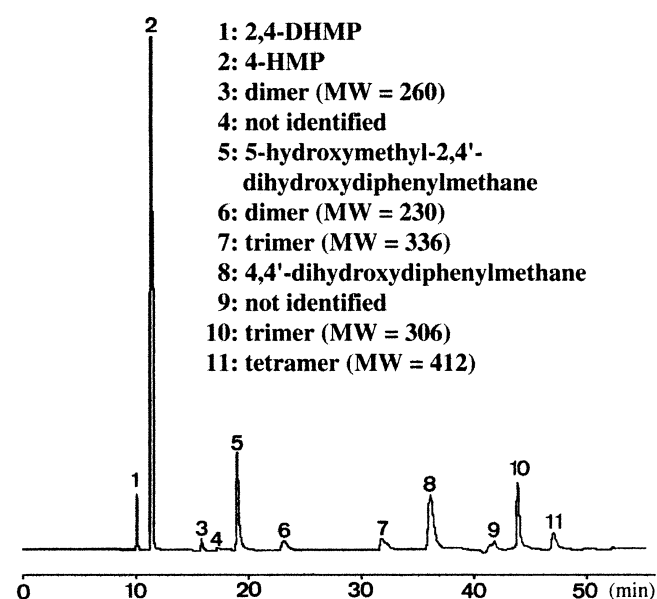
### NMR Analysis

A JEOL JNM-AL 400 FT NMR Spectrometer was used. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained with the use of deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as a solvent and tetramethylsilane as the internal standard.

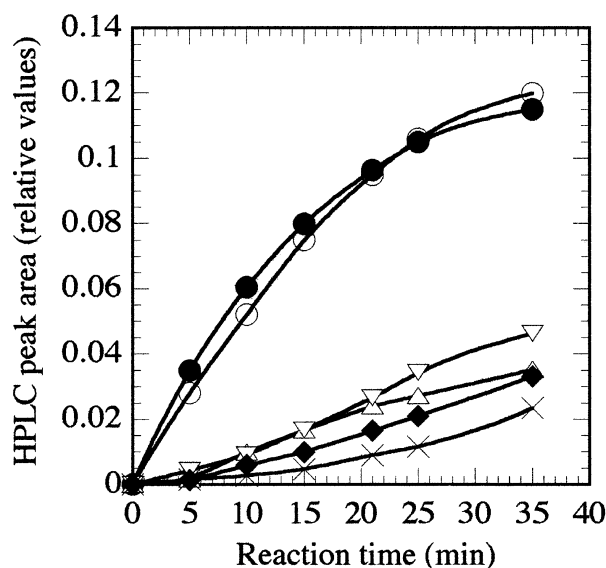
## RESULTS AND DISCUSSION

### Reaction Products in the Early Stage of Reaction

Figure 1 shows a HPLC chromatogram of the reaction system in an intermediate stage of reaction. Eleven absorption peaks exist in this chromatogram. LC/MS and <sup>13</sup>C NMR analyses gave the assignment



**Figure 1.** HPLC chromatogram of a reaction system. Reaction conditions:  $[4\text{-HMP}]_i$ : 0.1 mol L<sup>-1</sup>; NaOH/4-HMP molar ratio, 0.5; temperature, 100°C; time, 120 min.

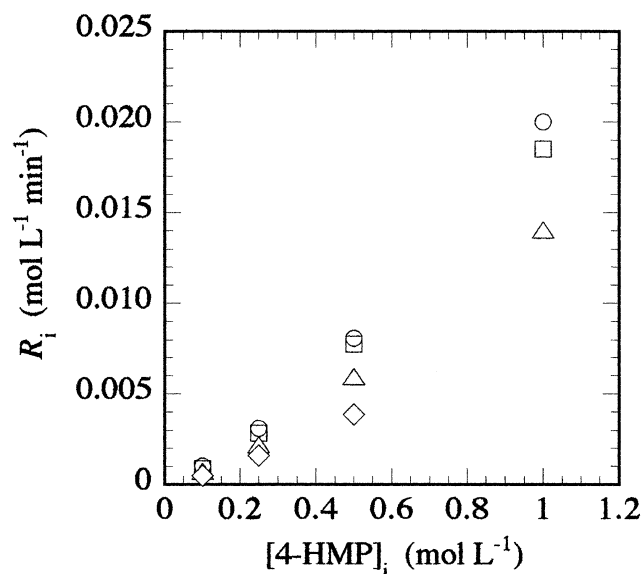


**Figure 2.** A time-course of the formation of reaction products. ●, 5-HM-2,4'-DPM, ○, 4,4'-DPM, ▽, trimer (MW = 306), △, trimer (MW = 336), ◆, tetramer (MW = 412), ×, 2,4-DHMP. Reaction conditions:  $[4\text{-HMP}]_i$ ,  $0.1 \text{ mol L}^{-1}$ ; NaOH/4-HMP molar ratio, 0.5; temperature,  $100^\circ\text{C}$ .

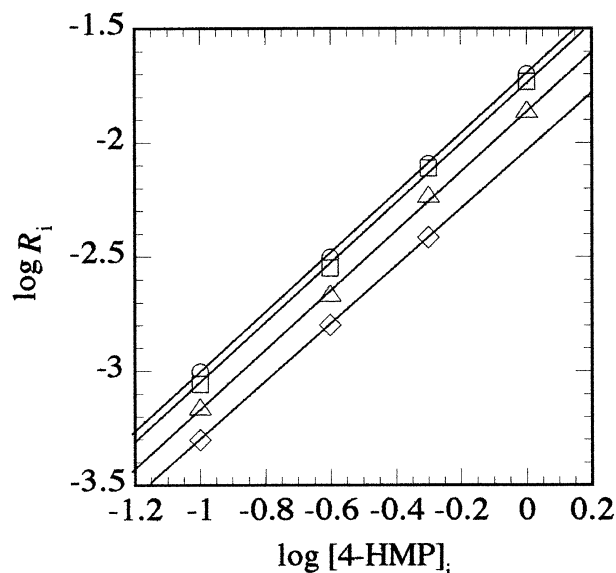
of each peak as shown in the figure. In the early stage of reaction two dimmers, 5-hydroxymethyl-2,4'-dihydroxydiphenylmethane (5-HM-2,4'-DPM), and 4,4'-dihydroxydiphenylmethane (4,4'-DPM) appeared as the reaction products, and then emerged two trimers with the molecular weight of 306 and 336 followed by a tetramer with the molecular weight of 412 and 2,4-dihydroxymethylphenol (2,4-DHMP). Figure 2 shows a time-course for the formation of reaction products. In this figure, the amounts of reaction products are shown in terms of relative peak areas in the HPLC chromatograms on the basis of the peak area for 4-HMP at reaction time of zero. It can be seen that the formation of two trimers, a tetramer and 2,4-DHMP (reaction product of 4-HMP with formaldehyde) starts in a fairly early stage of reaction and becomes significant as the reaction progresses. This indicates that the rate of decrease in the concentration of 4-HMP,  $-d[4\text{-HMP}]/dt$ , cannot be expressed by a simple equation composed of only one term of  $[4\text{-HMP}]$ . That is, the previously mentioned graphing method based on the integral form of the first-order or the second-order rate equation is not suitable for the analysis. Figure 2 also shows that the two dimmers (5-HM-2',4-DPM, and 4,4'-DPM) are formed nearly in the same rate in agreement with the statement by Grenier-Loustalot and others.<sup>8</sup>

#### Order of Reaction

To determine the order of reaction strictly, the dependence of the rate of reaction in the very early stage ( $R_i$ ,  $(-d[4\text{-HMP}]/dt)_i$ ) on the initial concentration ( $[4\text{-HMP}]_i$ )

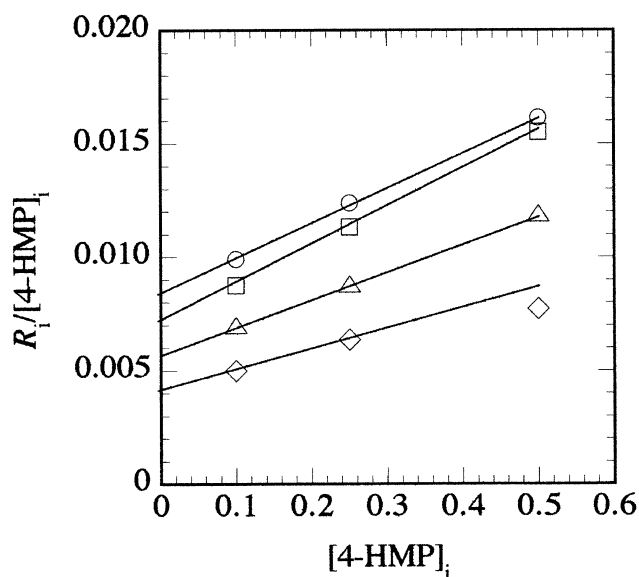


**Figure 3.** Initial rates of reaction plotted against the initial concentrations of 4-HMP. Reaction temperature:  $100^\circ\text{C}$ . NaOH/4-HMP molar ratios: ○, 0.25; □, 0.5; △, 0.75; ◇, 1.0.



**Figure 4.**  $\log R_i$  vs.  $\log [4\text{-HMP}]_i$  plot. Reaction conditions: the same as those in Figure 3.

$R_i$ ) was investigated. Figure 3 shows the  $R_i$  vs.  $[4\text{-HMP}]_i$  plots for the reactions carried out with various NaOH/4-HMP molar ratios. As this figure shows,  $R_i$  is not proportional to  $[4\text{-HMP}]_i$ . That is, the reaction is not of first-order. Figure 4 shows the logarithms of  $R_i$  plotted against the logarithms of  $[4\text{-HMP}]_i$ . Nearly linear relationships were obtained. From the slopes of the lines it was found that the order of reaction was around 1.3 in the region of NaOH/4-HMP molar ratio of 0.3–1.0 and of the 4-HMP concentrations below  $1.0 \text{ mol L}^{-1}$ . Incidentally, the order of reaction at NaOH/4-HMP molar ratios lower than 0.3 could not be determined because of the low solubility of 4-HMP.



**Figure 5.**  $R_i/[4\text{-HMP}]_i$  vs.  $[4\text{-HMP}]_i$  plot. Reaction conditions: the same as those in Figure 3.

#### Dependence of $R_i$ on the NaOH/4-HMP Molar Ratio

The value of  $R_i$  increased with an increase in the NaOH/4-HMP molar ratio until it reaches the maximum at around the NaOH/4-HMP molar ratio of 0.3; thereafter it decreased as the molar ratio increased (refer to Figure 10).

#### Energy of Activation

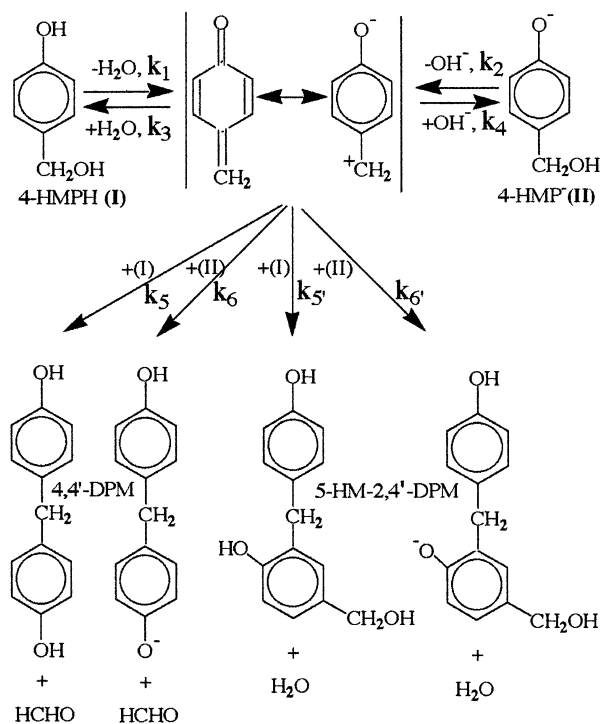
The energy of activation was found to be  $78 \pm 3$  kJ mol<sup>-1</sup> from the initial rates of reactions carried out at 80, 90, and 100°C with  $[4\text{-HMP}]_i$  of 0.1 mol L<sup>-1</sup> and NaOH/4-HMP molar ratio of 0.5. This value is 25 kJ mol<sup>-1</sup> smaller than that in the case of 2-HMP.<sup>6</sup>

#### Mechanisms of Reaction

The fractional number for the order of reaction, 1.3, indicates that two or more reactions of different mechanisms occur simultaneously as the rate-determining step. When the values of  $R_i$  divided by  $[4\text{-HMP}]_i$  were plotted against  $[4\text{-HMP}]_i$  linear relationships were obtained in the region of  $[4\text{-HMP}]_i$  below 0.5 mol L<sup>-1</sup> as shown in Figure 5. Thus the following empirical formula holds:

$$R_i = R_{i-1} + R_{i-2} = k_{(1)}[4\text{-HMP}]_i + k_{(2)}[4\text{-HMP}]_i^2 \quad (1)$$

where  $R_{i-1}$  and  $R_{i-2}$  represent the initial rates of reactions by the unimolecular process and by the bimolecular process, respectively,  $k_{(1)}$  and  $k_{(2)}$  denote the apparent rate constants for the unimolecular reaction and the bimolecular reaction, respectively. The values of  $k_{(1)}$  and  $k_{(2)}$  obtained from the intercepts on the vertical axis and slopes of the lines in Figure 5, respectively, are listed in Table I. Using these values we can calcu-



**Figure 6.** Quinone methide intermediate hypothesis applied to the self-condensation of 4-HMP.

late both the rates of reactions by the unimolecular process and by the bimolecular process separately at fixed NaOH/4-HMP molar ratios of 0.25, 0.5, 0.75, and 1.0.

It must be noted that eq 1 does not hold in the region of 4-HMP concentrations above 0.5 mol L<sup>-1</sup>. There may be some change in the state of molecular association as the reactant concentration increases. However, we have not obtained a reasonable explanation based on experimental data.

#### Rate of Reaction by the Unimolecular Process

To look closely into the unimolecular process, we assumed the formation of a quinone methide intermediate. The reactions involved can be illustrated as shown in Figure 6. And the following rate equation can be obtained (refer to Appendix 1):

$$\begin{aligned} R_{i-1} &= (-d[4\text{-HMP}]/dt)_i \\ &= [4\text{-HMP}]_i^2 \{ (k_5 + k_{5'}) / (1 + A) \\ &\quad + (k_6 + k_{6'}) A / (1 + A) \} \{ k_1 / (1 + A) \\ &\quad + k_2 A / (1 + A) \} / \{ k_3 [\text{H}_2\text{O}] + k_4 [\text{OH}^-] \\ &\quad + [4\text{-HMP}]_i \{ (k_5 + k_{5'}) / (1 + A) \\ &\quad + (k_6 + k_{6'}) A / (1 + A) \} \} \quad (2) \end{aligned}$$

where  $A$  is  $K_a[\text{OH}^-]/K_w$ ,  $K_a$ , and  $K_w$  are the dissociation constant of 4-HMP and the ion product of water, respectively.

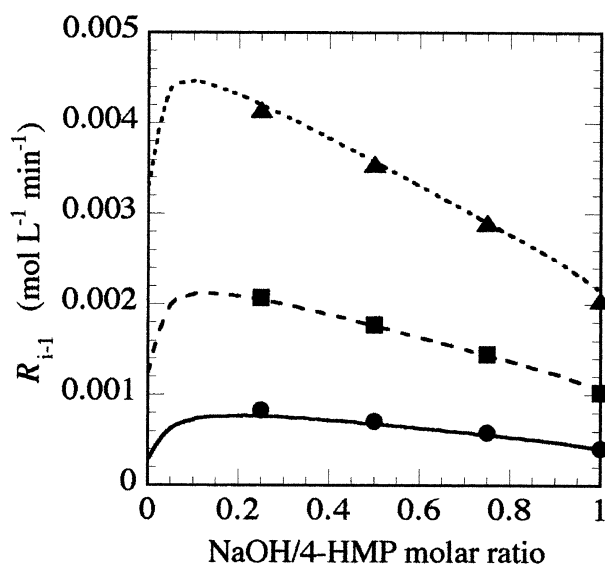
To determine the rate constants of eq 2, we made numerical calculations to find out a set of rate constant values that fit the experimental data. That is, we put a

**Table I.** Values of the apparent rate constants for the unimolecular and bimolecular reactions<sup>a</sup>

NaOH/4-HMP molar ratio	0.25	0.50	0.75	1.0
$k_{(1)}$ (min <sup>-1</sup> )	0.0083	0.0071	0.0058	0.0041
$k_{(2)}$ (L mol <sup>-1</sup> min <sup>-1</sup> )	0.0155	0.0168	0.0122	0.0090

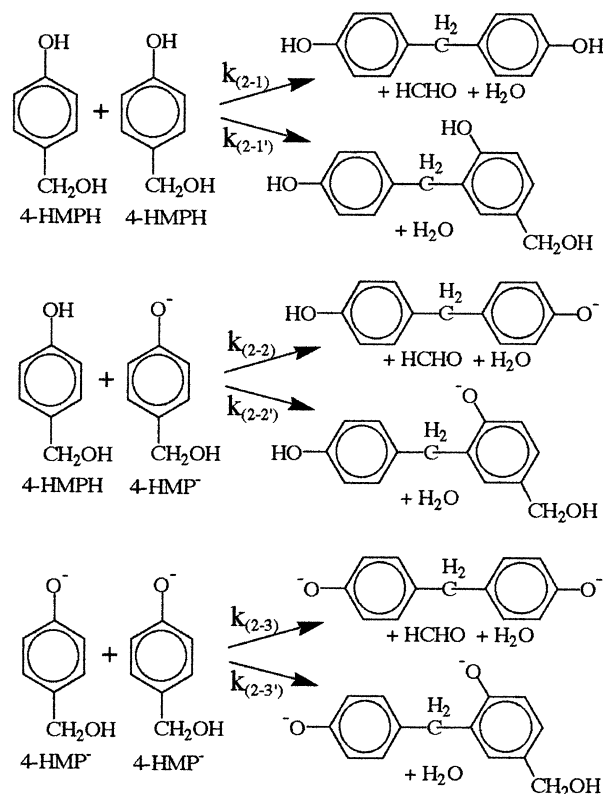
<sup>a</sup>Temperature: 100°C, [4-HMP]<sub>i</sub>: below 0.5 mol L<sup>-1</sup>.**Table II.** Values of the rate constants for the unimolecular process<sup>a</sup>

	$k_1^b$	$k_2^b$	$k_3^c$	$k_4^c$	$(k_5 + k_5')^d$	$(k_6 + k_6')^e$
4-HMP	$1.0 \times 10^{-2}$	$4.6 \times 10^{-3}$	$2.5 \times 10^5$	$2.0 \times 10^8$	$5.0 \times 10^5$	$4.0 \times 10^7$
2-HMP	$6.8 \times 10^{-3}$	$1.5 \times 10^{-3}$	$2.5 \times 10^5$	$2.0 \times 10^8$	$2.5 \times 10^5$	$2.0 \times 10^7$

<sup>a</sup>Temperature: 100°C. <sup>b</sup>min<sup>-1</sup>. <sup>c</sup>L mol<sup>-1</sup> min<sup>-1</sup>. <sup>d</sup> $k_5$  only in the case of 2-HMP (L mol<sup>-1</sup> min<sup>-1</sup>). <sup>e</sup> $k_6$  only in the case of 2-HMP (L mol<sup>-1</sup> min<sup>-1</sup>).**Figure 7.** Comparison of the values of  $R_{i-1}$  calculated by eq 2 with those calculated by eq 1. Reaction temperature: 100°C. [4-HMP]<sub>i</sub>: ●: 0.1; ■: 0.25; ▲: 0.5 (mol L<sup>-1</sup>). ●, ■, ▲: calculated by eq 1. —, ---, ···: calculated by eq 2.

set of values on the rate constants in eq 2 and calculated the values of  $R_{i-1}$  at various NaOH/4-HMP molar ratios, and then compared them with those calculated by eq 1 with the use of the values of  $k_{(1)}$  listed in Table I. Modification of the values of the rate constants of eq 2 was continued until the calculated values of  $R_{i-1}$  agreed with those calculated by eq 1. It was assumed that the temperature dependence of  $K_a$  ( $5.37 \times 10^{-9}$  at 25°C<sup>9</sup>) was the same as that of  $K_w$ . Values  $108.4 \times 10^{-10}$  and  $58.2 \times 10^{-14}$  were adopted as  $K_a$  and  $K_w$  at 100°C, respectively, and  $[\text{OH}^-]$  was calculated numerically by the method described in our previous paper<sup>10</sup> (refer to Appendix 2). Figure 7 shows the result. The values of rate constants obtained are listed in Table II.

*Rate of Reaction by the Bimolecular Process.* As to the bimolecular reactions, three combinations of reactants are possible. Figure 8 shows the presumable reactions. Thus the initial rate of the disappearance of 4-HMP can be expressed by the following equation:

**Figure 8.** Presumable bimolecular reactions.**Table III.** Values of the rate constants of the bimolecular reactions<sup>a</sup>

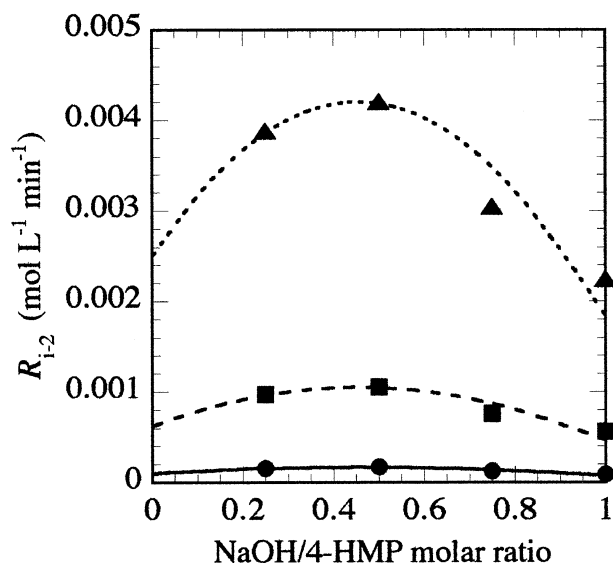
$(k_{(2-1)} + k_{(2-1')})$	$(k_{(2-2)} + k_{(2-2')})$	$(k_{(2-3)} + k_{(2-3')})$
$1.0 \times 10^{-2}$	$5.0 \times 10^{-2}$	$7.0 \times 10^{-3}$ (L mol <sup>-1</sup> min <sup>-1</sup> )

<sup>a</sup>Temperature: 100°C, [4-HMP]<sub>i</sub>: below 0.5 mol L<sup>-1</sup>.

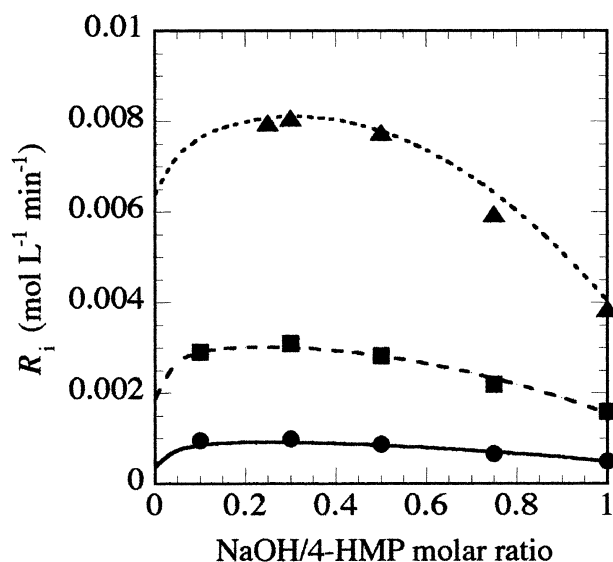
$$\begin{aligned}
 R_{i-2} &= (k_{(2-1)} + k_{(2-1')})[4\text{-HMPH}]_i^2 + (k_{(2-2)} \\
 &\quad + k_{(2-2')})[4\text{-HMPH}]_i[4\text{-HMP}^-]_i + (k_{(2-3)} \\
 &\quad + k_{(2-3')})[4\text{-HMP}^-]_i^2 \\
 &= [4\text{-HMP}]_i^2 \{ (k_{(2-1)} + k_{(2-1')}) + (k_{(2-2)} \\
 &\quad + k_{(2-2')})A + (k_{(2-3)} + k_{(2-3')})A^2 \} / (1 + A)^2 \quad (3)
 \end{aligned}$$

where  $A$  is  $K_a[\text{OH}^-]/K_w$ .

We made numerical calculations putting a set of values on the rate constants in eq 3 and compared the



**Figure 9.** Comparison of the values of  $R_{i-2}$  calculated by eq 3 with those calculated by eq 1. Reaction conditions: the same as those in Figure 7. ●, ■, ▲: calculated by eq 1. —, ---, ···: calculated by eq 3.



**Figure 10.** Comparison of the values of  $R_i$  calculated with those observed. Reaction conditions: the same as those in Figure 8. ●, ■, ▲: observed. —, ---, ···: calculated.

values of  $R_{i-2}$  obtained with those calculated by eq 1 with the use of the values of  $k_{(2)}$  listed in Table I. Figure 9 shows the result. The values of the rate constants obtained are listed in Table III. It is difficult to distinguish the two dimmers formed by the bimolecular process from those formed by the unimolecular process because, due to the low solubility of 4-HMP, we cannot conduct reactions at high 4-HMP concentrations where the bimolecular process predominates. Thus, we could obtain only the sums of the pairs of rate constants,  $k_{(2-1)} + k_{(2-1')}$ ,  $k_{(2-2)} + k_{(2-2')}$  and  $k_{(2-3)} + k_{(2-3')}$ .

Now we can calculate the values of  $R_i$  at any NaOH/4-HMP molar ratio by the combination of eqs

2 and 3 with the use of the values of rate constants listed in Tables II and III. Figure 10 shows the comparison of the dependence of the calculated  $R_i$  on the NaOH/4-HMP molar ratio with that of the observed  $R_i$ . It can be said that the calculated values of  $R_i$  are in good agreement with the observed ones. This verifies the theory we have assumed. The results on the kinetics obtained can explain the difference in the reactivity between 2-HMP and 4-HMP. It is known that the rate of self-condensation of 4-HMP is greater than that of 2-HMP. This can be attributed to the simultaneous occurrence of the unimolecular and bimolecular reactions and to the larger values of  $k_1$  and  $k_2$  (rate constants for the formation of the quinone methide intermediate) in the case of 4-HMP. The smaller values of  $k_1$  and  $k_2$  in the case of 2-HMP is considered to be due to the occurrence of intra-molecular hydrogen bonding that is considered to make the formation of the quinone methide intermediate slower increasing the electron density on the hydroxymethyl carbon. Incidentally, the energy of activation obtained for the self-condensation of 2-HMP,  $103 \text{ kJ mol}^{-1}$ ,<sup>6</sup> is about  $25 \text{ kJ mol}^{-1}$  greater than that,  $78 \text{ kJ mol}^{-1}$ , obtained for the self-condensation of 4-HMP at  $[4\text{-HMP}]_i$  of  $0.1 \text{ mol L}^{-1}$ . Although bimolecular reactions take place in the case of 4-HMP, the greater part of  $R_i$  at  $[4\text{-HMP}]_i$  of  $0.1 \text{ mol L}^{-1}$  is ascribed to the unimolecular reaction, the value of  $78 \text{ kJ mol}^{-1}$  is close to the energy of activation for the formation of the quinone methide intermediate. The difference in the energy of activation between 2-HMP and 4-HMP supports the above idea that the intra-molecular hydrogen bonding of 2-HMP has an inhibitory effect on the formation of the quinone methide intermediate.

As to the mechanisms for the bimolecular reactions, the  $S_N2$ -type mechanism in which the negatively charged *ortho* (C2) (or *para* (C4)) position of the phenolate ion attacks the hydroxymethyl carbon of the other molecule has been cited in many textbooks. However, there are some questions. Why does it not work in the case of 2-HMP? Is it because the electron densities on C2 and C4 are not high enough and that on the hydroxymethyl carbon is not low enough due to the intra-molecular hydrogen bonding? It may be possible that the  $S_N2$  mechanism works in the reaction between dissociated 4-HMP and undissociated 4-HMP. However, the dependence of  $R_{i-2}$  on the NaOH/4-HMP molar ratio (Figure 9) cannot be explained if we take only the reaction between dissociated 4-HMP and undissociated 4-HMP into consideration. We have to take the reactions between two undissociated 4-HMP molecules and between two dissociated 4-HMP molecules into account to describe the kinetics. In these two types of reactions, it is problematical that the  $S_N2$  mechanism

works. Therefore, we consider that there is a possibility of some unknown mechanisms working.

## CONCLUSION

It has been shown that there are differences in reaction mechanisms between 2-HMP and 4-HMP. In the case of 4-HMP, bimolecular reactions occur in addition to unimolecular reactions as the rate-determining step. The rate constants obtained for the unimolecular process occurring in the case of 4-HMP are considered to be reasonable in comparison with those in the case of 2-HMP. The greater values of  $k_1$  and  $k_2$ , the rate constants for the formation of quinone methide, in addition to the occurrence of the bimolecular reactions explain the well-known fact that the self-condensation of 4-HMP is faster than that of 2-HMP. As to the bimolecular reactions, the  $S_N2$  mechanism in which the negatively charged *ortho* (or *para*) position of phenolate ion attacks the hydroxymethyl carbon of the other molecule seems to be inadequate: it is problematical that the  $S_N2$  mechanism works in the reactions between two undissociated 4-HMP molecules and between two dissociated 4-HMP molecules. However, the kinetics indicates that the reactions between two undissociated 4-HMP molecules and between two dissociated 4-HMP molecules do occur. Therefore, there is a possibility of some unknown mechanisms working.

## APPENDIX

### 1. Derivation of eq 2

According to the reaction scheme in Figure 6, the rate of the formation of the quinone methide intermediate is expressed by the following equation:

$$+d[Q]/dt = k_1[4\text{-HMPH}] + k_2[4\text{-HMP}^-] \quad (4)$$

where  $[Q]$ ,  $[4\text{-HMPH}]$ , and  $[4\text{-HMP}^-]$  denote the concentrations of quinone methide, undissociated 4-HMP and dissociated 4-HMP, respectively.

And the rate of the disappearance of the quinone methide intermediate is expressed as follows:

$$-d[Q]/dt = [Q]\{k_3[\text{H}_2\text{O}] + k_4[\text{OH}^-] + (k_5 + k_{5'})[4\text{-HMPH}] + (k_6 + k_{6'})[4\text{-HMP}^-]\} \quad (5)$$

where  $[\text{H}_2\text{O}]$  and  $[\text{OH}^-]$  represent the concentrations of water and hydroxide ion, respectively.

As it is assumed that the formation of the quinone methide intermediate is the rate-determining step, the following stationary state holds:

$$+d[Q]/dt = -d[Q]/dt \quad (6)$$

Thus, the concentration of the quinone methide intermediate is expressed by the following equation:

$$[Q] = (k_1[4\text{-HMPH}] + k_2[4\text{-HMP}^-]) / (k_3[\text{H}_2\text{O}] + k_4[\text{OH}^-] + (k_5 + k_{5'})[4\text{-HMPH}] + (k_6 + k_{6'})[4\text{-HMP}^-]) \quad (7)$$

and the rate of the decrease in the concentration of 4-HMP is expressed as follows:

$$-d[4\text{-HMP}]/dt = \{(k_5 + k_{5'})[4\text{-HMPH}] + (k_6 + k_{6'})[4\text{-HMP}^-]\}[Q] = \{(k_5 + k_{5'})[4\text{-HMPH}] + (k_6 + k_{6'})[4\text{-HMP}^-]\}(k_1[4\text{-HMPH}] + k_2[4\text{-HMP}^-]) / \{(k_3[\text{H}_2\text{O}] + k_4[\text{OH}^-] + (k_5 + k_{5'})[4\text{-HMPH}] + (k_6 + k_{6'})[4\text{-HMP}^-])\} \quad (8)$$

Here, the following relationships hold:

$$[4\text{-HMPH}] + [4\text{-HMP}^-] = [4\text{-HMP}] \quad (9)$$

$$[4\text{-HMPH}] = [4\text{-HMP}] / (1 + K_a[\text{OH}^-]/K_w) \quad (10)$$

$$[4\text{-HMP}^-] = [4\text{-HMP}](K_a[\text{OH}^-]/K_w) / (1 + K_a[\text{OH}^-]/K_w) \quad (11)$$

where  $K_a$  and  $K_w$  represent the dissociation constant of 4-HMP and the ion product of water, respectively. Thus eq 8 can be converted into eq 2.

$$R_{i-1} = (-d[4\text{-HMP}]/dt)_i = [4\text{-HMP}]_i^2 \{(k_5 + k_{5'}) / (1 + A) + (k_6 + k_{6'})A / (1 + A)\} \{k_1 / (1 + A) + k_2A / (1 + A)\} / \{k_3[\text{H}_2\text{O}] + k_4[\text{OH}^-] + [4\text{-HMP}]_i[(k_5 + k_{5'}) / (1 + A) + (k_6 + k_{6'})A / (1 + A)]\} \quad (2)$$

where  $A$  is  $K_a[\text{OH}^-]/K_w$ .

### 2. Calculation of the Concentration of Hydroxide Ion

In the aqueous 4-HMP-NaOH system the following equation holds:

$$[\text{Na}^+] + [\text{H}^+] = [4\text{-HMP}^-] + [\text{OH}^-] \quad (12)$$

As  $[\text{H}^+]$  and  $[4\text{-HMP}^-]$  can be expressed by the following equations:

$$[\text{H}^+] = K_w / [\text{OH}^-] \quad (13)$$

$$[4\text{-HMP}^-] = [4\text{-HMP}](K_a[\text{OH}^-]/K_w) / (1 + K_a[\text{OH}^-]/K_w) \quad (11)$$

the following equation holds:

$$[\text{Na}^+] = [\text{OH}^-] + [4\text{-HMP}](K_a[\text{OH}^-]/K_w) / (1 + K_a[\text{OH}^-]/K_w) - K_w / [\text{OH}^-] \quad (14)$$

where the values of  $[\text{Na}^+]$ ,  $[4\text{-HMP}]$ ,  $K_a$ , and  $K_w$  are known. This equation cannot be solved arithmetically, but it can be solved easily by a trial-and-error method using a computer.

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