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ORIGINAL ARTICLE

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Condensation reactions of phenolic resins IV: self-condensation of 2,4-dihydroxymethylphenol and 2,4,6-trihydroxymethylphenol (2)

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Abstract Kinetics of the self-condensation of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (THMP) were investigated to elucidate the mechanisms of the condensation of hydroxymethylphenols (HMPs). Rate equations were derived on the assumptions of the formation of quinone methide intermediates as unimolecular reactions and the occurrence of bimolecular reactions between undissociated HMPs, between undissociated HMP and dissociated HMP, and between dissociated HMPs. Rate constants were determined numerically by comparing the calculated reaction rates with observed ones. The results of analyses are as follows: (1) Both unimolecular and bimolecular reactions occur as the rate-determining steps during the self-condensation of 2,4-DHMP and THMP with low concentrations. (2) Nothing but bimolecular reactions occur as the rate-determining steps during the self-condensation of THMP with high concentrations. (3) Differences in the activation energy and the reaction rate due to the unimolecular process between 2,4-DHMP and THMP are small. (4) Rates of bimolecular reactions of THMP are about five times as large as those of 2,4-DHMP. (5) The values of the rate constants and the activation energy for the bimolecular reactions of THMP of low concentrations differ from those of THMP of high concentrations, indicating the difference in reaction mechanisms.

Key words Phenolic resin · Kinetics · Self-condensation · 2,4-Dihydroxymethylphenol · 2,4,6-Trihydroxymethylphenol

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Introduction

The major part of curing alkaline phenolic resins is ascribed to the condensation reactions of hydroxymethylphenols (HMPs). However, the mechanisms of the condensation reactions of HMPs have not yet been clarified. At present, as no attempts to observe directly the activated complexes or transient states of reactants have been successful, kinetics is the only available means to discuss the reaction mechanisms.

We have examined the self-condensation of 2-hydroxymethylphenol (2-HMP)[1] and 4-hydroxymethylphenol (4-HMP),[2] and confirmed the order of reaction of the self-condensation of 2-HMP to be 1.0 and that of 4-HMP to be 1.3. In the case of 2-HMP, the rate-determining step was ascribed to some unimolecular reactions, and the rate of the reaction was confirmed to obey a rate equation that assumed the formation of a quinone methide from both the dissociated and the undissociated 2-HMP. In the case of 4-HMP, it was thought that the unimolecular and bimolecular reactions took place simultaneously as the rate-determining step and that the reaction rate could be expressed by a combination of a first-order rate equation that assumed the formation of a quinone methide for the unimolecular reactions and a second-order rate equation that assumed bimolecular reactions occurred between two undissociated 4-HMPs, between undissociated 4-HMP and dissociated 4-HMP, and between two dissociated 4-HMPs. These results indicate that the reaction mechanisms change with the species of reactant.

In this paper we discuss the self-condensation of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (THMP). In the previous paper,[3] we reported the dependence of the initial reaction rates (R_i) on the initial concentrations of reactants ($[2,4\text{-DHMP}]_i$ and $[\text{THMP}]_i$). For 2,4-DHMP, the relation was found to be $R_i = k[2,4\text{-DHMP}]_i^{1.1}$ (i.e., the order of the reaction was 1.1). In the case of THMP, the relation shifted at a border zone of concentration; in the region of the initial concentration above 1.5 mol/l the order of reaction was 2.0, whereas in the

region of the concentrations below 1.0 mol/l the order of reaction changed with the NaOH/THMP molar ratio, showing fractional numbers between 1.2 and 1.6. In this paper, more detailed data are presented and quantitative analyses are done on the basis of the rate equations.

Materials and methods

Preparation of 2,4-DHMP and THMP

The procedures for preparing 2,4-DHMP and THMP are the same as those described in our previous paper.[3]

Analyses of the self-condensation reactions

The experimental procedures are analogous with those described in our previous paper.[3] The concentrations of the reaction products were determined from the corresponding peak areas of the high-performance liquid chromatography (HPLC) chromatograms with the use of calibration curves prepared using authentic samples. With the application of the method described in our previous paper,[3] the initial rate of the formation of each reaction product (dimer) was calculated from the reaction time course. The initial rate of the formation of dimer was used for evaluating the variation in the dimer formation rate with reaction conditions.

HPLC, LC-MS, and NMR analyses

The experimental procedures – HPLC, liquid chromatography-mass spectrometry (LC-MS), nuclear magnetic resonance (NMR) – are similar with those described in our previous paper.[3]

Results and discussion

Dependence of R_i on the NaOH/HMP molar ratio

Figure 1 shows the dependence of R_i on the NaOH/2,4-DHMP molar ratio. The value of R_i increased with an increase in the NaOH/2,4-DHMP molar ratio until it reached the maximum at around a NaOH/2,4-DHMP molar ratio of 0.2. Thereafter it decreased as the molar ratio increased.

Figures 2 and 3 show the dependence of R_i on the NaOH/THMP molar ratio in the higher and lower regions of $[THMP]_i$, respectively. In the region of $[THMP]_i$ above 1.5 mol/l, R_i increased with an increase in the NaOH/THMP molar ratio until it reached a maximum at around an NaOH/THMP molar ratio of 0.5, thereafter it decreased as the molar ratio increased. This behavior is in agreement with the result reported by Tohmura et al.[4] However, in the region of $[THMP]_i$ below 1.0 mol/l, the NaOH/THMP molar ratio at which R_i reached the maximum decreased with a decrease in the initial concentration of THMP.

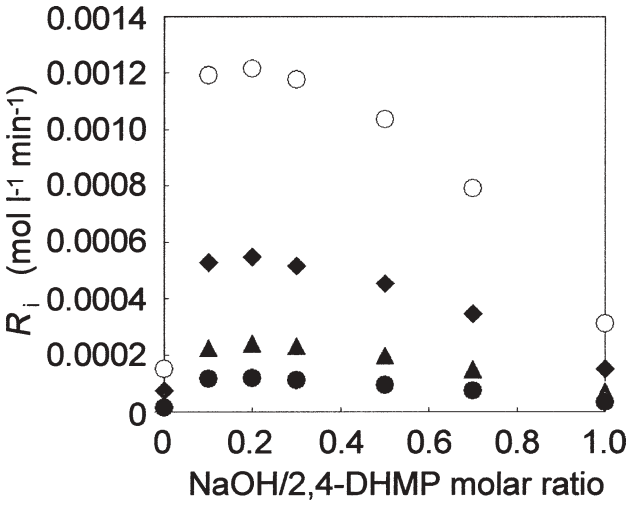

Fig. 1. Variation of R_i with the NaOH/2,4-DHMP molar ratio. Reaction conditions: temperature 70°C; $[2,4\text{-DHMP}]_i$: *filled circles*, 0.05 mol/l; *triangles*, 0.1 mol/l; *diamonds*, 0.2 mol/l; *open circles*, 0.4 mol/l

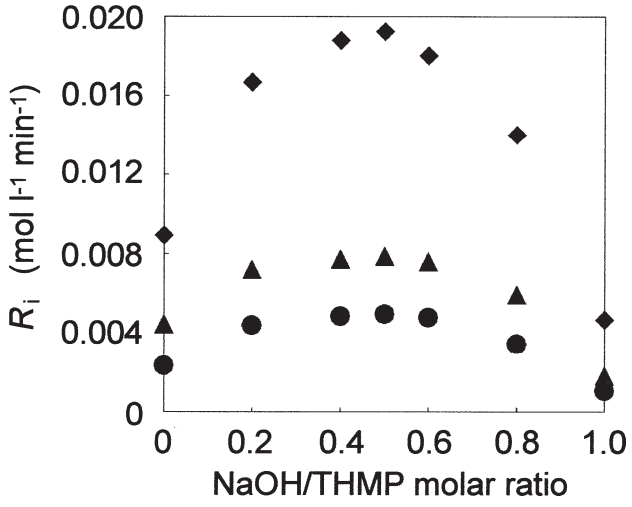

Fig. 2. Variation of R_i with the NaOH/THMP molar ratio in the high $[THMP]_i$ region. Reaction conditions: temperature 60°C; $[THMP]_i$: *circles*, 1.5 mol/l; *triangles*, 2.0 mol/l; *diamonds*, 3.0 mol/l

Variation of the ratio of dimer formation rate with the NaOH/HMP molar ratio and $[HMP]_i$

During the self-condensation of 2,4-DHMP, three dimmers – 3,3′-dihydroxymethyl-4,4′-dihydroxydiphenylmethane (3.3′-4,4′-DPM), 3,3′,5-trihydroxymethyl-2,4′-dihydroxydiphenylmethane (3,3′,5-2,4′-DPM), and 3′,5-dihydroxymethyl-2,4′-dihydroxydiphenylmethane (3′,5-2,4′-DPM) – were formed. The relative rates of the formation of the three dimers (3.1 for 3.3′-4,4′-DPM, 1.3 for 3,3′,5-2,4′-DPM, 1.0 for 3′,5-2,4′-DPM) neither changed with the NaOH/2,4-DHMP molar ratio nor with $[2,4\text{-DHMP}]_i$. In the case of THMP, two dimmers – 3,3′,5,5′-tetrahydroxymethyl-2,4′-dihydroxydiphenylmethane (3,3′,5,5′-2,4′-DPM) and 3,3′,5,5′-tetrahydroxymethyl-4,4′-dihydroxydiphenylmethane (3,3′,5,5′-4,4′-DPM) – were

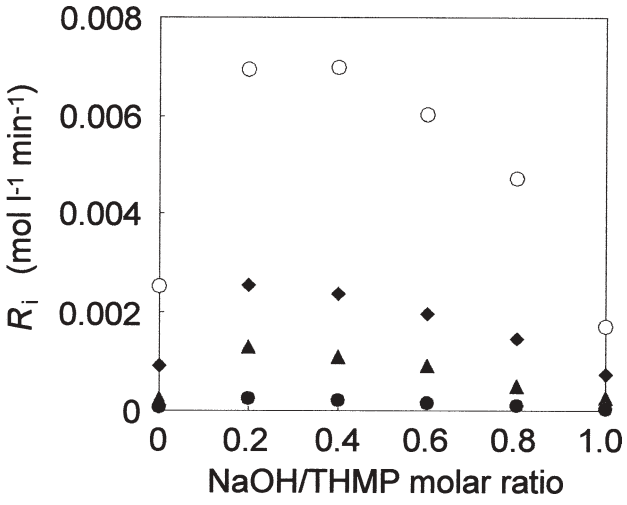

Fig. 3. Variation of R_i with the NaOH/THMP molar ratio in the low $[THMP]_i$ region. Reaction conditions: temperature 70°C; $[THMP]_i$: *filled circles*, 0.05 mol/l; *triangles*, 0.2 mol/l; *diamonds*, 0.4 mol/l; *open circles*, 1.0 mol/l

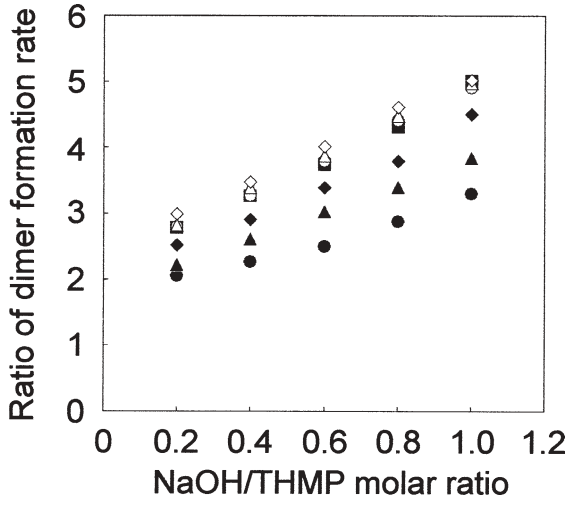

Fig. 4. Variation of the ratio of dimer formation rate with the NaOH/THMP molar ratio and $[THMP]_i$. Reaction conditions: temperature 60°C; $[THMP]_i$: *filled circles*, 0.05 mol/l; *filled triangles*, 0.2 mol/l; *filled diamonds*, 0.4 mol/l; *squares*, 1.0 mol/l; *open circles*, 1.5 mol/l; *open triangles*, 2.0 mol/l; *open diamonds*, 3.0 mol/l

formed. In contrast to 2,4-DHMP, the relative rates of the formation of the two dimers changed with the NaOH/THMP molar ratio; and in the region of $[THMP]_i$ below 1.0 mol/l, it changed also with $[THMP]_i$. Figure 4 shows the changes in the dimer formation ratio, (d[3,3′,5,5′-4,4′-DPM]/dt)/(d[3,3′,5,5′-2,4′-DPM]/dt), with the NaOH/THMP molar ratio and $[THMP]_i$. The relative rate of the formation of 3,3′,5,5′-4,4′-DPM increased with the increase in the NaOH/THMP molar ratio, and it increased with $[THMP]_i$ in the region below 1.0 mol/l. In the region of $[THMP]_i$ above 1.0 mol/l, the ratio was not dependent on $[THMP]_i$. These results suggest that the formation of *para-para* methylene bonds is favored by bimolecular reactions, and that the reaction of dissociated THMP favors the formation of *para-para* methylene bonds.

Analyses based on the rate equations

The results described above indicate that the mechanism for the self-condensation of THMP changes with the concentration. In the high concentration region, where the order of the reaction[3] is 2, bimolecular reactions must be the rate-determining steps. On the other hand, in the case of 2,4-DHMP and THMP with low concentrations, where the orders of reaction are 1.1 and 1.2–1.6, respectively,[3] both unimolecular and bimolecular reactions are considered to occur as the rate-determining steps.

Rate of unimolecular reactions of 2,4-DHMP and THMP in the low concentration region

The formation of quinone methide (benzyl cation) intermediates was assumed to be a unimolecular reaction (Figs. 5, 6). With application of the method described previously,[1,2] the following equations were derived for the initial rates due to the unimolecular reactions of 2,4-DHMP, R_{i-1D}, and THMP with a concentration below 1.0 mol/l (R_{i-1T})

$$R_{i-1D} = \left\{[2,4\text{-DHMP}]_i^2(k_1 + Ak_2)(k_5 + Ak_{5'} + k_6 + Ak_{6'} + k_7 + Ak_{7'})\right\} \Big/ \left\{(1 + A)^2\left(k_{-1}[H_2O] + k_{-2}[OH^-]\right) + [2,4\text{-DHMP}]_i(1 + A)(k_5 + Ak_{5'} + k_6 + Ak_{6'} + k_7 + Ak_{7'})\right\} + \left\{[2,4\text{-DHMP}]_i^2(k_3 + Ak_4)(k_8 + Ak_{8'})\right\} \Big/ \left\{(1 + A)^2\left(k_{-3}[H_2O] + k_{-4}[OH^-]\right) + [2,4\text{-DHMP}]_i(1 + A)(k_8 + Ak_{8'})\right\} \quad (1)$$

$$R_{i-1T} = \left\{[THMP]_i^2(k_1 + Ak_2)(k_5 + Ak_{5'} + k_6 + Ak_{6'})\right\} \Big/ \left\{(1 + A)^2\left(k_{-1}[H_2O] + k_{-2}[OH^-]\right) + [THMP]_i(1 + A)(k_5 + Ak_{5'} + k_6 + Ak_{6'})\right\} + \left\{[THMP]_i^2(k_3 + Ak_4)(k_8 + Ak_{8'})\right\} \Big/ \left\{(1 + A)^2\left(k_{-3}[H_2O] + k_{-4}[OH^-]\right) + [THMP]_i(1 + A)(k_8 + Ak_{8'})\right\} \quad (2)$$

where $[H_2O]$ and $[OH^-]$ represent the concentrations of water and hydroxide ions, respectively, and A is $K_a[OH^-]/K_w$. K_a and K_w represent the dissociation constants of HMP and the ion product of water, respectively. It was assumed that the temperature dependence of K_a was the same as that of K_w. Thus, the values 31.3×10^{-10}, 49.9×10^{-10}, and 15.3×10^{-14} were adopted as the K_a of 2,4-DHMP, the K_a of THMP, and the K_w at 70°C, respectively. $[OH^-]$ was calculated numerically by the method described previously.[1,2] Sets of values were assigned to the constants in Eqs. (1) and (2), and the values for R_{i-1D} and R_{i-1T} at various NaOH/

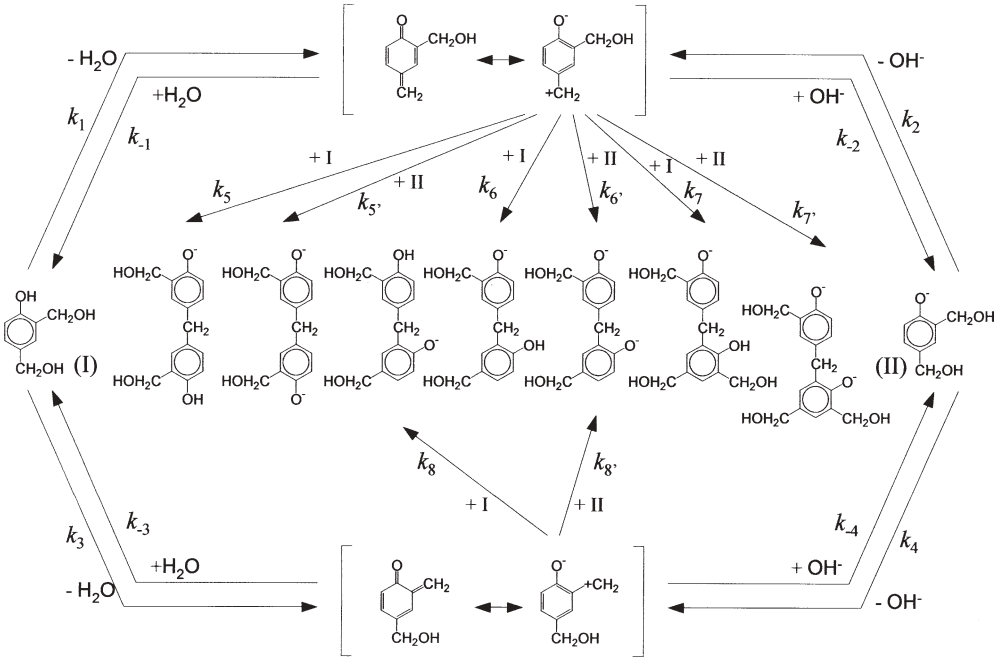

Fig. 5. Quinone methide intermediate hypothesis applied to the self-condensation of 2,4-DHMP

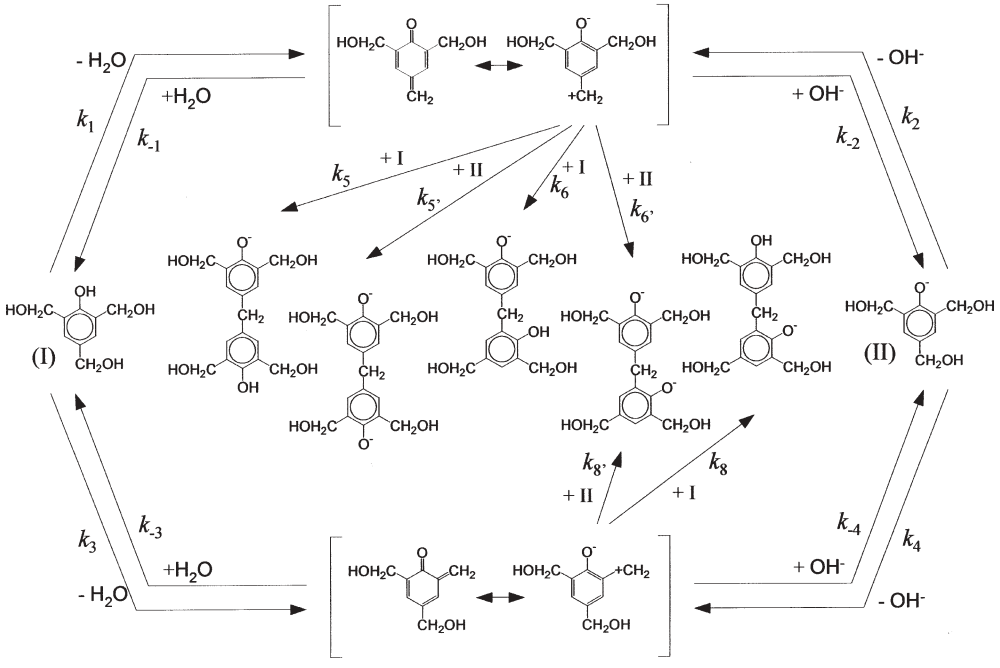

Fig. 6. Quinone methide intermediate hypothesis applied to the self-condensation of THMP

HMP molar ratios were calculated. Those calculated reaction rates were compared with observed ones.

Rate of bimolecular reactions of 2,4-DHMP and THMP in the low concentration region

As the bimolecular reactions, considering the difference of reactivity between undissociated HMP and dissociated HMP, the following three reactions were assumed to occur: (1) between two undissociated HMPs; (2) between undissociated HMP and dissociated HMP; and (3) between two dissociated HMPs (Figs. 7, 8). The initial rates of the bimolecular reactions of 2,4-DHMP (R_{i-2D}) and THMP with concentrations below 1.0 mol/l (R_{i-2T}) were expressed by the following equations:

$$\begin{aligned} R_{\text{i-2D}} &= \left(k_9 + k_{9'} + k_{9''}\right)\left[2,4\text{-DHMP}\right]_i^2\left(k_{10} + k_{10'} \right. \\ &\quad \left. + k_{10''}\right)\left[2,4\text{-DHMPH}\right]_i\left[2,4\text{-DHMP}^-\right]_i \\ &\quad + \left(k_{11} + k_{11'} + k_{11''}\right)\left[2,4\text{-DHMP}^-\right]_i^2 \\ &= \left\{k_9 + k_{9'} + k_{9''} + \mathrm{A}\left(k_{10} + k_{10'} + k_{10''}\right)\right. \\ &\quad \left. + \mathrm{A}^2\left(k_{11} + k_{11'} + k_{11''}\right)\right\}\left[2,4\text{-DHMP}\right]_i^2 \Big/ \left(1 + \mathrm{A}\right)^2 \end{aligned} \tag{3}$$

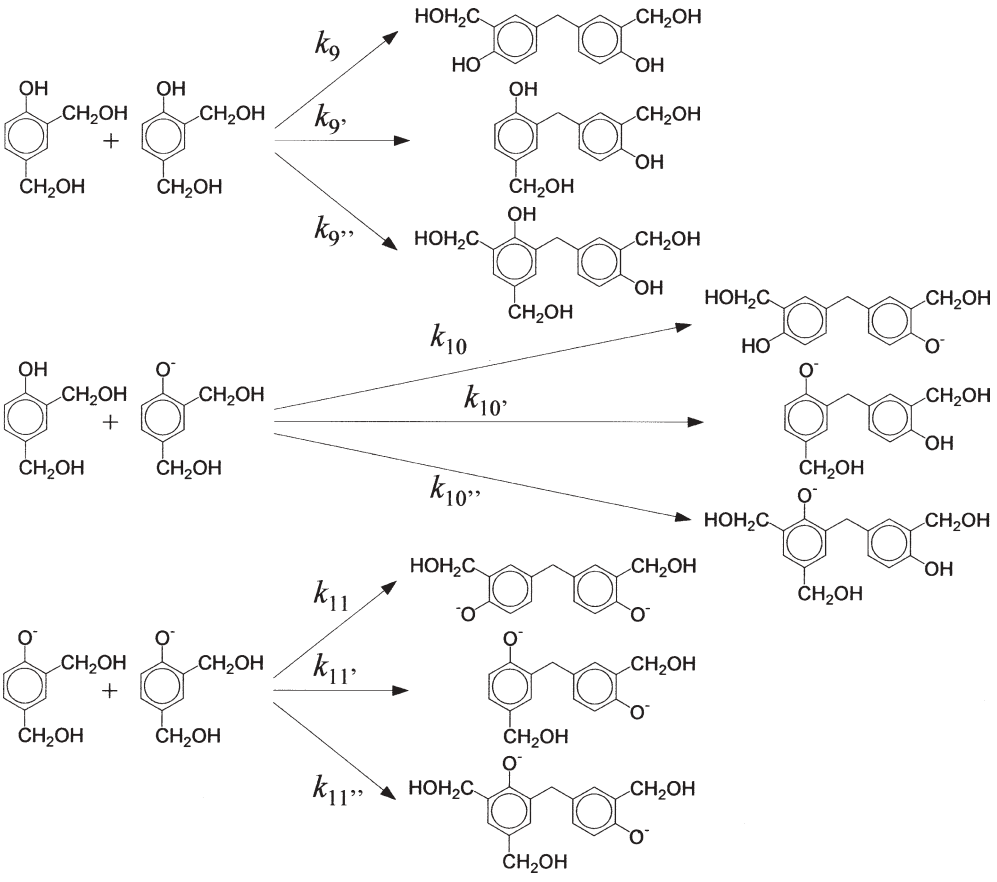

Fig. 7. Presumable bimolecular reactions in the self-condensation of 2,4-DHMP

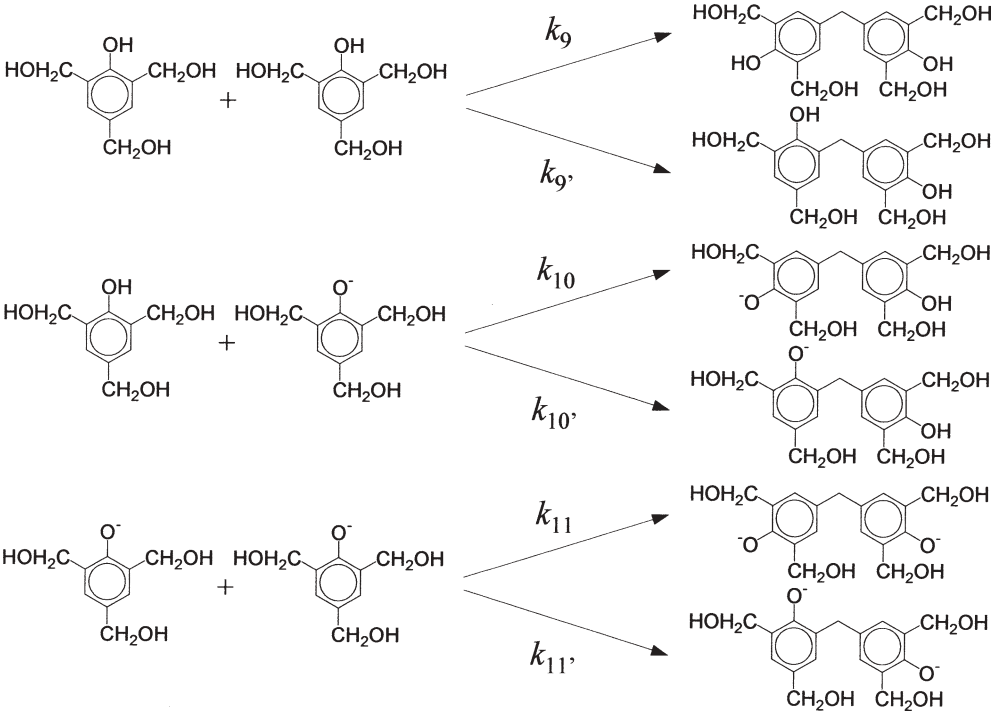

Fig. 8. Presumable bimolecular reactions in the self-condensation of THMP

Table 1. Rate constants for the unimolecular reactions

Substance	k_1 [a]	k_2 [a]	k_3 [a]	k_4 [a]	k_{-1} [b]	k_{-2} [b]	k_{-3} [b]	k_{-4} [b]	$(k_5 + k_6 + k_7)$ [b]	$(k_{5'} + k_{6'} + k_{7'})$ [b]	k_8 [b]	$k_{8'}$ [b]
2,4-DHMP	3.2×10^{-3}	7.3×10^{-4}	8.7×10^{-4}	6.0×10^{-5}	1.7×10^{3}	7.0×10^{7}	2.0×10^{3}	2.0×10^{7}	4.9×10^{5}	2.5×10^{7}	5.0×10^{3}	2.5×10^{5}
THMP	6.6×10^{-3}	3.0×10^{-5}	3.0×10^{-4}	3.0×10^{-5}	4.5×10^{3}	2.7×10^{8}	3.0×10^{4}	3.0×10^{4}	1.2×10^{6}	1.2×10^{9}	2.1×10^{7}	3.0×10^{9}

Temperature 70°C
[a] min^{-1}
[b] $\mathrm{l\,mol}^{-1}\,\mathrm{min}^{-1}$

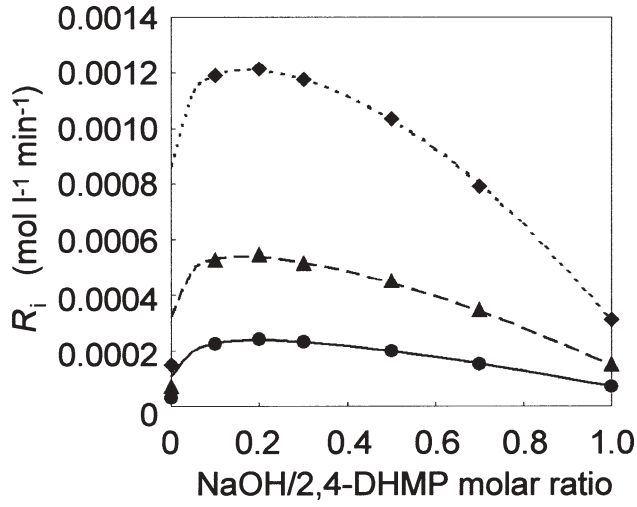

Fig. 9. Comparison of R_i calculated by Eqs. (1) and (3) versus observed values. Reaction conditions: temperature 70°C; $[2,4\text{-DHMP}]_i$: *circles*, 0.1 mol/l; *triangles*, 0.2 mol/l; *diamonds*, 0.4 mol/l (all observed). The curves of *solid lines*, *long-dashed lines*, and *short-dashed lines* were all calculated

$$
\begin{aligned}
R_{\text{i-2D}} &= \left(k_9 + k_{9'}\right)\left[\text{THMPH}\right]_i^2 \\
&\quad + \left(k_{10} + k_{10'}\right)\left[\text{THMPH}\right]_i\left[\text{THMP}^-\right]_i \\
&\quad + \left(k_{11} + k_{11'}\right)\left[\text{THMP}^-\right]_i^2 \\
&= \left\{k_9 + k_{9'} + \text{A}\left(k_{10} + k_{10'}\right)\right. \\
&\quad \left. + \text{A}^2\left(k_{11} + k_{11'}\right)\right\}\left[\text{THMP}\right]_i^2 \Big/ \left(1 + \text{A}\right)^2
\end{aligned}
\tag{4}
$$

where $[2,4\text{-DHMPH}]_i$, $[2,4\text{-DHMP}^-]_i$, $[\text{THMPH}]_i$, and $[\text{THMP}^-]_i$ denote the initial concentrations of undissociated 2,4-DHMP and dissociated 2,4-DHMP, undissociated THMP, and dissociated THMP, respectively.

Modification of the values of rate constants of Eqs. (1)–(4) was continued until the calculated values of $R_i (= R_{i-1} + R_{i-2})$ agreed with the observed ones. Figures 9 and 10 show the results, and the values of the rate constants determined are listed in Tables 1–3. As seen in Fig. 9, the calculated values for the R_i of 2,4-DHMP were in good agreement with the observed ones. In the case of THMP, the calculated values of R_i were in good agreement with the observed ones except for $[\text{THMP}]_i$ of 1.0 mol/l. As is described later, a zone of transition in the reaction mechanisms is considered to exist at around a $[\text{THMP}]_i$ of 1.0 mol/l. Additionally, whereas the reaction rate due to the unimolecular reactions of THMP were little different from those of 2,4-DHMP, the reaction rate due to the bimolecular reactions of THMP were about five times as large as those of 2,4-DHMP.

Rate of bimolecular reactions of THMP in the high concentration region

As the bimolecular reactions of THMP with concentrations above 1.5 mol/l, the same reactions as those in the concentration region below 1.0 mol/l were assumed (Fig. 8), and the following equation was applied.

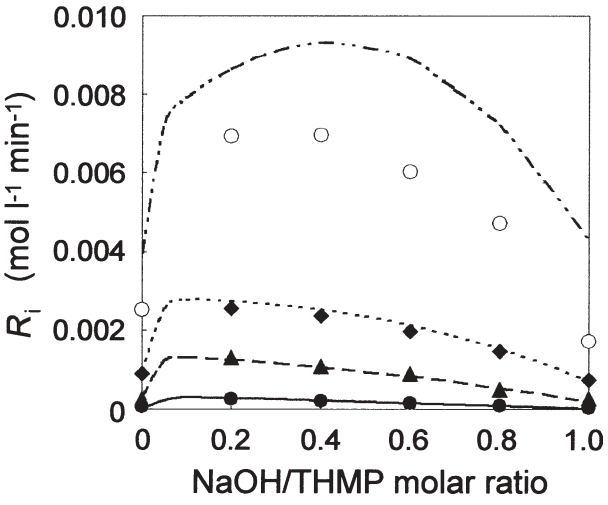

Fig. 10. Comparison of R_i calculated by Eqs. (2) and (4) versus observed values. Reaction conditions: temperature 70°C; $[THMP]_i$: *filled circles*, 0.05 mol/l; *triangles*, 0.2 mol/l; *diamonds*, 0.4 mol/l; *open circles*, 1.0 mol/l (all observed). The line curves are all calculated

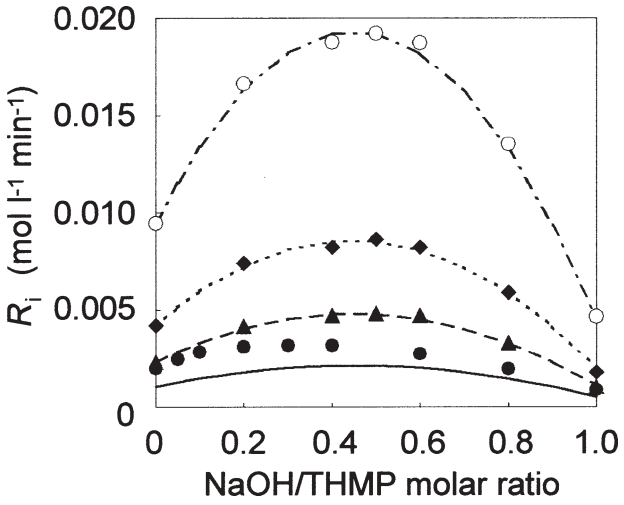

Fig. 11. Comparison of R_i calculated by Eq. (5) versus observed values. Reaction conditions: temperature 60°C; $[THMP]_i$: *filled circles*, 1.0 mol/l; *triangles*, 1.5 mol/l; *diamonds*, 2.0 mol/l; *open circles*, 3.0 mol/l (all observed). The line curves are all calculated

Table 2. Rate constants for the bimolecular reactions of 2,4-DHMP

Parameter	Rate constant
$k_9 + k_{9'} + k_{9''}$	4.0×10^{-6}
$k_{10} + k_{10'} + k_{10''}$	5.2×10^{-3}
$k_{11} + k_{11'} + k_{11''}$	1.0×10^{-5}

l mol^{-1} min^{-1}; temperature 70°C

Table 3. Rate constants for the bimolecular reactions of THMP

Region	$(k_9 + k_{9'})$	$(k_{10} + k_{10'})$	$(k_{11} + k_{11'})$
Low concentration	5.0×10^{-5}	9.3×10^{-3}	1.0×10^{-3}
High concentration	1.1×10^{-3}	7.0×10^{-3}	4.9×10^{-4}

l mol^{-1} min^{-1}; temperature 60°C

$$
\begin{aligned}
R_{\text{i-TD}} &= (k_9 + k_{9'})[\text{THMPH}]_i^2 \\
&\quad + (k_{10} + k_{10'})[\text{THMPH}]_i[\text{THMP}^-]_i \\
&\quad + (k_{11} + k_{11'})[\text{THMP}^-]_i^2 \\
&= \{k_9 + k_{9'} + A(k_{10} + k_{10'}) \\
&\quad + A^2(k_{11} + k_{11'})\}[\text{THMP}]_i^2/(1 + A)^2
\end{aligned}
\tag{5}
$$

Modification of the values of rate constants of Eq. (5) was continued until the calculated values of R_{i-Th} agreed with the observed ones. Figure 11 shows the results, and the values of rate constants determined are listed in Table 3. In the region of $[THMP]_i$ above 1.5 mol/l, the calculated values of R_{i-Th} were in good agreement with the observed ones. Thus, it can be said that nothing but bimolecular reactions occur as the rate-determining steps during the self-condensation of THMP with these high concentrations. At a $[THMP]_i$ of 1.0 mol/l, however, the values of R_{i-Th} calculated with the use of the rate constants that fit the reaction rates of THMP with concentrations above 1.5 mol/l differed from the observed ones. The initial concentration of THMP around 1.0 mol/l seems to be the border zone between the high concentration region and the low concentration region. Moreover, the values of the rate constants for the bimolecular reactions of THMP of high concentrations are different from those of THMP of low concentrations. This result suggests that the bimolecular reaction mechanisms change with the concentration of THMP.

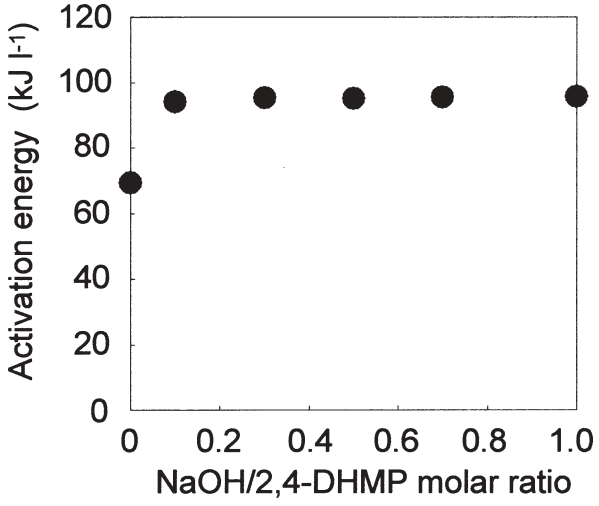

Fig. 12. Variation in the activation energy of unimolecular reactions with the NaOH/2,4-DHMP molar ratio. Reaction conditions: [2,4-DHMP]$_i$ 0.05 mol/l

Dependence of the energy of activation on the NaOH/HMP molar ratio

Figure 12 shows the dependence of the apparent energy of activation (E_a) for the self-condensation of 2,4-DHMP on

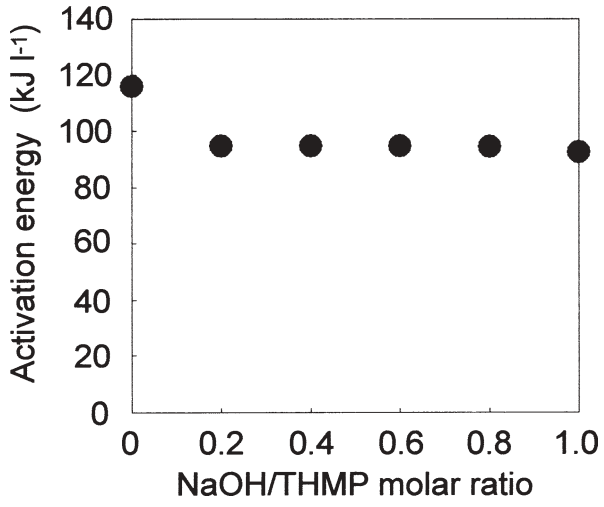

Fig. 13. Variation in the activation energy of unimolecular reactions with the NaOH/THMP molar ratio. Reaction conditions: $[THMP]_i$ 0.4 mol/l

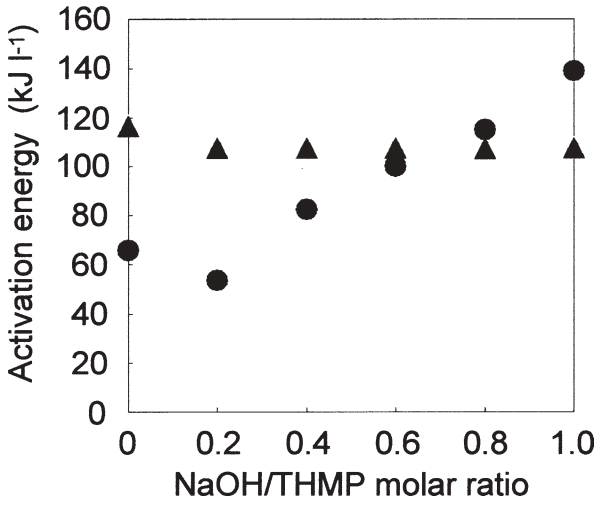

Fig. 14. Variation in the activation energy of bimolecular reactions with the NaOH/THMP molar ratio. Reaction conditions: $[THMP]_i$: *circles*, 0.4 mol/l; *triangles*, 2.0 mol/l

the NaOH/2,4-DHMP molar ratio. E_a was calculated from the Arrhenius plots of R_i obtained at 60°, 70°, and 80°C with $[2,4\text{-DHMP}]_i$ of 0.05 mol/l. At this low concentration, the bimolecular reaction rates can be neglected. That is, the obtained E_a is regarded as the energy of activation for the formation of the quinone methide intermediates. The value of E_a in the region of an NaOH/2,4-DHMP molar ratio of 0.1 to 1.0 differed from that (69 kJ/mol) at the NaOH/2,4-DHMP molar ratio of 0; but it varied little with the NaOH/2,4-DHMP molar ratio, with a value of 95 ± 1 kJ/mol. This value is about 8 kJ/mol smaller than that of 2-HMP[1] and 17 kJ/mol larger than that of 4-HMP[2].

In the case of THMP with concentrations below 1.0 mol/l, the bimolecular reactions are great, and it is experimentally difficult to trace the reactions of THMP at very low concentrations where the rate of bimolecular reactions can be ignored. Thus we measured R_i at various temperatures and calculated the rate of unimolecular and bimolecular reactions by Eqs. (2) and (4). The values for E_a were then calculated from the Arrhenius plots of R_{i-1T} and R_{i-2T} obtained at 50°, 60°, and 70°C. Figure 13 shows the dependence of the obtained E_a of unimolecular reactions on the NaOH/THMP molar ratio. The value of E_a for the unimolecular reactions in the region of NaOH/THMP molar ratio from 0.2 to 1.0 differed from that (116 kJ/mol) at the NaOH/THMP molar ratio of 0, but it varied little with the NaOH/THMP molar ratio having a value of 94 ± 1 kJ/mol. This value is close to that of 2,4-DHMP. Because the intramolecular hydrogen bonding between the phenolic hydroxy group and the *ortho*-hydroxymethyl group is thought to inhibit formation of the quinone methide intermediate, E_a, for the self-condensation of 2-HMP is greater than that of 4-HMP[2]. 2,4-DHMP and THMP have one or two hydroxymethyl groups in the *ortho*-position and one hydroxymethyl group on the *para*-position. Thus, it is reasonable that the values of E_a for the unimolecular reactions of 2,4-DHMP and THMP lie between the values for 2-HMP (103 kJ/mol) and 4-HMP (78 kJ/mol). Incidentally, because E_a for the unimolecular reactions of 2,4-DHMP and THMP were irrelevant to the NaOH/HMP molar ratio, it can be said that there is no difference between the E_a of the formation of quinone methide from undissociated HMP and that of dissociated HMP.

Figure 14 shows the dependence of the obtained E_a of bimolecular reactions on the NaOH/THMP molar ratio at high and low THMP concentrations. There was no dependence of E_a on the $[THMP]_i$ in the two concentration regions. In the high concentration region the value of E_a for the bimolecular reactions was 108 ± 1 kJ/mol, and it did not change with the NaOH/THMP molar ratio except at the NaOH/THMP molar ratio of 0 (117 kJ/mol). In the low concentration region, however, E_a for the bimolecular reactions varied with the NaOH/THMP molar ratio from 53 to 139 kJ/mol. This indicates that the mechanisms of bimolecular reactions change with the NaOH/THMP molar ratio in the low concentration region of THMP. In addition, differences in the rate constants and activation energy for the bimolecular reactions of THMP between the low and high concentration regions indicate that bimolecular reaction mechanisms change with the concentration of THMP.

Conclusions

By assuming the formation of quinone methide (benzyl cation) intermediates as the unimolecular reactions, and assuming the reactions to occur between two undissociated HMPs, between undissociated HMP and dissociated HMP, and between two dissociated HMPs as the bimolecular reactions, we derived the rate equations and could determine the rate constants numerically by comparing the calculated reaction rates with the observed ones. The analyses confirmed the following: (1) Both unimolecular and bimolecular reactions take place as the rate-determining steps during the self-condensation of 2,4-DHMP and THMP with con-

centrations below 1.0 mol/l. (2) Nothing but bimolecular reactions occur as the rate-determining step during the self-condensation of THMP with concentrations above 1.5 mol/l. The analyses revealed that the activation energy and the reaction rate due to the unimolecular process in the self-condensation of THMP differ little from those during self-condensation of 2,4-DHMP, whereas the bimolecular reaction rates of THMP are about five times as large as those of 2,4-DHMP. That the rate constants and the activation energy for the bimolecular reactions of THMP of high concentrations differ from those of THMP of low concentrations indicates the difference in the reaction mechanisms between the two concentration regions.

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