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Condensation reactions of phenolic resins III: self-condensations of 2,4-dihydroxymethylphenol and 2,4,6-trihydroxymethylphenol (1)

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Abstract This study reexamined the kinetics of the condensation reactions of hydroxymethylphenols with the purpose of elucidating the reaction mechanisms. This report discusses experimental results on the self-condensations of 2,4-dihydroxymethylphenols (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (THMP), focusing on the order of reaction. The relations between the initial rates of reaction and the initial concentrations of reactants were investigated. Results quite different from those of previous reports were obtained. The order of reaction of the self-condensation of 2,4-DHMP was found to be 1.1, which did not change with the alkali/2,4-DHMP molar ratio. The order of reaction of the self-condensation of THMP was found to vary with both the concentration of THMP and the alkali/THMP molar ratio. In the region of THMP concentrations above 1.5 mol/l, the order of reaction was confirmed to be 2.0, which did not change with the alkali/THMP molar ratio. In the region of THMP concentrations below 1.0 mol/l, the order of reaction varied with the alkali/THMP molar ratio, showing fractional numbers of 1.2–1.6. These results indicate that unimolecular reaction(s) and bimolecular reaction(s) take place simultaneously as the rate-determining step in the condensation reactions of 2,4-DHMP and THMP and that the reaction mechanism changes with the species of reactant and, in some cases, with the reaction conditions.

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

Introduction

The major part of curing alkaline phenolic resin is ascribed to the condensation reactions of hydroxymethylphenols (HMPs). Despite the long history and numerous research studies carried out, the mechanisms of the condensation reactions of HMPs have not yet been clarified.

There are many discrepant experimental results and interpretations. Francis and Yeddanapalli^{1,2} observed the self-condensation reactions of 2-hydroxymethylphenol (2-HMP), 4-hydroxymethylphenol (4-HMP), 2,4-dihydroxymethylphenol (2,4-DHMP), and 2,6-dihydroxymethylphenol (2,6-DHMP) to obey first-order rate equations with respect to the concentrations of the reacting HMPs. However, they considered the reactions to take place between dissociated (ionized) HMPs and undissociated HMPs. Their explanation was that because the concentrations of dissociated HMPs are constant for a constant alkali concentration the reactions appear to be kinetically of the first order. Freeman and Lewis³ once reported that the self-condensation of 2,4,6-trihydroxymethylphenol (THMP) appeared to be a first-order reaction. Later, Freeman⁴ reported that the self-condensation of THMP was a second-order reaction, occurring between dissociated THMP and undissociated THMP; and it became a pseudo-first-order reaction in the presence of excess alkali. Sekhar et al.⁵ also observed the reaction to be of pseudo-first-order, and they thought that the reaction was between dissociated THMP and undissociated THMP. Tohmura et al.⁶ explained kinetically the dependence of the reaction rate on the alkali/THMP molar ratio, assuming that three reactions occurred: between undissociated THMP and undissociated THMP; between dissociated THMP and undissociated THMP; and between dissociated THMP and dissociated THMP. These reports are based on a concept that an S_N2 -type mechanism works in the condensation reactions of HMPs. On the other hand, Jones⁷ proposed a quinone methide intermediate hypothesis to explain the kinetics of the self-condensation of THMP, which he observed to be a first-order reaction.

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Such being the case, we cannot draw any conclusion on the mechanisms of the condensation of HMPs. Incidentally, as no successful attempts have been reported on the direct observation of activated complexes formed by bimolecular reactions or the quinone methide intermediates formed by unimolecular reactions, kinetics is the last means to obtain information on the reaction mechanisms. The order of reaction provides information on the rate-determining step of the whole reaction.

As to the order of reaction, we noted that almost all of the authors of previous reports adopted only a graphing method that plots a function of the reactant concentration against the reaction time, e.g., $\log(a - x)$ versus t or $x/(a - x)$ versus t , where a and x represent the initial reactant concentration and the decrease in the reactant concentration in time t , respectively. They then concluded the reactions to be first order or second order. This graphing method, however, sometimes leads to misunderstanding. It gives correct results only in cases 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 in the previous findings. We believe that close reexamination is needed for each of the condensation reactions of HMPs.

The most reliable way to determine the order of reaction is to observe the dependence of the initial reaction rate on the initial concentration of reactant. In this way, we confirmed the order of reaction of the self-condensation of 2-HMP⁸ to be 1.0 and that of 4-HMP⁹ to be 1.3. This finding indicates that the unimolecular reaction is the rate-determining step in the case of 2-HMP, whereas both the unimolecular reaction and the bimolecular reaction occur simultaneously as the rate-determining step in the case of 4-HMP. That is, the reaction mechanism is different for the two monohydroxymethylphenols, one having a hydroxymethyl group in the *ortho* position and the other one having a hydroxymethyl group in the *para* position, suggesting that the reaction mechanism changes with the species of reactant.

This paper deals with the self-condensation of 2,4-DHMP and THMP. Incidentally, 2,4-DHMP and THMP are major products in the early stage of the synthesis of ordinary alkaline phenolic resins and are thought to play important roles in the early stage of condensation reactions.

Materials and methods

Chemicals

Phenol (99%), formaldehyde (37% solution), and sodium hydroxide (NaOH 96%) were purchased from Wako Pure Chemical Industries.

Preparation of 2,4-DHMP

Phenol (0.3 mol), formaldehyde (0.6 mol), and NaOH (0.3 mol, 50% aqueous solution) were mixed under cooling, and hydroxymethylation was carried out at 20°C for 50 h. The mixture was then neutralized with acetic acid. 2,4-DHMP was separated from the mixture solution by column chromatography using silica gel and an ethyl acetate–hexane mixture as eluent. Crystals (9.7 g) obtained by evaporation of solvent were dissolved in 20 ml of ethyl acetate and purified by recrystallization with the addition of a large amount of hexane. The crystals were analyzed by proton nuclear magnetic resonance spectroscopy (¹H-NMR) and liquid chromatography mass spectroscopy (LC-MS) and identified as pure 2,4-DHMP (>99.9%).

Preparation of THMP

Phenol (2 mol), formaldehyde (6 mol), and NaOH (2 mol, 50% aqueous solution) were mixed under cooling, and hydroxymethylation was carried out at 20°C for 3 days. The mixture was then poured into 5 l of isopropanol to precipitate the sodium salt of THMP. The precipitate was washed with isopropanol and then dispersed in a large amount of acetone. Acetic acid was added to the dispersed mixture to liberate THMP. The precipitate of sodium acetate was filtered off, and the filtrate was concentrated with a rotary evaporator. THMP crystals formed during the concentration process. The crystals (ca. 200 g) were purified by repeated recrystallization from acetone. The purified crystals were analyzed by ¹H-NMR and LC-MS and identified as pure THMP (>99.9%).

Analyses of the self-condensation reactions

2,4-DHMP and THMP were each dissolved in an aqueous NaOH solution under cooling, 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 cause the reaction to progress. Then the ampule was cooled in an ice-containing bath and was thereafter diluted with an acetonitrile–water solution containing enough acetic acid to neutralize the reaction system. After being made up to a known volume with the use of a volumetric flask, the reaction system was subjected to high-performance liquid chromatography (HPLC) and LC-MS analyses. The reactions were carried out with various concentrations of reactants and NaOH/hydroxymethylphenol (NaOH/HMP) molar ratios. The changes in the concentrations of the HMPs during the reactions were calculated from the corresponding peak areas of the HPLC chromatograms. The errors involved in the concentrations of the HMPs determined by this method were confirmed to be less than 3%, and the reproducibility of each reaction was checked by a duplicate experiment. The reaction rate at an arbitrary time was determined as $([HMP]_0 - [HMP]_t)/t$, and it was plotted against time ($t/2$). The value at time zero obtained by extrapolation was taken as the initial rate of reaction (R_i),

where $[HMP]_0$ and $[HMP]_t$ denote the concentrations of HMP at time zero and t , respectively. The dependence of R_t on the initial concentration of the HMP was investigated with fixed NaOH/THMP molar ratios.

HPLC analysis

For analysis of the 2,4-DHMP reactions, a Hitachi L-7000 system was used. The following conditions were adopted: column: Inertsil ODS-3 ($5\mu\text{m}$, $4.6 \times 250\text{ mm}$) (GL Science); water-acetonitrile gradient system (starting with a water/acetonitrile volume ratio of 95/5, 92/8 at 20 min, 88/12 at 30 min, 82/18 at 40 min, 77/23 at 50 min, 63/37 at 60 min, 0/100 after 70 min); flow rate 1.0 ml/min; column temperature 25°C ; UV detection 280 nm. For analysis of the THMP reactions, a Waters 600 liquid chromatograph was used. The following conditions were adopted: column: Inertsil ODS-3 ($5\mu\text{m}$, $4.6 \times 250\text{ mm}$) (GL Science); water-acetonitrile gradient system (starting with a water/acetonitrile volume ratio of 85/15, 30/70 at 10 min, 0/100 after 30 min); flow rate 1.0 ml/min; column temperature 25°C ; UV detection 280 nm.

LC-MS analysis

A Hitachi M-1200 AP mass spectrometer was used for the LC-MS analysis. The following conditions were adopted: column, solvent, gradient ratios, column temperature, flow rate, and detection for LC: as described for HPLC analysis; ionization: APCI (negative); nebulizer temperature 200°C ; desolvator temperature 400°C ; drift 60 V.

NMR analysis

A Jeol JNM-AL 400FT NMR spectrometer was used. ^1H - and ^{13}C -NMR spectra were obtained using deuterated dimethylsulfoxide ($\text{DMSO}-d_6$) as solvent and tetramethylsilane (TMS) as the internal standard.

Results and discussion

General aspects of the self-condensations of 2,4-DHMP and THMP in the early stage

Figure 1 shows a typical HPLC chromatogram of the reaction system of 2,4-DHMP. During the early stage of the reaction, three dimers (A, B, D) were formed. The rate of formation for D was about twice as large as those for A and B; A and B were formed at nearly the same rate. As the reaction proceeded, another dimer (C) and a trimer were formed. By NMR analyses, they were identified as 3,5,3'-trihydroxymethyl-2,4'-dihydroxydiphenylmethane (A), 5,3'-dihydroxymethyl-2,4'-dihydroxydiphenylmethane (B), 3,5,3'-trihydroxymethyl-4,4'-dihydroxydiphenylmethane (C), and 3,3'-dihydroxymethyl-4,4'-dihydroxydiphenylmethane (D) (Fig. 2). Apparently, compound C was formed by a reaction of D with formaldehyde liberated by the

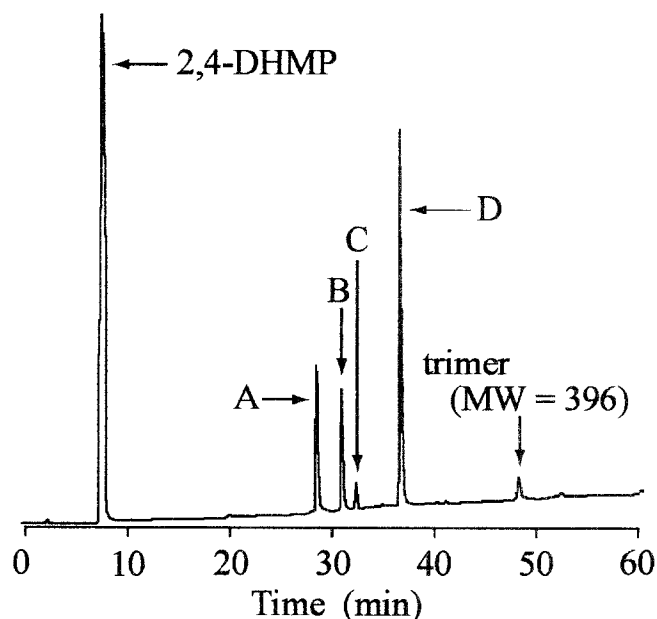


Fig. 1. High-performance liquid chromatography (HPLC) chromatogram of a reaction system of 2,4-dihydroxymethylphenol (2,4-DHMP). A, 3,5,3'-trihydroxymethyl-2,4'-dihydroxydiphenylmethane; B, 5,3'-dihydroxymethyl-2,4'-dihydroxydiphenylmethane; C, 3,5,3'-trihydroxymethyl-4,4'-dihydroxydiphenylmethane; D, 3,3'-dihydroxymethyl-4,4'-dihydroxydiphenylmethane; MW, molecular weight. Reaction conditions: $[2,4\text{-DHMP}]_0$: 0.2 mol/l; NaOH/2,4-DHMP molar ratio 0.3; temperature 70°C ; time 30 min

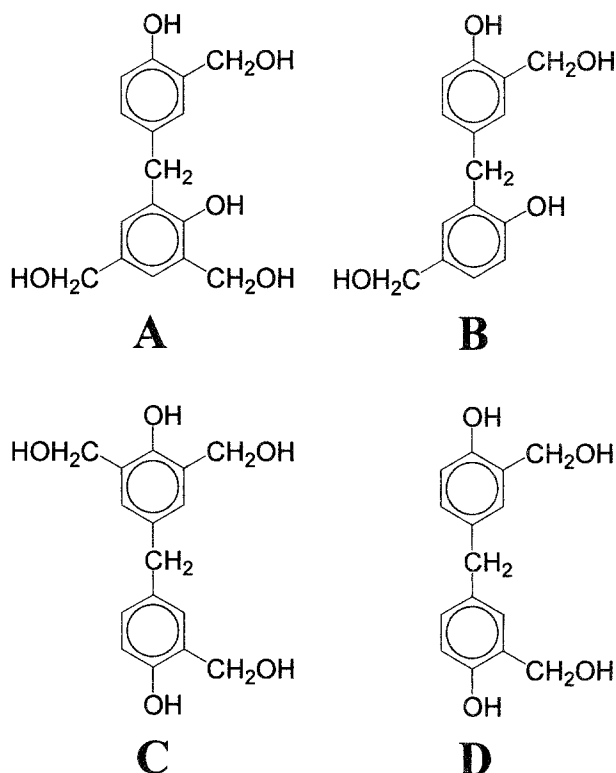


Fig. 2. Dimers detected during self-condensation of 2,4-DHMP

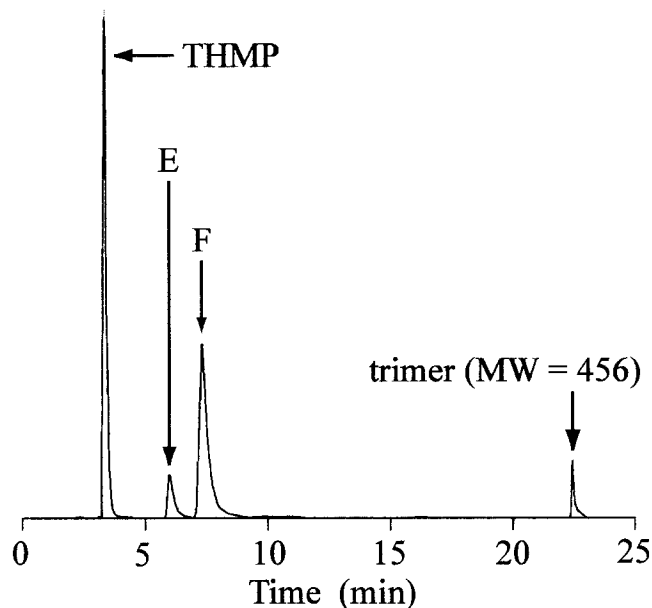


Fig. 3. HPLC chromatogram of a reaction system of trihydroxymethylphenol (THMP). *E*, 3,3',5,5'-tetrahydroxymethyl-2,4'-dihydroxydiphenylmethane; *F*, 3,3',5,5'-tetrahydroxymethyl-4,4'-dihydroxydiphenylmethane. Reaction conditions: [THMP]: 2.0 mol/l; NaOH/THMP molar ratio 0.5; temperature 60°C; time 360 min

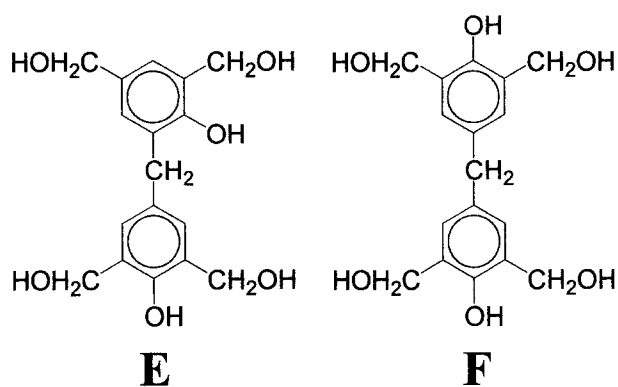


Fig. 4. Dimers detected during self-condensation of THMP

formation of D (and B). Incidentally, no dimers with *ortho-ortho* methylene bonds were detected.

Figure 3 shows a typical HPLC chromatogram of the reaction system of THMP. During the early stage of the reaction, two dimers (E and F) were formed. The rate of the formation of F was several times higher than that of E. Then a trimer was formed, increasing the rate of formation as the reaction progressed. The two dimers were identified as 3,3', 5,5'-tetrahydroxymethyl-2,4'-dihydroxydiphenylmethane (E) and 3,3',5,5'-tetrahydroxymethyl-4,4'-dihydroxydiphenylmethane (F) by NMR analyses (Fig. 4). Incidentally, in this case too, no *ortho-ortho* methylene-bonded dimer could be detected during the early stage of reaction.

The concentrations of 2,4-DHMP and THMP decreased smoothly, slowing down the rates of disappearance. Figure 5 shows the examples of $\log [\text{HMP}]$ versus t plots for refer-

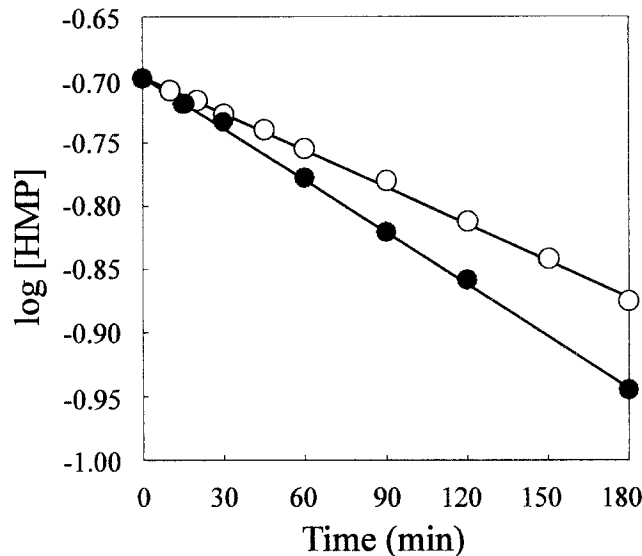


Fig. 5. Logarithms of the concentrations of 2,4-DHMP and THMP plotted against the reaction time. Reaction conditions: 2,4-DHMP ([2,4-DHMP]_i: 0.2 mol/l; temperature 70°C; NaOH/2,4-DHMP molar ratio 0.2); THMP ([THMP]_i: 0.2 mol/l; temperature 60°C; NaOH/THMP molar ratio 0.4). Filled circles, 2,4-DHMP; open circles, THMP

ence. Linear relations can be observed for both of the reactions of 2,4-DHMP and THMP. This indicates that the rates of the disappearance of the two HMPs obey first-order rate equations. That is, the following equations hold.

$$-d[2,4\text{-DHMP}]/dt = k[2,4\text{-DHMP}] \quad (1)$$

$$-d[\text{THMP}]/dt = k'[\text{THMP}] \quad (2)$$

However, this is merely an appearance. The reaction products of the self-condensations of 2,4-DHMP and THMP, as shown Figs. 2 and 4, have hydroxymethyl groups and can affect (increase) the rates of disappearance of the starting reactants by taking part in the reactions with the reactants. Moreover, particularly in the case of THMP, formaldehyde accumulates in the system as the reaction progresses and may affect the rate of the reaction. Therefore, we must investigate the relation between the reactant concentration and the rate of reaction in the very early stage, where the effects of the reaction products can be neglected.

Order of reaction of the self-condensation of 2,4-DHMP

Figure 6 shows the relation between the initial rate of reaction (R_i) and the initial concentration of 2,4-DHMP ($[2,4\text{-DHMP}]_i$) at a NaOH/2,4-DHMP molar ratio of 0.2. It can be seen that R_i is not directly proportional to $[2,4\text{-DHMP}]_i$. That is, the self-condensation reaction of 2,4-DHMP is not first order, at least at a NaOH/2,4-DHMP molar ratio of 0.2. Thus, we investigated the relation at various NaOH/2,4-DHMP molar ratios. No linear relation was observed at any NaOH/2,4-DHMP molar ratio. When the logarithms of R_i were plotted against the logarithms of $[2,4\text{-DHMP}]_i$, linear relations were obtained, as shown in Fig. 7. The lines show

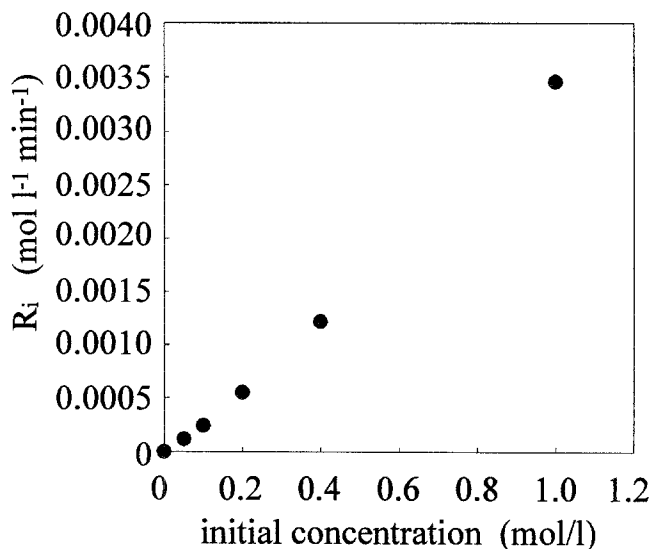


Fig. 6. R_i plotted against the initial concentrations of 2,4-DHMP. Reaction conditions: temperature 70°C; NaOH/2,4-DHMP molar ratio 0.2

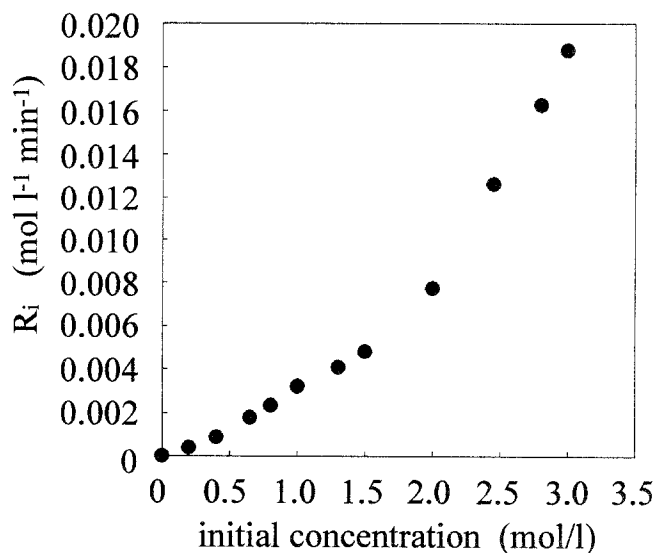


Fig. 8. R_i plotted against the initial concentrations of THMP. Reaction conditions: temperature 60°C; NaOH/THMP molar ratio 0.4

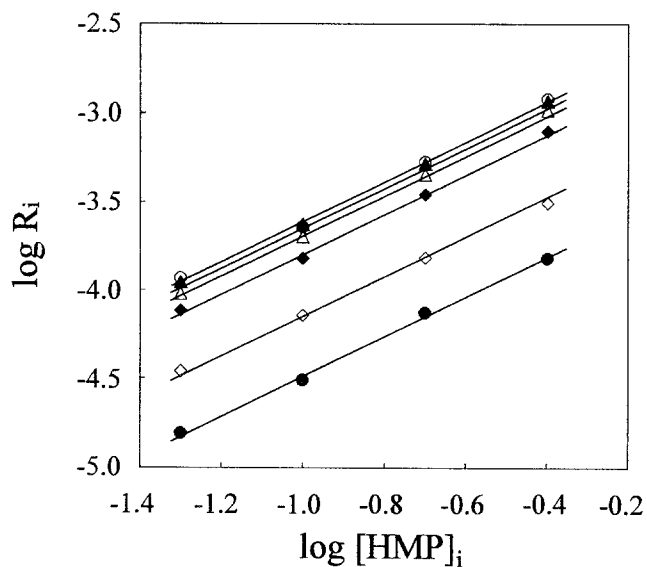


Fig. 7. $\log R_i$ plotted against $\log [2,4\text{-DHMP}]_i$. Reaction conditions: temperature 70°C; NaOH/2,4-DHMP molar ratio: filled circles, 0; open circles, 0.1; filled triangles, 0.3; open triangles, 0.5; filled diamonds, 0.7; open diamonds, 1.0

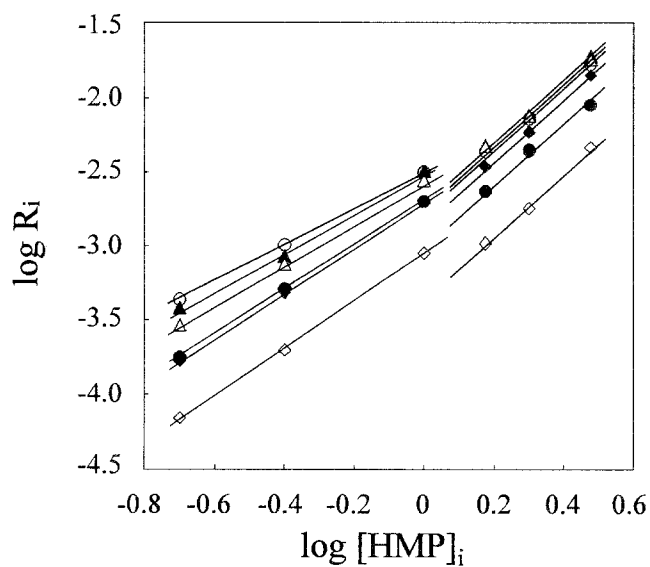


Fig. 9. $\log R_i$ plotted against $\log [THMP]_i$. Reaction conditions: temperature 60°C; NaOH/THMP molar ratio: filled circles, 0; open circles, 0.2; filled triangles, 0.4; open triangles, 0.6; filled diamonds, 0.8; open diamonds, 1.0

nearly the same slope of 1.1 (± 0.01). Thus, it can be said that the order of this reaction is 1.1. It can also be said that two or more reactions involving unimolecular and bimolecular reactions take place simultaneously as the rate-determining step.

Order of reaction of the self-condensation of THMP

Regarding the order of reaction of the self-condensation of THMP, no linear relations were observed between R_i and $[THMP]_i$, as shown in Fig. 8. Thus, it can be said that the self-condensation of THMP is not first order, contrary to

Jones's report. Figure 9 shows $\log R_i$ versus $\log [THMP]_i$ plots. Surprisingly, the relations changed at a THMP concentration of 1.0–1.5 mol/l. In the region of $[THMP]_i$ higher than 1.5 mol/l, all lines in Fig. 9 show the same slope (2.0). Thus, it can be said that the order of reaction is 2.0 in this high concentration region. Therefore, the rate-determining step is ascribed to some bimolecular reactions in this high THMP concentration region. In the region of $[THMP]_i$ lower than 1.0 mol/l, too, linear relations can be observed. However, the slope of the line (i.e., the order of reaction) varies with the NaOH/THMP molar ratio. Figure 10 shows the variation in the order of reaction in this low concentration region with the NaOH/THMP molar ratio. Because the

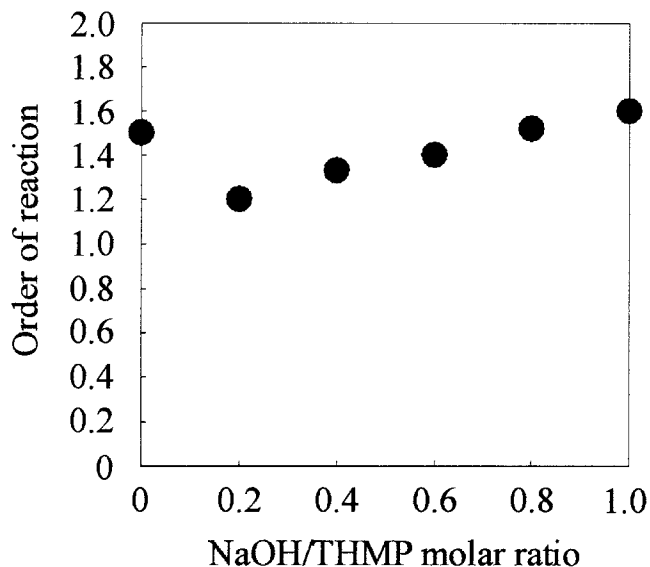


Fig. 10. Variation of the order of reaction with the NaOH/THMP molar ratio in the low $[\text{THMP}]_i$ region. Reaction conditions: $[\text{THMP}]_i < 1.0 \text{ mol/l}$; temperature 60°C

values of the order of reaction lie between 1.2 and 1.6, it is thought that both unimolecular and bimolecular reactions take place simultaneously as the rate-determining step in this low-THMP concentration region.

Conclusions

The order of reactions of the self-condensations of 2,4-DHMP and THMP were determined through investigation of the relations between the initial rates of reactions and the initial concentrations of reactants. The order of reaction for 2,4-DHMP was found to be 1.1 and unrelated to the NaOH/

2,4-DHMP molar ratio. In the case of THMP, the order of reaction was found to change with the reaction conditions. In the region of the initial concentration of THMP below 1.0 mol/l , the order of reaction changed with the NaOH/THMP molar ratio, and the values were between 1.2 and 1.6. In the region of the initial concentration of THMP above 1.5 mol/l , the order of reaction was 2.0, which did not change with the NaOH/THMP molar ratio. These findings, together with the previous findings reported by us on the self-condensations of 2-HMP and 4-HMP, clearly indicate that the kinetics changes with the species of reactant and in some case with the reaction conditions.

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