

Kinetics on Cocondensation between Phenol and Urea through Formaldehyde I.

Pseudo-first-order reaction of monomethylolphenol and urea*¹

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フェノールとユリアのホルムアルデヒドによる共縮合反応の動力学 (第1報)

モノメチロールフェノールとユリアの擬一次反応*¹

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フェノール-ユリア共縮合樹脂の生成反応の解析を目的として、2-および4-ヒドロキシベンジルアルコールとユリアの反応の動力学を検討した。逆相クロマトグラフィーによりヒドロキシベンジルアルコールと反応生成物のヒドロキシベンジルユリアが分離することを利用して両者のピーク比を得、これをC-13 NMR 測定の結果と比較して定めた換算係数を用いることにより両者のモル濃度の比を求め動力学解析を行った。ユリアを大過剰に用いると反応は、擬一次反応に従うことが判明し、種々の反応条件下で反応速度定数を求めたところ、一般に4-ヒドロキシベンジルアルコールの反応性は2-ヒドロキシベンジルアルコールのそれに比べ10倍以上高いことが見出された。擬一次反応定数のpH依存性を検討すると同時に、反応性に及ぼす酸触媒の種類の影響を検討したところ、酢酸亜鉛と硫酸の混合触媒を用いると2-ヒドロキシベンジルアルコールの反応性が他の酸触媒に比べて2倍程度高まることが判明した。

The kinetics of the reactions of methylolphenols and urea were investigated using 2- and 4-hydroxybenzyl alcohols. The high-performance liquid chromatography (HPLC) using a reverse-phase column gave a clear separation between methylolphenols and hydroxybenzylureas. The molar ratios of hydroxybenzylureas to the corresponding methylolphenols in reaction mixtures were obtained from the ratios of peak areas of the chromatograms by using transfer factors corrected by quantitative ¹³C-NMR (carbon 13 nuclear magnetic resonance) measurements. The reactions of 2- and 4-hydroxybenzyl alcohols with excessive amounts of urea were found to follow the pseudo-first-order reaction. It was found that the pseudo-first-order rate constant for the formation of 4-hydroxybenzylurea is at least ten times greater than that of 2-hydroxybenzylurea. The reactivities of the two hydroxybenzyl alcohols also were investigated in terms of pH and kinds of acids used as catalysts. The pH dependencies of the pseudo-first-order rate constants were represented by linear equations in terms of hydrogen ion concentrations. It was found that the reactivity of 2-hydroxybenzyl alcohol is enhanced considerably by a zinc acetate/sulfuric acid system.

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1. INTRODUCTION

Combining urea into phenol-formaldehyde (PF) resins as true copolymers would bring together the durability of PF resin with the low cost of urea-formaldehyde (UF) resin. Minimum effort has been directed to developing this type of resin system heretofore because of the basic incompatibility of the curing properties of the two resins. Water-soluble PF resins are normally cured in the alkaline state, whereas urea-formaldehyde resins are cured in the acidic state. In a previous work, bridging between PF and UF resins by reactions under acidic conditions was detected by ^{13}C -NMR (carbon 13 nuclear magnetic resonance) spectroscopy.^{1,2)}

Our recent works has resulted in the isolation of the basic cocondensation products of methylolphenol and urea.^{3,4)} Several new cocondensed compounds and cocondensed resins have been identified and verified for the first time by ^{13}C -NMR spectroscopy. These results will provide a scientific and technological basis for the development of long-sought cocondensed phenol-urea-formaldehyde resins. There is every expectation that these co-condensation products could lead to many innovative application if the effects of the reaction conditions on kinetics were determined.

When these copolymers are synthesized from polymethylolphenols and urea, *o*- and *p*-methylol groups will react with urea simultaneously. Therefore, these cocondensations are considered to involve two different reactions: namely, concurrent or competitive reactions. The chemical structures of the copolymers were influenced greatly by the differences of the reactivities between *o*- and *p*-methylol groups.⁵⁾

This paper discusses the establishment of the analytical method to determine the chemical kinetics of cocondensation using two model compounds, 2-hydroxybenzyl alcohol (*o*-methylolphenol) and 4-hydroxybenzyl alcohol (*p*-methylolphenol). Furthermore, the effects of acidity (pH) and kinds of acids used as catalysts on the cocondensations are discussed.

2. EXPERIMENT

2.1 Reaction of urea with 2- and 4-hydroxybenzyl alcohols

Industrial grade urea and reagent grades 2- and 4-hydroxybenzyl alcohols (Aldrich Chemical Company, Inc.) were used. Several reactions were performed by changing the reaction conditions. Each hydroxybenzyl alcohol (1.0 g, 0.0081 mol) and urea (10.0 g, 0.17 mol) were dissolved in 200 ml of water. The mixtures were adjusted to the desired pH levels by using sulfuric acid, hydrochloric acid, nitric acid acetic acid, oxalic acid, citric acid, and zinc acetate/sulfuric acid. The molar concentrations of the hydroxybenzyl alcohols and urea were maintained the same through all experiments. The mixtures were put in three-necked flasks equipped with condensers and stirrers, and maintained at 80°C. Each pH was adjusted during the reaction by sodium hydroxide or a corresponding acid, and a sample was taken every 10 min and freeze-dried after neutralizing.

2.2 ^{13}C -NMR measurement

Each freeze-dried sample was dissolved in pyridine-*d*₅, and its quantitative NMR spectrum was obtained with an AC-P 300 spectrometer (Bruker) at a frequency of 75.0 MHz and a pulse delay of 4 sec with inverse decoupling of the proton. Quantitative data were based on integration values. Chemical shifts were calculated by defining the center of three signals of pyridine-*d*₅, that appeared in the upper magnetic field at 123.6 ppm.

2.3 High performance liquid chromatography

Each dried sample was dissolved in a mixture of water and acetonitrile, and analyzed by a liquid Chromatograph ALC/GPC with R-401 Differential Refractometer (Waters Associates). One reverse phase column, Zorbax CN (Du Pont), was run using the mixture of water-acetonitrile (8/2 v/v for the reaction of 2-hydroxybenzyl alcohol and 8.5/1.5 for that of 4-hydroxybenzyl alcohol). The flow rates were 0.5 ml/min. Quantitative analyses were based on peak areas.

3. RESULTS AND DISCUSSION

3.1 Analysis of reactions of monomethylolphenols and urea

The reaction of monomethylolphenol with urea under acidic conditions involves two kinds of condensations: one is cocondensation, and the other is self-condensation of the methylolphenol. If an excessive amount of urea is employed, the self-condensation of the methylolphenol will be suppressed, and the condensation will dominate the reaction to produce hydroxybenzylurea derivatives.

In a previous report,¹⁰ gel-permeation chromatography was used to analyze the reactants of urea and 2-hydroxybenzyl alcohol or 4-hydroxybenzyl alcohol. However, the separation of chromatograms was too poor to be applied in the determinations of chemical kinetics. On the other hand, ¹³C-NMR spectroscopy was powerful enough to determine kinetic data.¹¹ However, the quantitative measurements of ¹³C-NMR require many accumulation times and are not very available for kinetic works. During the course of finding other analytical methods, high-performance

liquid chromatography (HPLC) using a reverse-phase column was found to show a clear separation of the reaction mixtures.

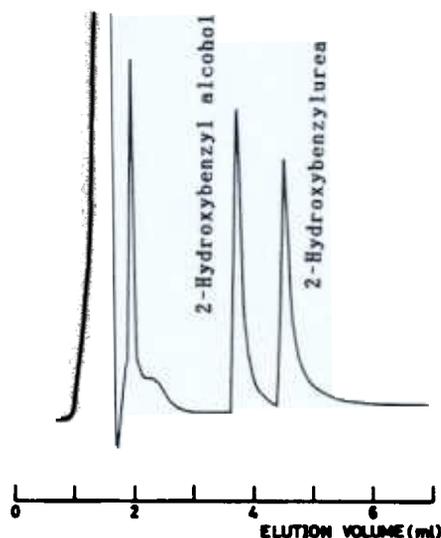


Fig. 1. Liquid chromatogram of the reaction mixture of 2-hydroxybenzyl alcohol and an excessive amount of urea.

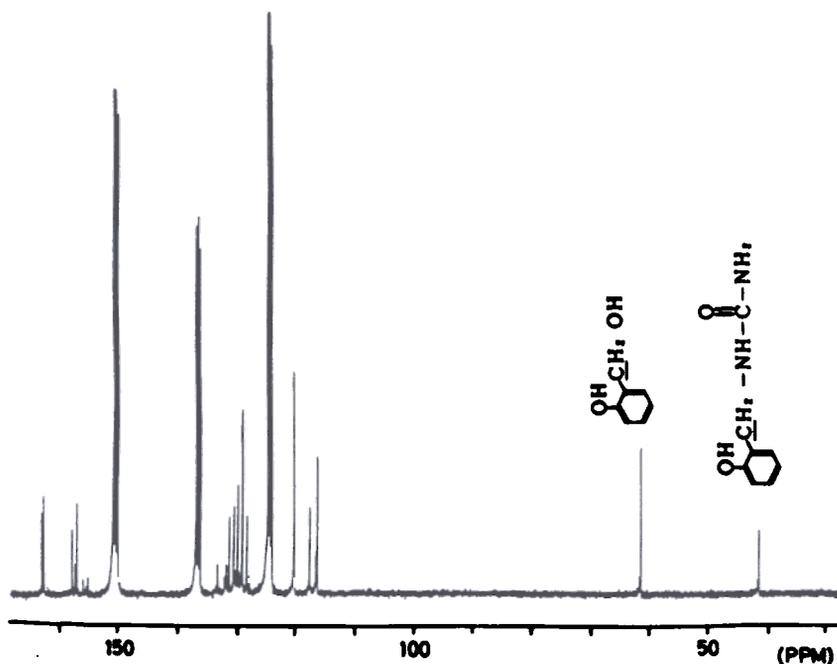


Fig. 2. ¹³C-NMR spectrum of the reaction mixture of 2-hydroxybenzyl alcohol and an excessive amount of urea.

Note: The same sample as used in Fig. 1 was measured.

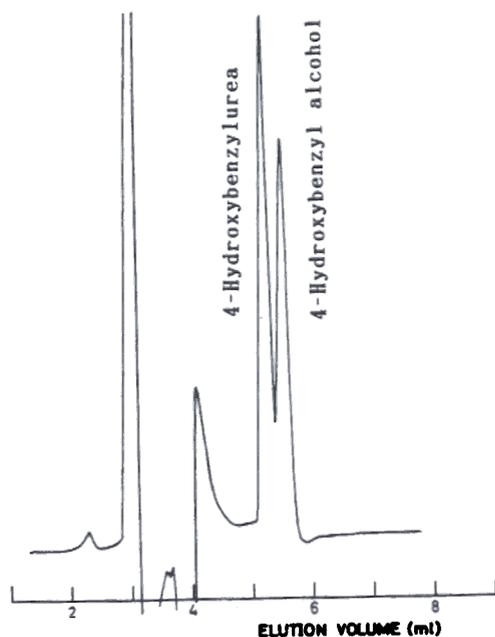


Fig. 3. Liquid chromatogram of the reaction mixture of 4-hydroxybenzyl alcohol and an excessive amount of urea.

Figure 1 shows the chromatogram of one of the reaction mixtures of 2-hydroxybenzyl alcohol and an excessive amount of urea. A good separation of the cocondensed product, 2-hydroxybenzylurea, from the starting compound, 2-hydroxybenzyl alcohol, is observed. In the ^{13}C -NMR spectrum of the same sample (Fig. 2), the formation of 2-hydroxybenzylurea was identified by the presence of the signal at 40.5 ppm.²⁰ Furthermore, the formation of self-condensation with methylolphenol was denied by the absence of a signal at about 36 and 30 ppm.^{6,7}

Figure 3 shows the chromatogram of the reaction mixture of 4-hydroxybenzyl alcohol and an excessive amount of urea. A good separation between the starting compound and the product is recognized. The ^{13}C -NMR analysis confirmed the formation of 4-hydroxybenzylurea because a signal due to the cocondensed methylene carbon was observed at 44.2 ppm.²¹ It also excluded the occurrence of self-condensation with the methylolphenol because of the absence of signals in the magnetic field between 30 and 42 ppm as shown in Fig. 4.^{6,7}

3.2 Determination of pseudo-first-order rate constant

From the results in the previous section, it can be

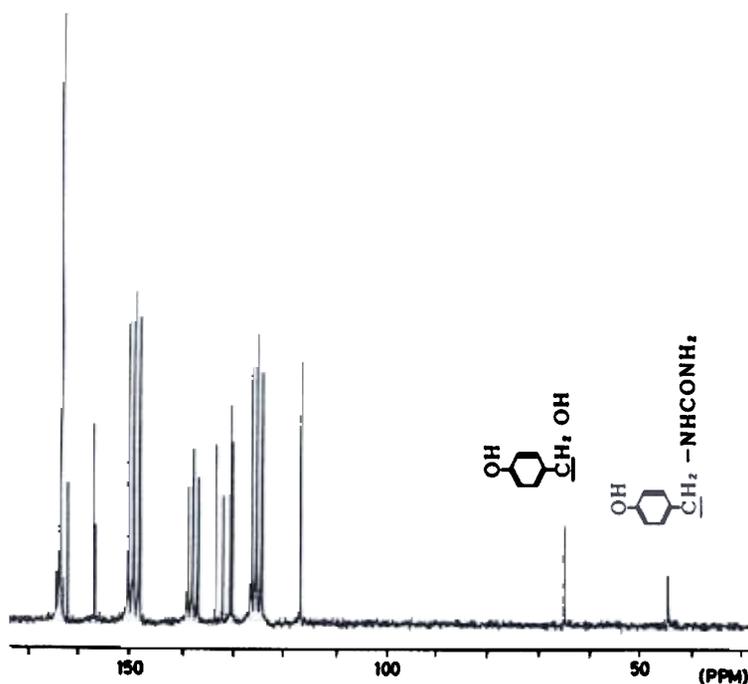
said that the suppression of the self-condensation of methylolphenols was achieved. Therefore, the cocondensations were suggested to follow the pseudo-first-order partly because the concentration of urea can be considered to have stayed constant during the reaction by employing an excessive amount of urea.

The equation of integral form for the pseudo-first-order reaction can be written as:

$$-kt = \ln ([\text{MP}]_t / [\text{MP}]_0),$$

where $[\text{MP}]_0$ is the initial molar concentration of methylolphenol, $[\text{MP}]_t$ is the molar concentration of methylolphenol at the reaction time of t , and k (min^{-1}) is the pseudo-first-order rate constant. Therefore, if the reaction follows the pseudo-first-order, the plot of $\ln ([\text{MP}]_t / [\text{MP}]_0)$ against reaction time will give a straight line, and the slope will indicate the rate constant.

The data required for the kinetics were obtained by the HPLC analyses of the reactants in the process of reaction. However, the peak intensities of HPLC generally are dependent on the sensitivities of the compounds to be analyzed. On the other hand, it is accepted that the relative ratios of signal intensities in quantitative ^{13}C -NMR spectra represent the molar ratio, and the quantitative errors are considered to be within 5% because measurements are performed with enough of a pulse delay time of 4 sec with the inverse decoupling of the proton. For example, a methylene carbon of 4-hydroxybenzyl alcohol gave a signal at 64.7 ppm, and a methylene carbon of 4-hydroxybenzylurea gave one at 44.2 ppm as shown in Fig. 4. Therefore, the ratio of intensities of these two signals indicates that the molar ratio of the two compounds is within a 5% error. The quantitative data between the HPLC and the NMR analyses, which were averages of four measurements, are compared in Table 1. The ratio of 4-hydroxybenzylurea/4-hydroxybenzyl alcohol was 0.96 in the NMR analysis, and 1.27 in the HPLC analysis for the same sample. Therefore, the transfer factor to obtain the molar ratio from HPLC data was determined to be 0.76 (0.96/1.27). Thus, the molar ratio can be obtained by multiplying the HPLC ratio by the transfer factor. For the ratio of 2-hydroxybenzylurea/4-hydroxybenzyl alcohol, it also was determined to be 0.72 as shown in Table 1. It is noted that these transfer factors always include quantitative errors within 5%, and that they are applicable



^{13}C -NMR spectrum of the reaction mixture of 4-hydroxybenzyl alcohol and an excessive amount of urea.

The same sample as used in Fig. 3 was measured.

Table Comparison of quantitative measurements of reaction mixtures of hydroxybenzyl alcohols with urea between HPLC and ^{13}C -NMR spectroscopy.

Kinds of reactions	Ratios of hydroxybenzylurea to hydroxybenzyl alcohol		Transfer ^{a)} factors
	^{13}C -NMR	HPLC	
2-Hydroxybenzyl alcohol	0.78	1.00	0.72
4-Hydroxybenzyl alcohol	0.96	1.27	0.76

Transfer factors are the ratios of HPLC data to NMR data.

only to the solvent systems used in this experiment. Other solvent systems will cause changes of the factors because of the differences of sensitivities.

Thus, the values of $[\text{MP}]_t/[\text{MP}]_0$ required for kinetic calculations could be obtained by assuming that the sum of the concentrations of hydroxybenzyl alcohol and corresponding hydroxybenzylurea has not changed during the reaction.

Figure 5 shows the result of kinetic plots for the reaction of an excessive amount of urea with 2-hydroxybenzyl alcohol as well as that with 4-hydroxybenzyl alcohol. Both reactions were performed under the same conditions of pH 2.5 catalyzed by oxalic acid. As these plots of $\ln ([\text{MP}]_t/[\text{MP}]_0)$

against reaction time gave straight lines, it was concluded that the co-condensations between the methylolphenols and urea well-follow the pseudo-first-order reaction. It also was concluded that the rate constant for the formation of 4-hydroxybenzylurea is at least ten times larger than that for the formation of 2-hydroxybenzylurea.

3.3 Effects of pH on the rate constant of cocondensation

The reaction of 4-hydroxybenzyl alcohol with an excessive amount of urea was performed at various levels of pH at 80°C. Original kinetic plots on the reaction catalyzed with oxalic acid are shown for various levels of pH in Fig. 6. The pseudo-first-order

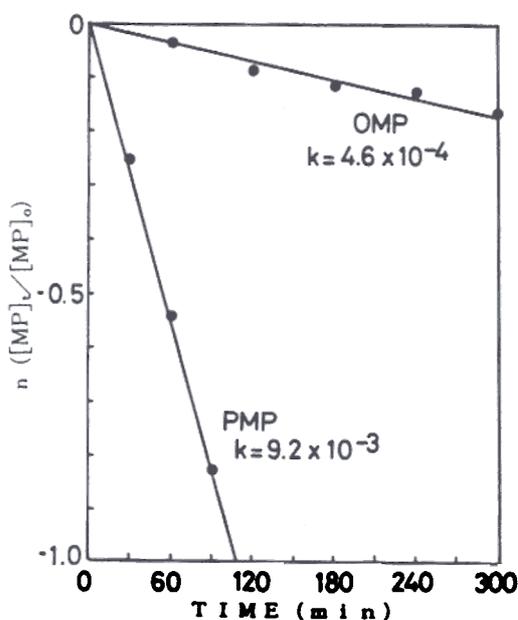
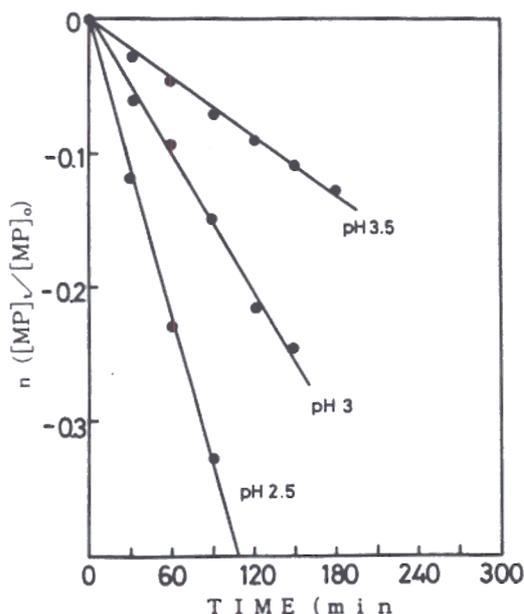


Fig. 5. Kinetic plots for the reactions of methylolphenols with excessive amounts of urea under pH 2.5 catalyzed by oxalic acid.

Legend: $[MP]_0$ is the initial concentration of methylolphenol. $[MP]_t$ is the concentration of methylolphenol at the reaction time of t . OMP is *o*-methylolphenol, and PMP is *p*-methylolphenol. k is the pseudo-first-order rate constant.



rate constants at respective pH levels were determined by the least-square method using data from several reaction times. As the reactivity of 2-hydroxybenzyl alcohol was quite small, which had been suggested in the preceding reports,^{3,4} it required a longer reaction time to obtain kinetic data under weakly acidic condition above pH 3.5. Therefore, the reactions were performed only at 2.5 and 3.0, and the kinetic plots for pH 2.5 and 3.0 are shown in Fig. 7. Both reactions also well-followed straight lines. The pseudo-first-rate constants also were determined by the least-square method using data from several reaction times.

Table 2 summarizes the pseudo-first-order rate constants determined for the formations of 2- and 4-hydroxybenzylureas at various pH levels catalyzed with oxalic acid and sulfuric acid. In the case of the reactions catalyzed with oxalic acid, the following two equations could be derived between the pseudo-first-order rate constants (k_0 and k_p , respectively)

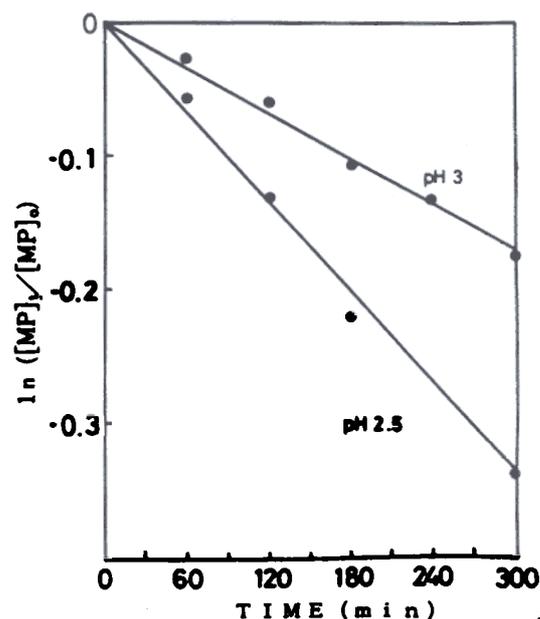


Fig. 7. Kinetic plots for the reactions of *o*-methylolphenol with an excessive amount of urea under the pHs of 2.5 and 3.0 catalyzed by oxalic acid.

Fig. 6. Kinetic plots for the reactions of *p*-methylolphenol with an excessive amount of urea under various pHs catalyzed by oxalic acid.

Table 2. The pseudo-first-order rate constants (k) for the reaction of hydroxybenzyl alcohol and an excessive amount of urea at various pH levels catalyzed with oxalic acid and sulfuric acid.

Kinds of hydroxybenzyl alcohol	Kinds of catalysts	pHs	Rate constant k , min ⁻¹
4-Hydroxybenzyl alcohol	Oxalic acid	2.5	9.2×10^{-3}
		3.0	3.3×10^{-3}
	Sulfuric acid	2.5	9.0×10^{-3}
		3.0	3.0×10^{-3}
2-Hydroxybenzyl alcohol	Oxalic acid		4.6×10^{-4}
			1.9×10^{-4}
	Sulfuric acid	2.5	1.2×10^{-3}
		3.0	5.2×10^{-4}

Table 3. Reactivity ratios (k_o/k_p)^{a)} of 2- and 4-hydroxybenzyl alcohols in the cocondensation with urea at pH 2.5 and 3.0 catalyzed by various acids.

Kinds of acids	pHs	k_o , min ⁻¹	k_p , min ⁻¹	k_o/k_p
Sulfuric acid	2.5	1.2×10^{-3}	9.0×10^{-3}	0.13
Oxalic acid	2.5	4.6×10^{-4}	9.2×10^{-3}	0.05
Hydrochloric acid	2.5	1.3×10^{-3}	9.3×10^{-3}	0.14
Nitric acid	2.5	1.4×10^{-3}	9.5×10^{-3}	0.15
Zinc acetate/sulfuric acid	2.5	2.1×10^{-3}	9.6×10^{-3}	0.22
Sulfuric acid	3.0	5.2×10^{-4}	3.0×10^{-3}	0.17
Oxalic acid	3.0	1.9×10^{-4}	3.3×10^{-3}	0.06
Acetic acid	3.0	9.9×10^{-5}	3.3×10^{-3}	0.03
Citric acid	3.0	6.6×10^{-4}	3.4×10^{-3}	0.20

^{a)} k_o is the pseudo-first-order rate constant for 2-hydroxybenzyl alcohol (*o*-methylolphenol), and k_p is that for 4-hydroxybenzyl alcohol (*p*-methylolphenol).

and the hydrogen ion concentration $[H^+]$.

For the formation of 2-hydroxybenzylurea :

$$k_o = 0.12 \times [H^+] + 6.6 \times 10^{-3}$$

For the formation of 4-hydroxybenzylurea :

$$k_p = 1.0 \times [H^+] + 4.7 \times 10^{-4}$$

The second terms of the equations represent the rate constants when the reactions are employed under the neutral condition of pH 7.0. Because pH is defined as the logarithm of a reciprocal of hydrogen ion concentration, both equations mean that the rate constants increase by almost one order of magnitude with decreases of the pH by one, that is, increases of $[H^+]$ by one order. It is easily realized from values of coefficients of the first terms of these two equations that the reactivity of 4-hydroxybenzyl alcohol is ten times more than that of 2-hydroxybenzyl alcohol at every pH level. It is noted that the absolute values of these rate constants will be changed by other reaction conditions including molar concentration, molar ratio, and temperature.

3.4 Effects of kinds of acids on reactivity of methylolphenols

The effects of types of acids on the reactivities of

methylolphenols in the cocondensation with urea were investigated at the two pH levels of 2.5 and 3.0 using seven kinds of catalysts. The molar concentrations of methylolphenols and urea were kept constant to exclude the effects of concentrations on kinetics. Each reaction well-followed the pseudo-first order within a small error. The average pseudo-first-order rate constants are summarized for seven catalysts at pH 2.5 and 3.0 in Table 3, where k_o is the rate constant for *o*-methylolphenol and k_p is for *p*-methylolphenol. There are not great differences in the reactivity ratio of k_o/k_p among the four catalysts; namely, sulfuric acid, hydrochloric acid, nitric acid, and oxalic acid. However, considerable enhancement of the reactivity of *o*-methylolphenol could be recognized when the mixture of zinc acetate/sulfuric acid was employed as the catalyst. Citric acid enhanced it slightly, and, on the other hand, acetic acid reduced it remarkably.

It is very interesting that the reactivity of *o*-methylolphenol was enhanced by the catalyst system of the zinc acetate/sulfuric mixture, whereas that of *p*-methylolphenol was maintained as almost the same level of other catalysts. The interpretation of the

enhancement depending upon the type of catalyst must be done with care. The formation of the chelates as transient compounds can be considered as occurring between zinc ion and *o*-methylolphenol.⁹⁾ If this transient complex enhances the strength of the benzylic cation, the reactivity of *o*-methylol group will be increased in the reaction with urea. In the present experiments, the chemical equivalent of zinc acetate employed was a half of methylolphenols. If the amount of zinc acetate is varied, more enhancement of the reactivity of the *o*-methylol group may be expected. Furthermore, the investigation of other compounds, including bi-valent metal, will be encouraged.

4. CONCLUSION

The cocondensations of 2- and 4-hydroxybenzyl alcohols with excessive amounts of urea under various acidic conditions were found to follow the pseudo-first-order reaction, and the reactivity of 4-hydroxybenzyl alcohol was approximately ten times greater than that of 2-hydroxybenzyl alcohol. Although great differences in the reactivity of 2-hydroxybenzyl alcohol could not be recognized among most of acid catalysts used in the present experiment, it was enhanced considerably by the catalyst system of the zinc acetate/sulfuric acid mixture. If the reactivity of the *o*-methylol group is so little, many unreacted methylol groups remain in the cocondensed resin, and the cocondensation is terminated at small molecular-weights when the resins are prepared from polymeth-

ylolphenols and urea. Therefore, an investigation on the kinetics of other catalysts, including bi-valent metal, is expected as well as is the synthesis of cocondensed resins using these types of catalysts.

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