

Kinetics on Cocondensation between Phenol and Urea through Formaldehyde III.[†]

Concurrent reactions of monomethylolphenol and urea involving cocondensation and self-codensation^{*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3報)[†]

モノメチロールフェノールとユリアの共縮合と自己縮合の併発反応^{*}

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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、*o*-および *p*-メチロールフェノールとユリアの反応の動力学を検討した。この系の反応は、メチロールフェノールがユリアと共縮合すると同時にそれ自身が自己縮合する併発反応系である。自己縮合と共縮合の反応性の比は式[4]を用い、反応生成物の C-13 NMR による定量結果より得た。水系における *o*-メチロールフェノールの自己縮合の反応速度は、共縮合のおよそ10倍程度であり、反応溶媒に水とジオキサンとの混合系を用いた場合に反応性比が減少した。また、混合溶媒系における *p*-メチロールフェノールの共縮合の反応速度は自己縮合のおよそ4倍程度であることが判明した。

Concurrent reactions involving cocondensation and self-codensation were determined simultaneously in the reactions of *o*- and *p*-methylolphenol, respectively, with urea. The results were as follow:

- (1) The reactivity ratio of self-condensation to cocondensation could be determined by Equation [4] for the concurrent reaction of monomethylolphenol with urea.
- (2) For the reaction of *o*-methylolphenol with urea in water, it was found that the second-order rate constant of the self-condensation due to the formation of a *o,p*-methylene linkage is approximately ten times greater than that of the cocondensation between *o*-methylolphenols with urea. The reaction solvent of the mixture of water and dioxane reduced the reactivity ratio.
- (3) For the reaction of *p*-methylolphenol with urea using a water/dioxane solvent, it was suggested that the rate constant of the cocondensation is approximately four times greater than that of the self-condensation between *p*-methylolphenols.

Keywords: cocondensation, urea/methylolphenols, kinetics, reactivity ratio, C-13 NMR.

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1. INTRODUCTION

In the previous works,^{1,2)} it was confirmed that the cocondensation of *o*- or *p*-methylolphenol (2- or 4-hydroxybenzyl alcohol) with an excessive amount of urea follows a pseudo first-order reaction, and that the reactivity of *p*-methylolphenol is almost ten times greater than that of *o*-methylolphenol. Moreover, it also was found that the reactivity of the *p*-methylol group was approximately ten times greater than that of the *o*-methylol group in the concurrent cocondensation of 2,4,6-trimethylolphenol with urea.

Nevertheless, methylolphenols themselves will react to form self-condensation, when the copolymers are synthesized practically from mixtures of methylolphenols and urea, where the excessive amount of urea can not be employed.^{3,4)} Then, it was considered that the reaction of *o*- or *p*-methylolphenol with urea under acidic conditions might involve self-condensations between methylolphenols besides the cocondensation when the amount of urea was not used excessively. In this case, the chemical kinetics must be determined as the concurrent reactions.

In this paper, the kinetics of the concurrent reactions involving the cocondensations and the self-condensations are determined simultaneously in the reactions of *o*- and *p*-methylolphenol with urea, respectively.

2. EXPERIMENT

2.1 Reaction of *o*- and *p*-methylolphenol with urea

Reagent grade urea, *o*- and *p*-methylolphenol (Tokyo Kasei Kogyo Co., Ltd) were used. Several reactions were performed by changing reaction conditions such as the molar ratio of urea to methylolphenol. For example of an equimolar reaction, *o*-methylolphenol (10.3 g) and urea (5.0 g) were dissolved in 200 ml of water. In this case, each molar concentration was 0.417 mol/l. For some reactions, a mixture of water (100 ml) and dioxane (100 ml) was used as the reaction solvent as well as for one of the reactions of *o*-methylolphenol. The mixture was adjusted to desired pH levels by using sulfuric acid, put into three-necked flask equipped with condenser, and maintained at 80°C with mechanically stirring. The pH of the mixture was adjusted every ten min by using sodium hydroxide or sulfuric acid during the

reaction. A sample for NMR (nuclear magnetic resonance) measurement was taken every ten min and freeze-dried after neutralizing.

2.2 Self-condensation of *o*-methylolphenol

The mixture of *o*-methylolphenol (10 g) and water (200 ml) was reacted at 80°C under pH 2.5 catalyzed with sulfuric acid. The pH adjustment and the preparation of the sample were performed as described in the previous section.

2.3 ¹³C-NMR measurement

Each freeze-dried sample was diluted with pyridine-*d*₅, and its quantitative ¹³C-NMR spectrum was obtained with an AC-P 300 (Bruker) at a frequency of 75.0 MHz, a pulse delay of 4 sec, a flip angle of 45° with inverse decoupling of the proton. Chemical shifts were determined by defining methylene carbon of a methylol group as 61.1 ppm for *o*-methylolphenol or 64.7 ppm for that of *p*-methylolphenol. Quantitative data were based on the integral value of each peak.

3. RESULTS AND DISCUSSION

3.1 Theory of kinetics

In the reactions of *o*- or *p*-methylolphenols with urea, the self-condensations of methylolphenols were considered to take place in addition to the cocondensations between methylolphenols and urea.

Assuming that both condensations followed the second-order, and that each rate constant kept constant during the reaction, the following two equations were derived:

$$-dx/dt = k_1x^2 + k_2xu \quad [1]$$

$$-du/dt = k_2xu. \quad [2]$$

Here,

k_1 : rate constant of the self-condensation of methylolphenol,

k_2 : rate constant of the cocondensation between methylolphenol and urea,

x : concentration of methylolphenol at the reaction time of t ,

u : concentration of urea at the reaction time of t .

From Equations [1] and [2], the linear differential Equation [3] was derived:

$$dx/du = k_1x/k_2u + 1. \quad [3]$$

The solution of Equation [3] is represented as Equation [4]:

$$x = u/(1-K) - U_0^{1-K} (1-a+aK)u^K/(1-K). \quad [4]$$

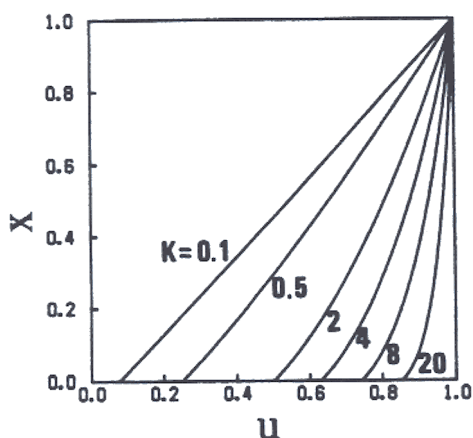


Fig. 1. Theoretical predictions of the concentrations of mono-methylolphenol and urea for concurrent condensations in the equimolar reactions for various reactivity ratios.

Legend: U and X are the molar concentrations of urea and methylolphenol at the reaction time t , respectively.

where

K : is the reactivity ratio of self-condensation to cocondensation (k_1/k_2),

U_0 : is the initial concentration of urea, and

a : is the ratio (X_0/U_0) of initial concentration of methylolphenol (X_0) to that of urea.

A theoretical prediction for the changing of the concentrations of u and x in the case of an equimolar reaction for concurrent condensations can be illustrated as shown in Fig. 1, which was obtained by computer calculations according to given K values using Equation [4].

3.2 Determination of kinetics on concurrent condensations of *o*-methylolphenol and urea

A quantitative ^{13}C -NMR spectrum of the reaction mixture of *o*-methylolphenol and urea is shown in Fig. 2. A signal due to the methylene carbon of self-condensation is observed at about 36 ppm (*o,p*-methylene linkage) and that of cocondensation is observed at about 41 ppm, as well as a methylene

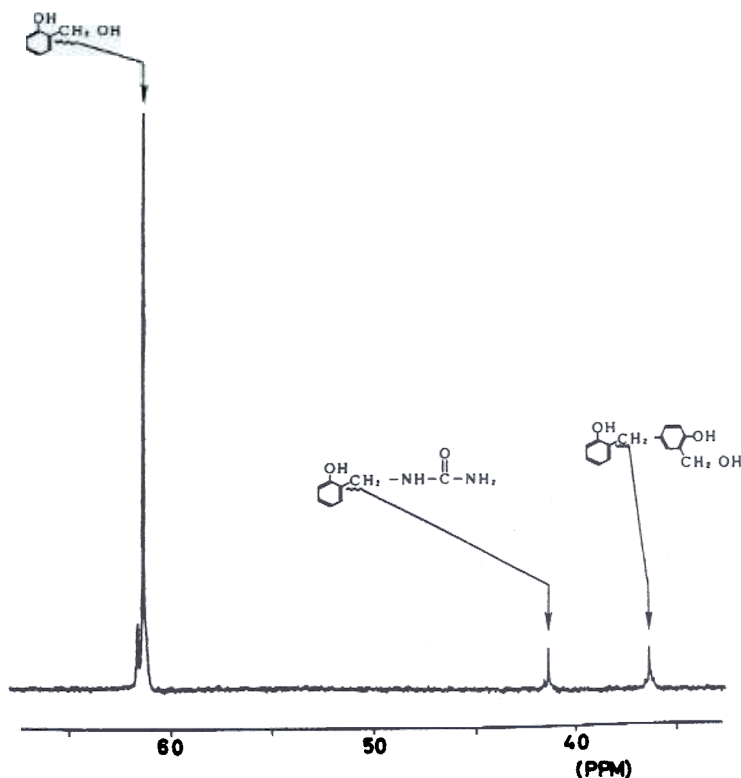


Fig. 2. ^{13}C -NMR spectrum of the reaction mixture of *o*-methylolphenol and urea with the molar ratio of $X_0/U_0=0.5$ at 80°C and pH 2.5 after two hours.

carbon of a methylol group of *o*-methylolphenol at about 61 ppm.¹⁻⁴⁾ Therefore, three kinds of concentrations required for the kinetic calculation can be obtained by NMR data as follows:

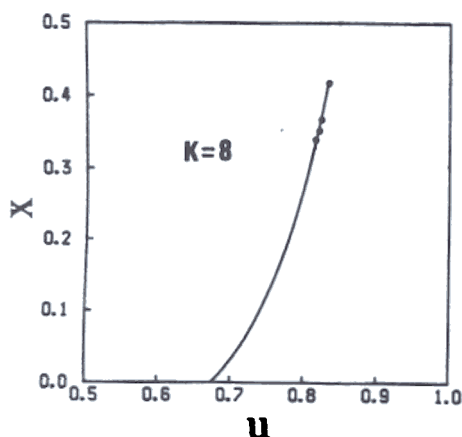
x : integral value of signal at 61 ppm,

$(U_0 - u)$: integral value of signal at 41 ppm, and

$[X_0 - (U_0 - u) - x]$: integral value of signal at 36 ppm.

Because the initial molar concentration of X_0 and U_0 are known from experimental conditions, the molar concentrations of x and u at certain reaction times are obtained from NMR data. Accordingly, the reactivity ratio (K) could be calculated according to Equation [4]. Figures 3 and 4 show the results of kinetic plots for the reaction using a water solvent at pH 2.5 on the theoretical prediction curve at the initial molar ratios ($a = X_0/U_0$) of 0.5 and 0.33, respectively, and the reactivity ratios were found to be approximately 8 and 10, respectively. Therefore, it was suggested that the rate constant of self-condensation due to the formation of a *o,p*-methylene linkage between *o*-methylolphenols is almost ten times greater than that of cocondensation between *o*-methylolphenol and urea. It should be noted, however, that the kinetic data were obtained only in early stages of the reaction. Because a longer reaction time in water solvent produced the precipitates, reliable data required for kinetics could not be obtained by NMR measurements of the solutions.

On the other hand, the reaction solvent of a water/dioxane mixture was found to prevent the formations of precipitates, although the reaction rate decreased



Kinetic plots for the reaction of *o*-methylolphenol and urea at pH 2.5 on the theoretical curve for the reactivity ratio of $K=8$.

Initial concentrations, U_0 and X_0 , are 0.833 mol/l and 0.417 mol/l, respectively. Reaction solvent was water.

U and X are common as in Fig. 1.

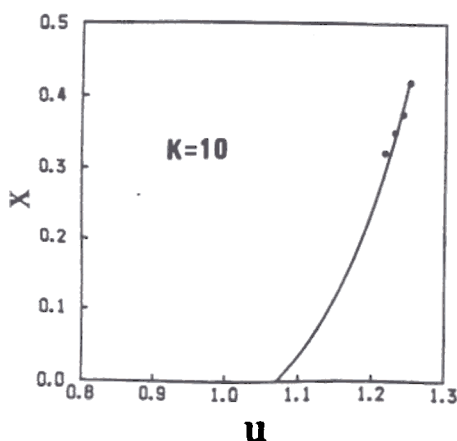


Fig. 4. Kinetic plots for the reaction of *o*-methylolphenol and urea at pH 2.5 on the theoretical curve for the reactivity ratio of $K=10$.

Notes: Initial concentrations of U_0 and X_0 , are 1.25 mol/l and 0.417 mol/l, respectively. Reaction solvent was water.

Legend: U and X are common as in Fig. 1.

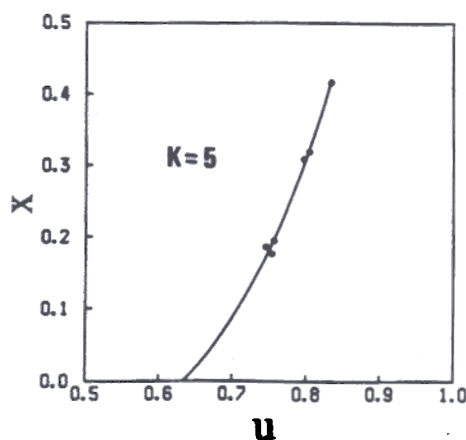


Fig. 5. Kinetic plots for the reaction of *o*-methylolphenol and urea at pH 1.6 on the theoretical curve for the reactivity ratio of $K=5$.

Notes: Initial concentrations of U_0 and X_0 , are 0.833 mol/l, and 0.417 mol/l, respectively. Reaction solvent was a mixture of water and dioxane.

Legend: U and X are common as in Fig. 1.

remarkably when compared with a water-solvent system. Figure 5 shows the kinetic plots for the reaction using this solvent system. Experimental results well-follow the theoretical curve assuming that the reactivity ratio is 5. Therefore, it was concluded that the reactivity ratio for a water/dioxane solvent is almost half of that for a water-solvent. The decreases of the reaction rate and the reactivity ratio will be due to the difference of solvation between water and the water/dioxane solvent.

3.3 Determination of the kinetics on concurrent condensations of *p*-methylolphenol and urea

The solubility of *p*-methylolphenol in water is so small that the reaction mixture was apt to produce precipitates at a very short reaction time even though the reaction was performed with a small concentration. Therefore, a mixture of water and dioxane was employed as a reaction solvent.

One of quantitative ^{13}C -NMR spectra of the reaction mixtures is shown in Fig. 6, where five signals are

observed besides a signal at about 67 ppm due to the methylene carbons of dioxane. The assignments of these signals could be made as indicated in Fig. 6 according to the preceding papers.^{3,4)}

If the formation of a dimethylene ether linkage can be considered as negligible in the initial stage of reaction, three kinds of concentrations required for kinetic calculation using Equation [4] are obtained by NMR data as follows:

x : integral value of signal at 64 ppm,

$(U_0 - u)$: total integral value of signals at 41 and 49 ppm, and

$[X_0 - (U_0 - u) - x]$: integral value of signal at 36 ppm.

Figure 7 shows the kinetic results for the equimolar reaction under pH 3.0, where the experimental changes of x and u are well-identical with the theoretical curve for reactivity ratio of 0.25. The reactivity ratio (K), calculated in accordance with Equation [4], also was estimated as about 0.25 within a small

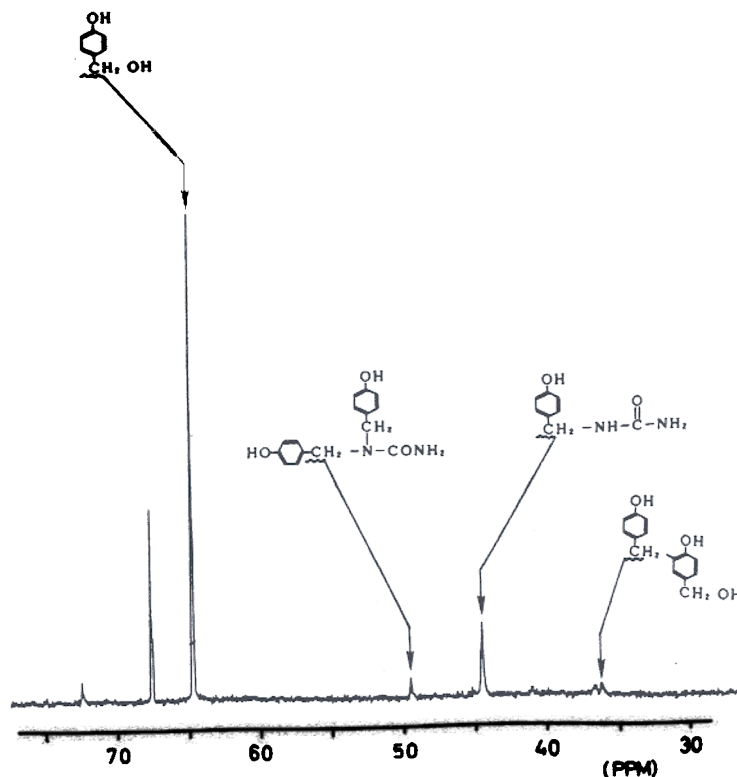


Fig. 6. ^{13}C -NMR spectrum of the reaction mixture of *p*-methylolphenol and urea with the molar ratio of $X_0/U_0=1$ at 80°C and pH 3.0 for after three hours.

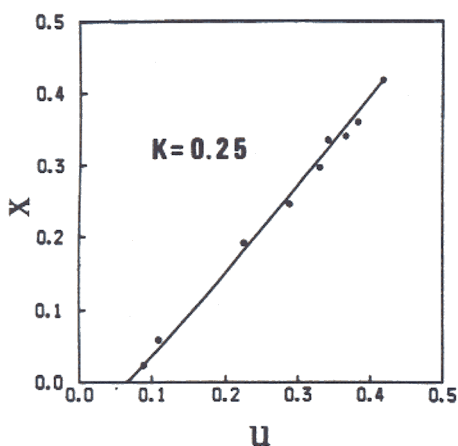


Fig. 7. Kinetic plots for the equimolar reaction of *p*-methylolphenol and urea at pH 1.6 on the theoretical curve for the reactivity ratio of $K=0.25$.

Notes: Initial concentrations of U_0 and X_0 are 0.417 mol/l. Reaction solvent was a mixture of water and dioxane.

Legend: U and X are common as in Fig. 1.

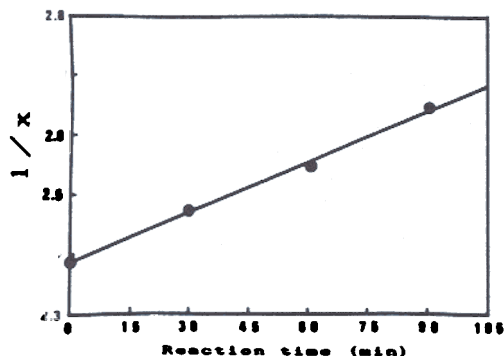


Fig. 8. Kinetic plots for the self-condensation of *o*-methylolphenol at pH 2.5.

Legend: X is the molar concentration of *o*-methylolphenol.

error. Therefore, it was concluded that the rate constant of cocondensation between *p*-methylolphenol and urea is about four times greater than that of self-condensation due to the formation of methylene linkages between *p*-methylolphenols.

3.4 Determination of the rate constants for the self-condensation of methylolphenol

To know the absolute values of the rate constants for the cocondensations, determinations of those for self-condensations were attempted. If the self-

condensations follow the second-order, the integral form of the equation can be written as [5]:

$$1/x = k_1 t + 1/X_0 \quad [5]$$

Figure 8 shows the results of kinetic plots for the reaction of *o*-methylolphenol in a water solvent at 80°C and under pH 2.5. From the slope of the straight line, the rate constant (k_1) was determined as 2.9×10^{-3} (mol⁻¹min⁻¹). Therefore, the rate constant (k_2) for the cocondensation between *o*-methylolphenol and urea was estimate as approximately 2.9×10^{-4} (mol⁻¹min⁻¹), because the reactivity ratio K was determined to be about 10. On the other hand, the reactivity ratio of *p*-methylolphenol was determined for the reaction in the mixture of water and dioxane. Thus, the reported data,⁷ which describes the rate constant for *o*-methylolphenol as being about ten times that of *p*-methylolphenol, were employed for the calculation of the rate constants. Accordingly, assuming that the rate constant (k_1) of self-condensation for *p*-methylolphenol is about 2.9×10^{-4} (mol⁻¹ min⁻¹), that for condensation (K_2) was estimated to be about 1.2×10^{-4} (mol⁻¹ min⁻¹). Considering that the water/dioxane solvent system reduced the reactivity ratio, it was concluded that the rate constant of the cocondensation for *p*-methylolphenol is more than four times that for *o*-methylolphenol.

4. CONCLUSION

The pseudo first-order rate constant for the formation of 4-hydroxybenzylurea was found to be approximately ten times more than that of 2-hydroxybenzylurea as reported in a previous paper.¹¹ Moreover, it also was concluded that the reactivity of *p*-methylol group with urea is almost 10 times more than that of *o*-methylolphenol in the concurrent reaction of 2,4,6-trimethylolphenol with urea.⁹ Therefore, with regard to the reactivity between *o*- and *p*-methylol groups, the results obtained as reported in this paper is in good agreement with those found as reported in the previous papers. Finally, it can be said that this is the first time in the kinetic works on formaldehyde-resin chemistry that the concurrent reactions involving self-condensation and cocondensation were investigated.

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