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

Concurrent cocondensations of 2,4,6-trimethylolphenol with 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2報）[†]

2,4,6-トリメチロールフェノールとユリアの併発共縮合反応[*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，2,4,6-トリ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。この系は，o-およびp-メチロール基が同時にユリアと反応する併発反応系であり，それぞれの素反応を2次反応と仮定し，両者の反応速度定数の比を求めた。使用した酸触媒は，硫酸，塩酸，シュウ酸，硝酸の4種類である。その結果，反応速度の比（o-メチロール基/p-メチロール基）は，4種の触媒で0.066から0.075と決定され，酸触媒による差はほとんど認められなかった。また，硫酸触媒の場合の反応速度の比は，o-メチロールフェノールとp-メチロールフェノールの共存状態で行った競争反応系で求めたそれとほぼ一致した。

The chemical kinetics of the concurrent reactions of 2,4,6-trimethylolphenol with urea, where o- and p-methylol groups reacted simultaneously with urea, were analyzed on four kinds of catalysts: namely, sulfuric acid, hydrochloric acid, nitric acid, and oxalic acid. The results were summarized as follows:

(1) Assuming that each reaction follows the second-order reaction, the reactivity ratio ($K=k_o/k_p$) of the o- to p-methylol group could be obtained from the kinetic plots of Equation [5] within small errors.

(2) The reactivity ratios were determined to be 0.066 to 0.075 by the least-square method for four kinds of acid catalysts.

(3) The reactivity ratio of the pseudo-first-order rate constants obtained by competitive cocondensations under the coexistence of o- and p-methylolphenols with a sulfuric acid catalyst was found to be almost identical with that obtained by the concurrent cocondensation of the trimethylolphenol.

Keywords: cocondensation/urea/methylolphenol, 2,4,6-trimethylolphenol, kinetics, reactivity ratio, catalyst.

1. INTRODUCTION

In previous works,[1,2] an alternating copolymer was synthesized by the reaction of 2,4,6-trimethylolphenol with urea, and cocondensates containing small amounts of self-condensed units between phenols by the reaction of mixtures of polymethylolphenols with urea have been evaluated. When these cocondensates are synthesized from polymethylolphenols and urea, o- and p-methylol groups react with urea simultaneously, although the self-condensations of polymethylolphenols can be suppressed. Therefore, these systems for the cocondensation are considered to involve two concurrent reactions, and the difference of reactivies between o-and p-methylol groups must greatly influence the formation of the cocondensates.[3] For example, polymerization will terminate in a low-molecular-weight region if the reactivity of the o-methylol group is too small when compared with that of the p-methylol group.

Furthermore, in the preceding paper,[4] the analytical method to determine the chemical kinetics, which involves certain quantitative errors, has been established for the cocondensation between methylolphenols and urea. As results, it was found that the cocondensations of 2- or 4-hydroxybenzyl alcohol (o- or p-methylolphenol) with an excessive amount of urea follows the pseudo-first-order reaction, and that rate constant for the formation of 4-hydroxybenzylurea is approximately ten times greater than that of 2-hydroxybenzylurea. In this paper, the difference of reactivity between o- and p-methylol groups is determined not only by analyzing the concurrent cocondensation of 2,4,6-trimethylolphenol with urea, but also by the competitive cocondensations under the coexistence of o- and p-methylol phenols with urea.

2. EXPERIMENT

2.1 Reaction of 2,4,6-trimethylolphenol with urea

Sodium 2,4,6-trimethylolphenate (10.0 g, 0.056 mol) prepared according to Freeman[5] was dissolved in water (200 ml) and acidified to pH 5.0 by acids. After adding urea (50 g, 0.83 mol), the solutions were adjusted to pH 2.5. Sulfuric acid, hydrochloric acid, nitric acid, and oxalic acid were used as catalyst. Each mixture was put in a three-necked flask equipped with a condenser, and maintained at 80°C with mechanical stirring. The pH was adjusted to 2.5 by sodium hydroxide or corresponding acid during the reaction. A sample was taken every ten min, and freeze-dried after neutralizing.

2.2 Reactions of mixtures of o- and p-menthylol-phenols with urea

An excessive amount of urea (6.0 g, 0.1 mol) and equimolar amounts of o- and p-methylolphenols (for each; 0.93 g, 0.0075 mol) were dissolved in 200 ml of water. Each mixture was put in a three-necked flask equipped with a condenser and a stirrer, and reacted at 80°C and pH 3.5 catalyzed with sulfuric acid. The pH adjustment was performed in the same way as described the previous section, and the sample was freeze-dried after neutralizing.

2.3 ¹³C-NMR measurements

Each freeze-dried sample was diluted with D_2O, and its quantitative ¹³C-NMR (carbon 13 nuclear magnetic resonance) spectrum was obtained with an AC-P 300 (Bruker) at a frequency of 75.0 MHz, a pulse delay of 4 sec, and a flip angle of 45° with inverse decoupling of the proton. Quantitative data were based on the integral value of each peak. Chemical shifts were calculated by defining methylene carbon of a p-methylol group as 64.7 ppm or that of a o-methylol group as 61.1 ppm.

2.4 High-performance liquid chromatography (HPLC)

The dried sample was dissolved in a mixture of water and acetonitrile, and analyzed by a liquid Chromatograph ALC/GPC with a R-401 Differential Refractometer (Waters Associates). One reverse phase column, Zorbax CN (Du Pont), was run using the mixture of water/acetonitrile (9/1, v/v). The flow rate was 0.5 ml/min.

3. RESULTS AND DISCUSSION

3.1 Theory of kinetics

The reaction of 2,4,6-trimethylolphenol with urea involves two kinds of cocondensations: namely, one the reaction of the o-methylol group with urea, and the other the reaction of the p-methylol group with urea.

Assuming the reaction of the methylol group with urea follows the second order and each rate constant for the formation of cocondensation is unchanged during the reaction, Equations [1] and [2] can be obtained:

$$dx/dt = k_p[X_0 - x][U_0 - u], \text{ and} \quad [1]$$

$$dy/dt = k_o[Y_0 - y][U_0 - u]. \quad [2]$$

Here, k_p : Rate constant for reaction of the p-methylol group with urea,

k_o : Rate constant for reaction of the o-methylol group with urea,

X_0 : Initial concentration of the p-methylol group,

Y_0 : Initial concentration of the o-methylol group,

U_0 : Initial concentration of urea,

x : Concentration of the reacted p-methylol group at the reaction time of t,

y : Concentration of the reacted o-methylol group at the reaction time of t, and

u : Concentration of reacted urea at the reaction time of t.

From Equations [1] and [2], the linear differential Equation [3] can be derived where K is the ratio of the rate constant, k_o/k_p.

$$dy/dx + Ky/[X_0 - x] = KY_0/[X_0 - x]. \quad [3]$$

The solution of Equation [3] is as following :

$$Y_0 - y = -C(X_0 - x)^K, \quad [4]$$

where C is a constant. Before starting the reaction, $C = -Y_0/X_0^K$ because x and y are zero. Consequently, the ratio of the rate constants : namely, the reactivity ratio, can be represented as Equation [5].

$$K = \log[(Y_0 - y)/Y_0]/\log[(X_0 - x)/X_0]. \quad [5]$$

3.2 Determination of reactivity ratio (K)

Figure 1 shows the ^{13}C-NMR spectrum of the solution of sodium 2,4,6 - trimethylolphenate after acidification. Although the spectrum showed the presence of two small signals because of free formaldehyde at 81 ppm and a methylene linkage between two p-positions at 41 ppm, the presences of two large

signals because of the methylene carbons of a o-methylol group at 61.7 ppm and a p-methylol group at 64.7 ppm, indicated that 2,4,6-trimethylolphenol was considered to be a main component of the solution. Therefore, it was judged that the solution is practically suitable as a starting compound for kinetic work.

The reaction processes of 2,4,6-trimethylolphenol and urea were analyzed with ^{13}C-NMR spectroscopy. For example, Fig. 2 shows an expanded spectra on a higher magnetic field for the reaction mixture catalyzed with sulfuric acid. Each signal was assigned easily to methylene carbons as follows : 64 ppm (p-Ph-$\underline{C}H_2OH$), 61 ppm (o-Ph-$\underline{C}H_2OH$), 44 ppm (p-Ph-$\underline{C}H_2$- NHCONH$_2$), and 41 ppm (o - Ph - $\underline{C}H_2$-NHCONH$_2$), where Ph is a phenolic ring. The signal
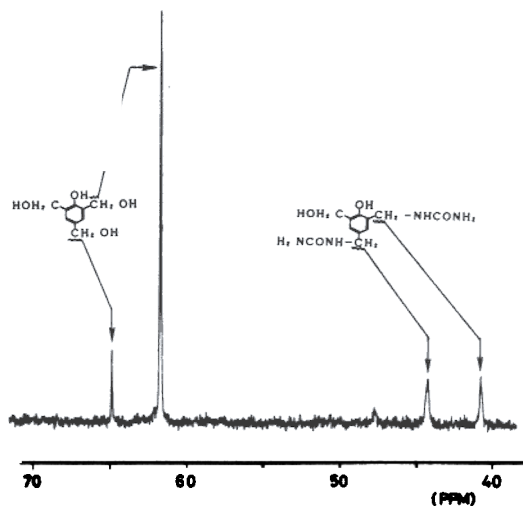

Fig. 2. ^{13}C-NMR spectrum of the reaction mixture of 2,4,6-trimethylolphenol and urea at 80°C under pH 2.5 catalyzed with sulfuric acid.
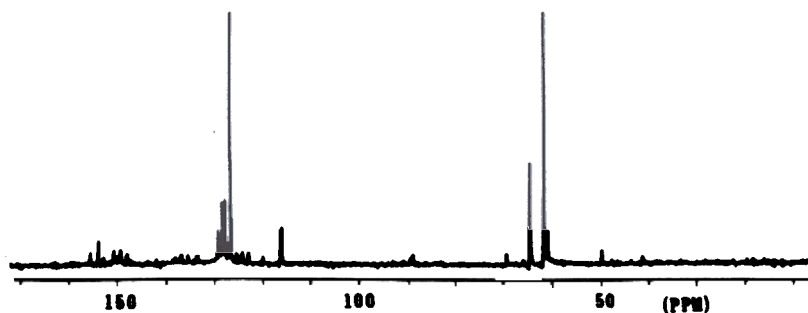

Fig. 1. ^{13}C-NMR spectrum of sodium 2,4,6-trimethylolphenate after acidification in D_2O.

at 47.5 ppm also was assigned to the methylene carbons of methylenediurea,[6] which might be derived from the reaction of free formaldehyde with urea. However, the formation of methylenediurea practically was excluded from the kinetic treatment because of its very small amount.

From the quantitative spectra, X_0, Y_0, x, and y in Equation [5] can be obtained as follows:

x : Integral value of signal at 44 ppm,

y : Integral value of signal at 41 ppm,

(X_0-x) : Integral value of signal at 64 ppm, and

(Y_0-y) : Integral value of signal at 61 ppm.

The starting compound, 2,4,6-trimethylolphenol, was found to already have a small signal at about 41 ppm as an impurity which was derived from self-condensed methylene carbons between two *p*-positions[1] as shown in Fig. 1. Therefore, it was concluded that this
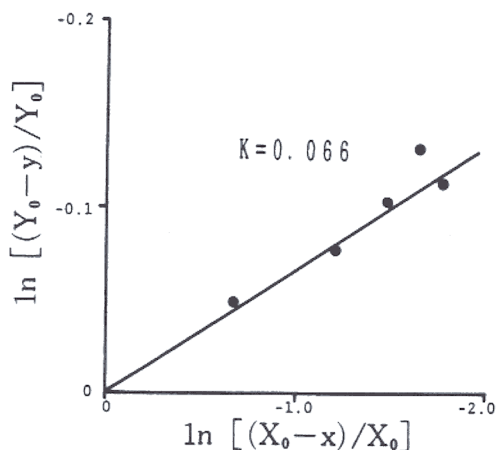

Fig. 3. Kinetic plots of the reaction of 2,4,6-trimethylolphenol and urea at 80°C under pH 2.5 catalyzed with sulfuric acid.

Table 1. Reactivity ratios for the concurrent cocondensation of 2,4,6-trimethylolphenol with urea at pH 2.5 catalyzed with four kinds of acids.

Kinds of acids	Reactivity ratios[a] $(K = k_o/k_p)$
—	0.067
	0.066
	0.073
	0.076

Notes: [a] K is the reactivity ratio. k_o and k_p are the second order rate constants for the *o*- and *p*-methylol groups, respectively.

signal overlapped with the cocondensed methylene carbon (o-Ph-$\underline{C}H_2$-NHCONH$_2$) in the spectra of the reaction mixtures. Consequently, the value of y was obtained by subtracting the intensity of the signal at 41 ppm before starting the reaction, from that after the reaction. The value corrected was determined as 3.8% of the integral value of the initial methylol group (Y_0). If the value of $\log[(Y_0-y)/Y_0]$ is plotted against that of $\log[(X_0-x)/X_0]$ at various reaction times, the ratio (K) of the two rate constants can be obtained from the slope of the straight line as represented by Equation [5]. Figure 3 shows these plots for the reaction catalyzed with sulfuric acid, which resulted in a well fit straight line relationship. The values of K were calculated for the four kinds of reactions different in catalyst by the least-square method, and are summarized in Table 1. It was found that all of the K values were in the range of 0.066 to 0.076. Therefore, the reactivity of the *o*-methylol group was evaluated as one-tenth smaller than that of the *p*-methylol group. It also was found that the differences among the four kinds of catalysts used in this work do not influence greatly the reactivity ratio.

Because an excessive amount of urea was employed, the reactions were considered to follow the pseudo-first-order as found in the previous paper.[4] Figure 4 shows the plots of $\ln[(X_0-x)/X_0]$ and ln
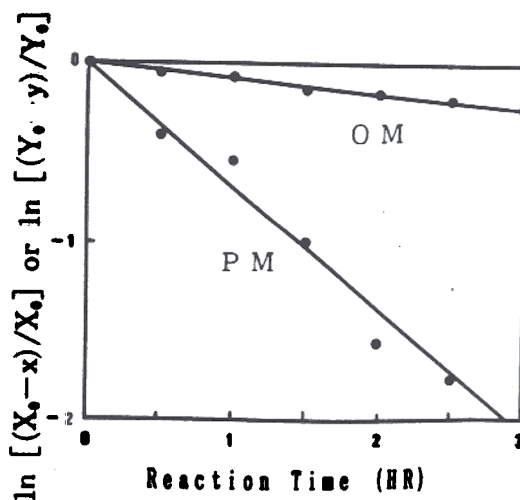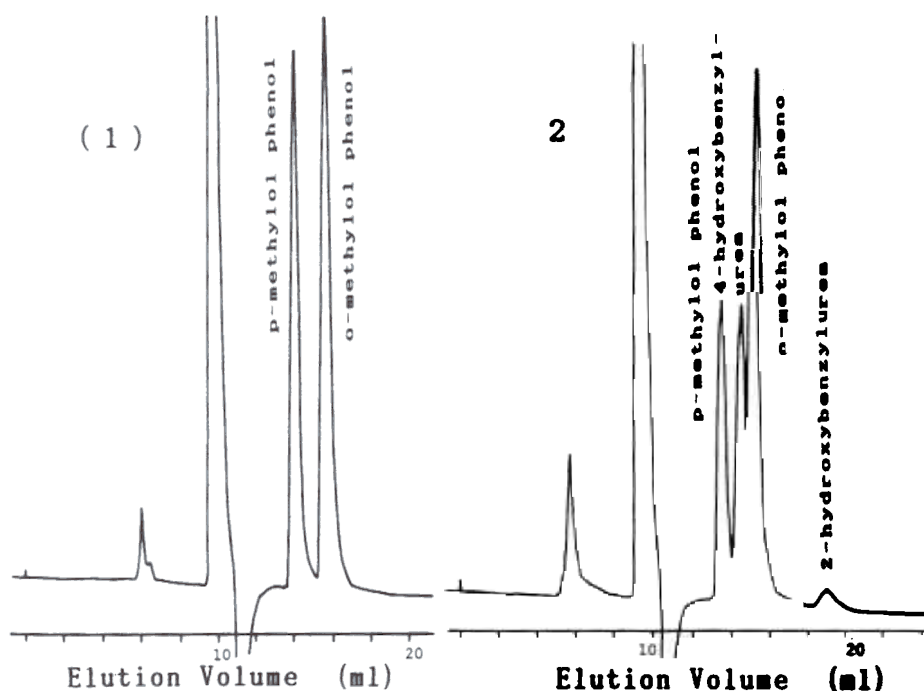

Fig. 4. Kinetic plots for the reaction of 2,4,6-trimethylolphenol and urea at 80°C under pH 2.5 catalyzed with oxalic acid.

Notes: OM : plots for *o*-methylol group, PM : plots for *p*-methylol group.

Liquid chromatgrams of the reaction mixtures of the equimolar amounts of o- and p-methylolphenols with excessive amounts of urea at 80°C under pH 3.5 catalyzed with sulfuric acid.

(1): before reacting, (2): after reacting for 70 min.

$[(Y_0-y)/Y_0]$ against reaction time for the reaction catalyzed with oxalic acid. Both plots were found to follow well a straight line, respectively.

In the preceding paper,[4] the reactivity ratios (K) for the pseudo-first-order reactions at pH 2.5 were evaluated as 0.14 for oxalic acid, 0.13 for sulfuric acid, 0.14 for hydrochloric acid, and 0.15 for nitric acid. When these previous results were compared with the present K values, it was concluded that the reactivity ratio for the trimethylolphenol is approximately a half of that between monomethylolphenols. It is possible that once one of the two methylol groups of the trimethylolphenol reacts with urea, the reactivity of the second methylol group may decrease substantially, which in turn results in the small reactivity ratio of the trimethylolphenol.

3.3 Competitive reactions of o- and p-methylolphenols with urea

The equimolar mixture of o- and p-methylolphenols was reacted with an excessive amount of urea at less than pH 3.5 catalyzed with sulfuric acid. The

^{13}C NMR spectrum of the sample after reacting for 70 min indicated the suppression of the occurrences of self-condensations between methylolphenols. Furthermore, Fig. 5 shows the liquid chromatograms of the mixtures before and after reacting, in which both of the formations of 2- and 4-hydroxybenzylureas are recognized clearly. The kinetic calculations also were performed by the least-square method using the data from several reaction times. The pseudo-first-order rate constant for o-methylolphenol was determined as 0.00060 min^{-1}, and that for p-methylolphenol was 0.0080 min^{-1}. The reactivity ratio was calculated as 0.075, which is almost equal to the value (0.066) obtained for the concurrent reaction of the trimethylolphenol at pH 2.5. From these results, the reaction under the coexistence of o- and p-methylolphenols can be considered to have almost the same effect on the reactivity ratio as the concurrent reaction of the trimethylolphenol.

4. CONCLUSION

The kinetics of the concurrent reactions of 2,4,6-trimethylolphenol with urea were analyzed for four kinds of acid used as catalysts. The reactivity of the p-methylol group was more than ten times that of the o-methylol group. The reactivity ratio $(K=k_o/k_p)$ was almost the same as that obtained by the competitive cocondensation of o- and p-methylolphenols with an excessive amount of urea. Furthermore, no significant differences in the reactivity ratios could be recognized between four kinds of catalysts used in the present work. Accordingly, the investigation to find a catalyst which can enhance the reactivity of the o-methylol group is expected.

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