

Kinetics on Cocondensation of Phenol and Urea

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ABSTRACT

The chemical kinetics on cocondensation between methylolphenols and urea under acidic condition were investigated using 2- and 4-hydroxybenzyl alcohols as well as 2,4,6-trimethylolphenol as model compounds. The reactivity of the cocondensation were compared between o- and p-methylol groups. Moreover, the kinetics on self-condensations of monomethylolphenols and cocondensation between monomethylolphenols and urea were determined simultaneously.

INTRODUCTION

Amino resins such as urea- and melamine-formaldehyde resins have been widely used for manufacturing wood based materials, and taken advantage on bonding of hardwood including tropical hardwood. On the other hand, alkaline-type phenolic resins, resol, have been generally employed as adhesives for softwood. Recently so-called "phenol-melamine cocondensed resins" have become to be widely used for manufacturing of hardwood plywoods in Japan. However, the occurrence of true cocondensation between phenol and melamine or urea has been determined with ¹³C-NMR spectroscopy in the investigations reacting methylolphenols with an excessive amount of urea or melamine (1). Nevertheless, further informations is still

needed to develop the cocondensed adhesives between phenol and urea or melamine in wood industry. Our recent work has resulted in isolation of basic cocondensation products of methylolphenols and urea (2). These new cocondensed compounds have been identified for the first time by ^{13}C -NMR spectroscopy. We have also succeeded in synthesizing an alternative copolymer by the reaction of 2,4,6-trimethylolphenol with urea as well as copolymers which contains a small amount of self-condensed units between methylolphenols (3). These results provide a scientific and technological basis for the development of long sought cocondensed phenol-urea-formaldehyde resins. There is every expectation that these cocondensation products could lead to many innovative applications if the effects of pH, temperature, and molar ratio on the reaction 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 reaction. In these systems, the chemical structures of the copolymers were greatly influenced by the difference of the reactivity between o- and p-methylol groups. This paper will discuss on the three kinds of chemical kinetics on the cocondensation of phenol with urea: 1) concurrent reactions of o- and p-methylol groups of trimethylolphenol with urea; 2) pseudo-first order reactions of monomethylolphenols and urea; and 3) concurrent reactions involving cocondensation of methylolphenols with urea and self-condensation of methylolphenols.

Concurrent Reactions of o- and p-Methylol Groups of Trimethylolphenol with Urea

The reaction of trimethylolphenol with urea involves two kinds of condensations: one is the reaction of o-methylol group with urea and the other is p-methylol group with urea. The reaction mixtures of 2,4,6-trimethylolphenol and urea were analyzed with ^{13}C -NMR spectroscopy as shown in figure 1. The signal at around 41 ppm was already assigned to o-benzyl carbon of cocondensation and that at around 44 ppm to p-benzyl carbon (1,2).

Here, assuming that the reactions of methylol groups with urea follow the second-order, and that each rate constant for the formation of cocondensation is unchanged during reaction, two equations can be obtained.

$$-dx/dt = k_1xu \quad [1]$$

$$-dy/dt = k_2yu \quad [2]$$

where

- k_1 : rate constant for reaction of p-methylol group with urea
- k_2 : rate constant for reaction of o-methylol group with urea
- x : concentration of p-methylol group at reaction time of t
- y : concentration of o-methylol group at reaction time of t
- t : reaction time.

From the equation [1] and [2], the ordinary linear differential equation [3] can be derived.

$$dy/dx = k_2y/k_1x \quad [3]$$

The solution of equation [3] can be represented as the equation [4].

$$K = \log (y/Y_o)/\log (x/X_o) \quad [4]$$

where

$$K = k_2/k_1$$

X_o : initial concentration of p-methylol group

Y_o : initial concentration of o-methylol group.

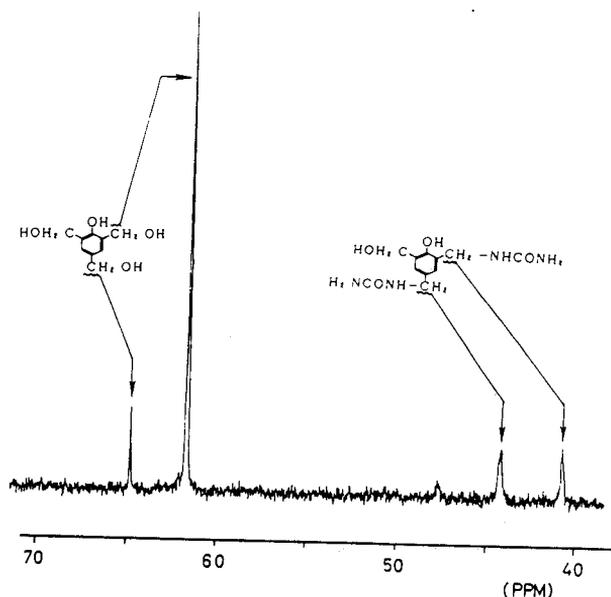


Figure 1. ^{13}C -NMR spectrum of the reaction mixture of 2,4,6-trimethylolphenol and urea at 80 °C under pH 2.5 catalyzed with sulfuric acid.

Consequently, if the values of $\log (y/Y_o)$ are plotted against those of $\log (x/X_o)$ on various reaction times, the reactivity ratio (K) of two rate constants will be obtained from the slope of the straight line as represented by the equation [4]. Figure 2 shows the results of these plots for the reaction catalyzed by hydrochloric acid. The plots well followed a straight line and the values of K were calculated by least square.

Reactivity ratios at pH 2.5 for four kinds of acid used as catalyst are summarized in table 1. The value of K is in the range from 0.066 to 0.075. Therefore, it was concluded that the reactivity of *o*-methylol group is quite low, compared with *p*-methylol group. It was also confirmed that difference of acid catalyst does not influence greatly on the reactivity ratio. In order to find the catalyst enhancing the reactivity of *o*-methylol group, further works were encouraged.

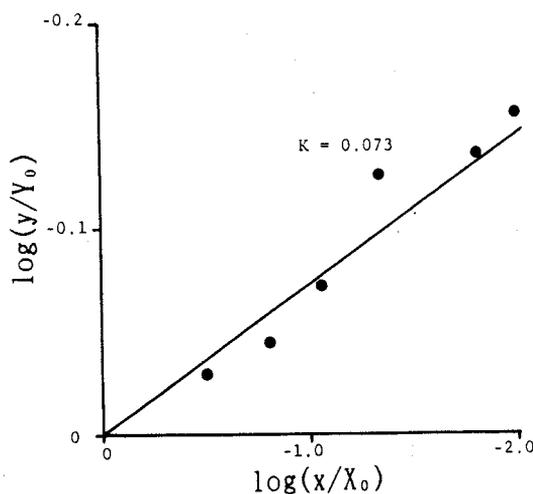


Figure 2. Kinetic plots of the reaction of trimethylolphenol and urea at 80 °C under pH 2.5 catalyzed with hydrochloric acid.

Table 1. Reactivity ratio of *p*- and *o*-methylol groups of trimethylolphenol in concurrent reaction with urea for four kinds of acid.

Kind of acid	Ratio of rate constant $K = k_2/k_1$
Oxalic acid	0.067
Sulfuric acid	0.066
Hydrochloric acid	0.073
Nitric acid	0.076

Pseudo-First Order Reactions of Monomethylolphenols and Urea

The reaction of methylolphenol with urea involves two kinds of condensations: one is cocondensation and the other self-condensation of methylolphenols. If an excessive amount of urea is employed, the self-condensation of methylolphenols will be suppressed and the cocondensation will follow the pseudo-first order. Figure 3 shows the liquid chromatogram of the reaction mixture of *o*-methylolphenol and urea. A good separation of cocondensed product, 2-hydroxybenzylurea, from the starting compound, 2-hydroxybenzyl alcohol, was observed. In the ^{13}C -NMR spectrum (fig. 4), the formation of 2-hydroxybenzylurea was confirmed by the presence of the signal at 40.5 ppm (2). Further, the formation of self-condensation between methylolphenol was denied by the absence of signals at around 36 and 30 ppm (4,5). Figure 5 shows also the liquid chromatogram of the reaction mixture of *p*-methylolphenol and urea. A good separation between starting compound and the product is also recognized. The self-condensation was also denied in its ^{13}C -NMR spectrum as shown in Figure 6. The integral form of the pseudo-first order reaction is represented as the equation [5].

$$-kt = \ln ([\text{Mp}]_t / [\text{Mp}]_0) \quad [5]$$

where

k : rate constant for pseudo-first order reaction

$[\text{Mp}]_0$: initial concentration of methylolphenol

$[\text{Mp}]_t$: concentration of methylolphenol at reaction time of t

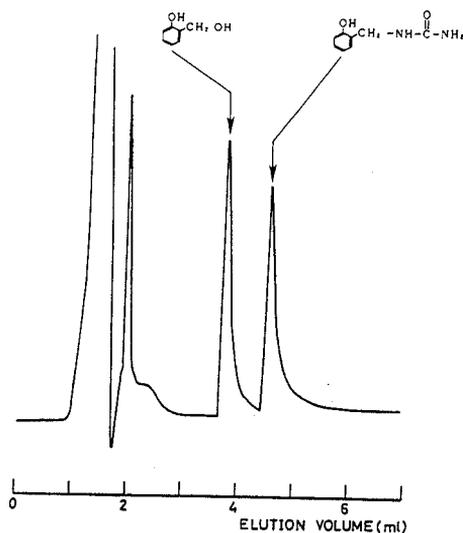


Figure 3. Liquid chromatogram of the reaction mixture of *o*-methylolphenol and urea

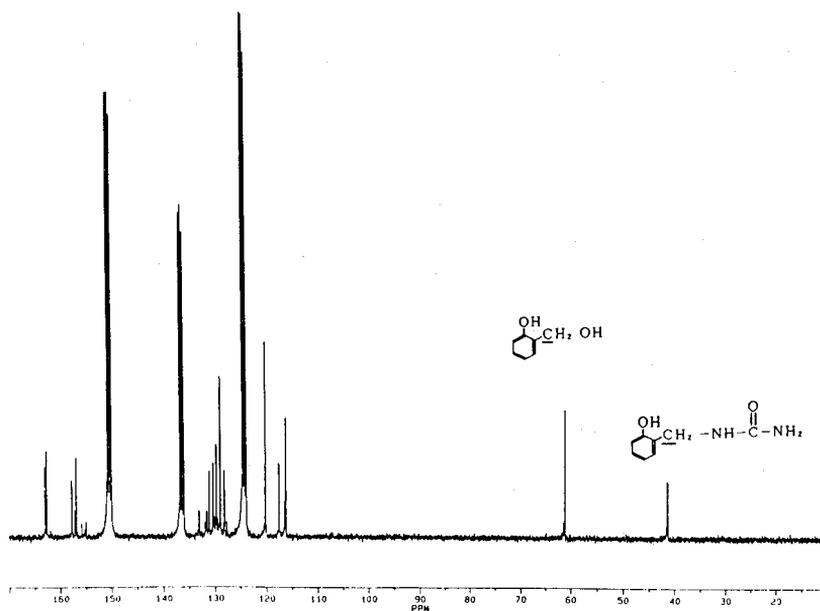


Figure 4. ^{13}C -NMR spectrum of the reaction mixture of o-methylphenol and urea.

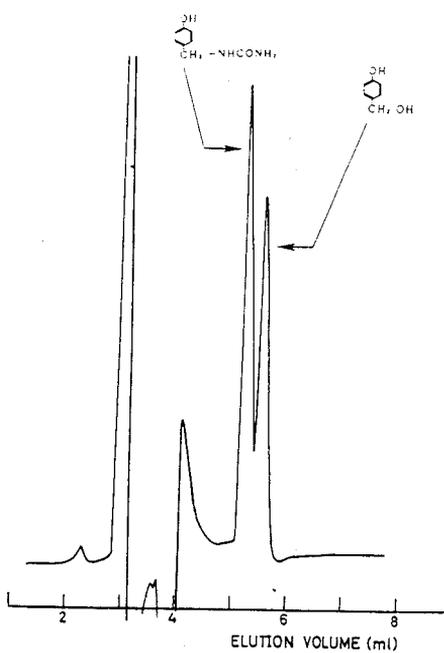


Figure 5. Liquid chromatogram of the reaction mixture of p-methylphenol and urea

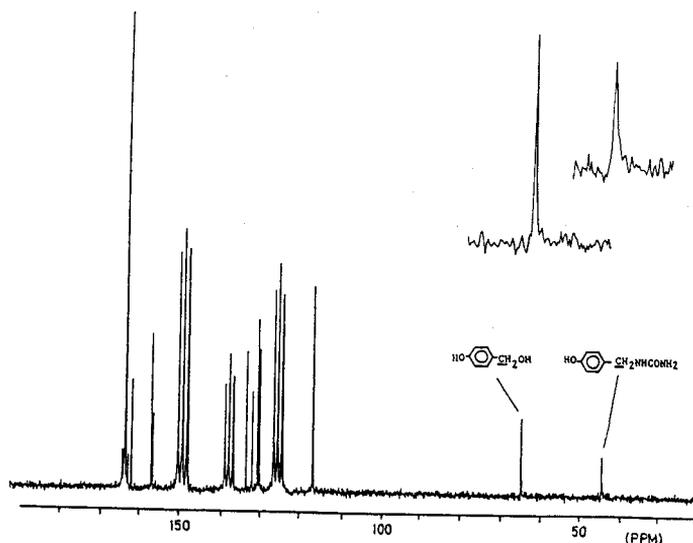


Figure 6. ^{13}C -NMR spectrum of the reaction mixture of p-methylolphenol and urea.

Therefore, the plots of $\ln ([\text{Mp}]_t / [\text{Mp}]_0)$ against reaction time will give a straight line and its slope will indicate the rate constant. Figure 7 shows the plots for the reaction of p-methylolphenol and an excessive amount of urea at various pH levels. Each plot well follows a straight line. Figure 8 also shows results of the reaction for o-methylolphenol. However, the scale is different by one order from the figure 7. It is obvious that the reactivity of p-methylolphenol is larger by almost one order than that of o-methylolphenol.

The reactivity ratios are summarized for seven catalysts at pH 2.5 and 3.0 in table 2. There are not great differences of the reactivity ratio among four catalysts: sulfuric acid, hydrochloric acid, nitric acid, and oxalic acid. However, a considerable enhancement of the reactivity of o-methylolphenol can be recognized when the mixture of zinc acetate and sulfuric acid was employed as catalyst. Citric acid enhanced reactivity slightly. On the other hand, acetic acid reduced it remarkably.

It is very interesting that the reactivity of o-methylolphenol was enhanced by zinc acetate/sulfuric acid system while that of p-methylolphenol was maintained at almost the same level as other catalysts. The interpretation of the enhancement depending upon the type of catalyst must be performed with care. However, the formation of the chelates as transient compounds can be considered between zinc ion and o-methylol group. If this transient complex enhance the strength of the benzyl cation, the reactivity of o-methylol group will be increased in the reaction with urea. Further investigations on other catalysts including bi-valent metal will be encouraged.

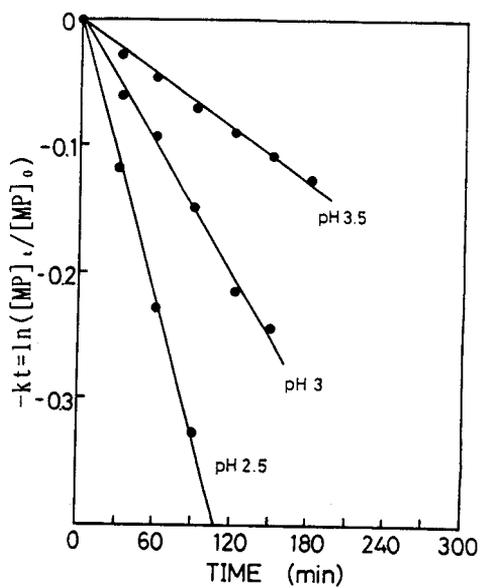


Figure 7. Kinetic plots for the pseudo-first order reactions of p-methylolphenol and urea at various pH.

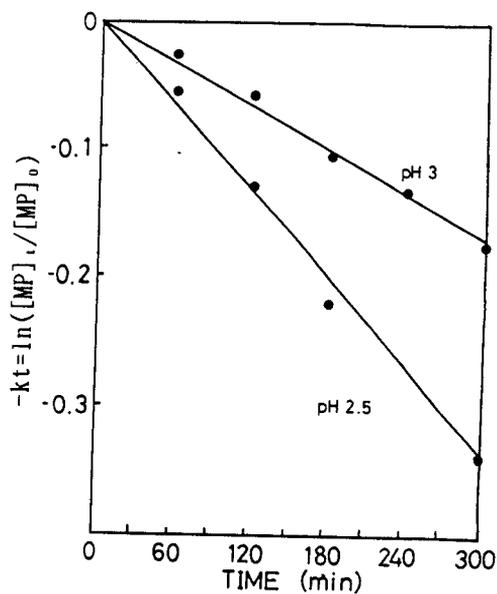


Figure 8. Kinetic plots for the pseudo-first order reactions of o-methylolphenol and urea at various pH.

Table 2. Reactivity ratios of p- and o-methylolphenol in cocondensation with urea for various acids.

Acid	ph	$K = K_2 / K_1$
H ₂ SO ₄	2.5	0.133
(COOH) ₂	2.5	0.141
HCl	2.5	0.137
HNO ₃	2.5	0.147
H ₂ SO ₄ /Zinc	2.5	0.219
H ₂ SO ₄	3.0	0.173
(COOH) ₂	3.0	.0170
CH ₃ COOH	3.0	0.033
Citric acid	3.0	0.202

Concurrent Reactions Involving Cocondensation of Methylol-phenols with Urea and Self-Condensation of Methylolphenols

The reaction of o- or p-methylolphenol with urea under acidic condition might involve self-condensation between methylolphenols besides the cocondensation when urea is not employed excessively. In this case, the chemical kinetics must be determined as the concurrent reactions, competitive reactions.

A quantitative ¹³C-NMR spectrum of reaction mixture of o-methylolphenol and urea is shown in figure 9. A residual signal due to the methylene carbon of self-condensation is observed at around 36 ppm and that of cocondensation is observed at around 41 ppm as well as methylene carbon of methylol group of o-methylolphenol at around 61 ppm. Therefore three kinds of quantity, formations of cocondensation and self-condensation and unreacted methylol group, required for kinetic calculation can be obtained by NMR data.

Here, assuming that both condensations follow the second-order, and that each rate constant keeps constant during reaction, following equations can be derived.

$$-dx/dt = k_1x^2 + k_2xu \quad [6]$$

$$-du/dt = k_2xu \quad [7]$$

where

k_1 : rate constant of self-condensation of methylolphenol

k_2 : rate constant of cocondensation between methylolphenol and urea

x : concentration of methylolphenol at reaction time of t

u : concentration of urea at reaction time of t .

From the equations [6] and [7], the ordinary linear differential equation [8] is derived.

$$dx/du = k_1x/k_2u + 1 \quad [8]$$

The solution of [8] is represented as the equation [9].

$$x = u/(1 - k) - U_0^{1-k} (1 - a + aK)u^K/(1 - K) \quad [9]$$

where

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

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

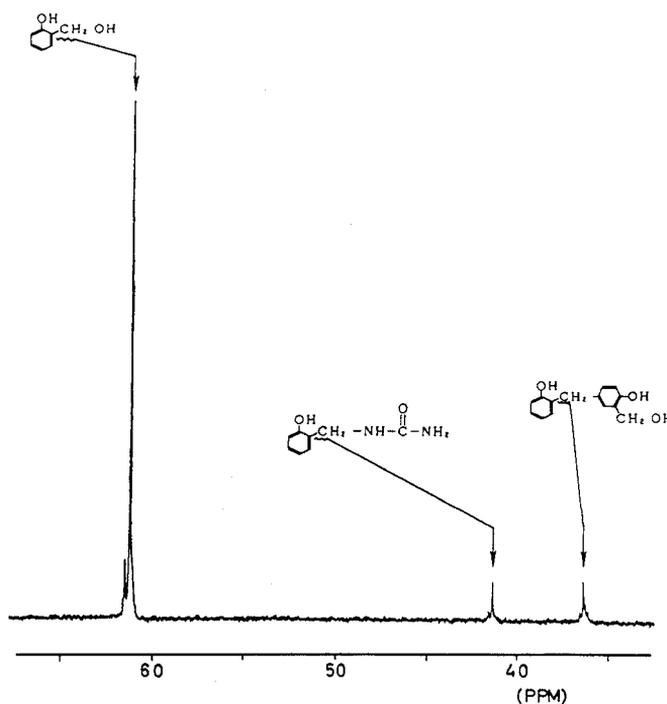


Figure 9. ^{13}C -NMR spectrum of the reaction mixture of *o*-methylol and urea.

Theoretical outline for changing of concentrations in the case of equimolar reaction for the concurrent condensations can be illustrated as shown in figure 10, which was obtained by computer calculation according to given K values using equation [9].

Since both molar concentrations of x and u at a certain reaction time were obtained from NMR data, the ratio (K) of rate constants could be calculated according to the equation [9]. In figure 11, the reactivity ratio was estimated as about 5. Therefore, it was concluded that the rate constant of self-condensation due to the formation of *o,p*-methylene linkage between *o*-methylolphenol is five times larger than that of cocondensation between 2-hydroxybenzyl alcohol and urea.

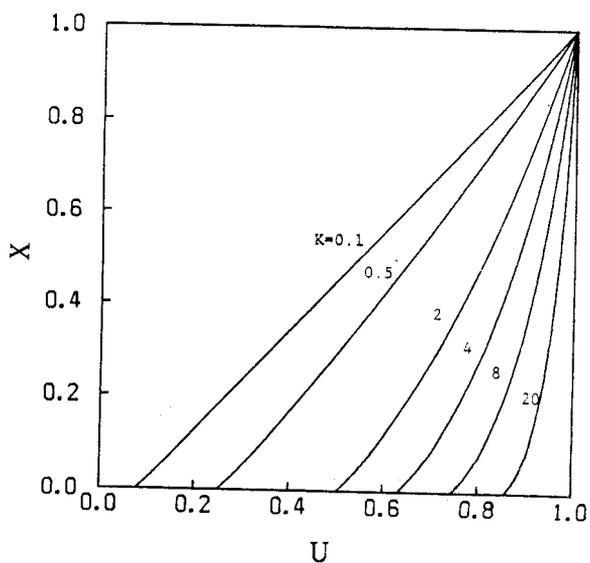


Figure 10. Theoretical prediction for concurrent condensation of monomethylolphenol and urea at equimolar reaction for various reactivity ratios (K).

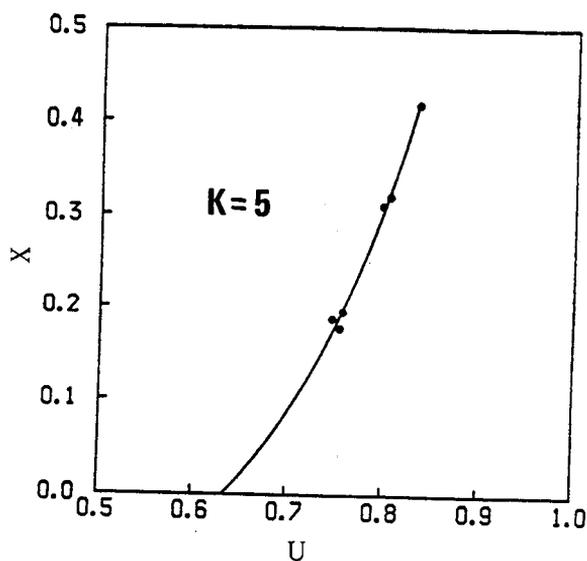


Figure 11. Kinetic plots on the theoretical curve for the concurrent condensations of 0-methylolphenol and urea at the reactivity ratios ($K=5$).
Initial concentration: $U_0 = 0.833 \text{ mol/l}$, $MP_0 = 0.417 \text{ mol/l}$

Figure 12 shows the kinetic results for the equimolar reaction of p-methylolphenol and urea under pH 3.0. The reactivity ratio (K) calculated in accordance with the equation [9] was estimated as about 0.25 within a small error. Therefore, it was confirmed that the rate constant of cocondensation between p-methylolphenol and urea is approximately four times larger than that of self-condensation due to the formation of methylene linkage between p-methylolphenols.

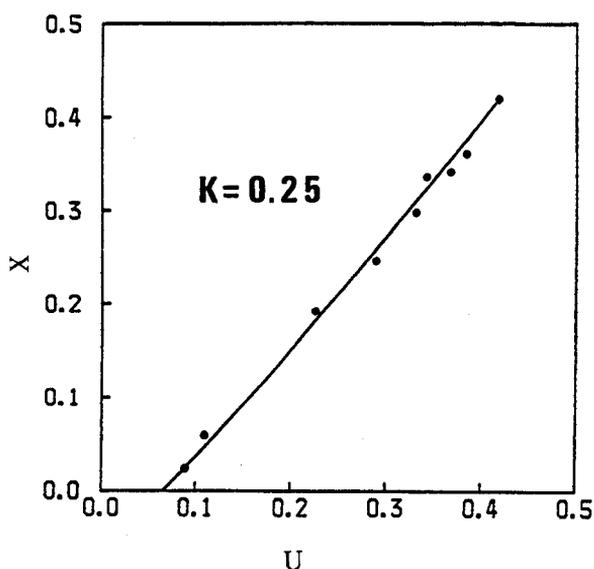


Figure 12. Kinetic plots on the theoretical curve for the concurrent condensations of p-methylolphenol and urea at the reactivity ratios ($K=0.25$).
Initial concentration: $U_0 = 0.417 \text{ mol/l}$, $MP_0 = 0.417 \text{ mol/l}$

CONCLUSION

The results were concluded: (1) the cocondensations of trimethylolphenol with urea were determined as concurrent reactions of o- and p-methylol groups; (2) reactivity ratio of o- methylol group to p-methylol group was 0.66-0.076 for the concurrent cocondensation of 2,4,6-trimethylolphenol and urea; (3) kinds of acid catalyst (sulfuric acid, hydrochloric acid, nitric acid and oxalic acid) did not influence on the reactivity ratio of o- to p-methylol group in the cocondensation with urea; (4) cocondensation of 2- and 4-hydroxybenzyl alcohol with an excessive amount of urea were determined as the pseudo-first order reaction; (5) the

pseudo-first order rate constant for a formation of 4-hydroxybenzylurea was larger by one order than that of 2-hydroxybenzylurea; (6) the reactivity of o-methylolphenol was enhanced by zinc acetate/sulfuric acid catalyst; (7) the reactivity ratio of self-condensation to cocondensation was determined for the concurrent reaction of monomethylolphenols with urea; (8) the rate constant of the self-condensation of 2-hydroxybenzyl alcohol was larger by one order than that of the cocondensation of 2-hydroxybenzyl alcohol and urea; and (9) the rate constant of the cocondensation between 4-hydroxybenzyl alcohol with urea was approximately four times larger than that of the self-condensation between 4-hydroxybenzyl alcohols.

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