Kinetics and mechanism of urea–formaldehyde reaction

B. Raveendran Nair and D. Joseph Francis*
Department of Applied Chemistry, University of Cochin 682 022, India
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The various initial reactions in the urea–formaldehyde reaction have been isolated and the course of the reaction investigated using a quantitative thin-layer chromatographic technique developed for the purpose. The rate constants for the formation of monomethylol urea pass through a minimum in the pH range 4.5–8, thereby proving catalysis by H^+ and OH^-. Whereas the reaction under alkaline conditions leads to methylol formation, acidic conditions favour formation of methylene bridges. It was found that the higher homologues were formed through the methylolation of methylene urea followed by its condensation with free urea and not by the reaction of methylene urea with methylol urea.

Keywords Urea; formaldehyde; kinetics; thin-layer chromatography; condensation polymerization; resins

INTRODUCTION

A study of the literature[1–6] on the reaction of urea with formaldehyde under acidic, alkaline and neutral conditions shows that so far no kinetic investigation has been carried out with a view to isolating the various initial reactions leading to resinification. Because of the complexity of the reaction between urea and formaldehyde, it is not very easy to control the reaction to form expected product alone, so that its formation and dissociation can be studied separately. Such an investigation has now been carried out using the quantitative thin-layer chromatography (t.l.c.) method for the separation and estimation of the reaction products reported earlier[7] and the results are reported here.

EXPERIMENTAL

Materials

Urea (U). BDH, AR grade, recrystallized from water, m.p. 133°C.

Formaldehyde (F). BDH, AR grade aqueous solution (38%) containing less than 2% methanol was used.

Monomethylol urea (MMU). M.p. 110°–111°C.

Dimethylol urea (DMU). M.p. 132°C.

Methylene diurea (MeDU). M.p. 207–208°C.

Monomethylol methylene diurea (MMMeDU) and dimethylol methylene diurea (DMMeDU). These were prepared by standard methods[8].

Dimethylene triurea (DMeTU) and trimethylene tetraurea (TMeTeU). DMeTU, m.p. 243°C, and TMeTeU, m.p. 248°C, were prepared by the method reported earlier[7].

Procedure

The reactions were carried out in a 250 ml four-necked flask fitted with a mercury sealed stirrer, a water condenser, a sensitive thermometer and a vacuum sampling device. The flask was heated using a thermostat to maintain the required temperature within ± 0.1°C. The urea solution at the desired concentration was first introduced into the reaction vessel. After the required temperature was attained, catalyst was added followed by the measured amount of formaldehyde solution, preheated to the required temperature so that the expected volume, concentration and pH of the final reaction mixture was obtained. For reactions involving addition of formaldehyde to methylol derivatives, the formaldehyde was first introduced into the reaction vessel to which the methylol urea was then added. Aliquots were withdrawn using the vacuum sampling device kept in ice-cold water to slow down the reaction. From this unreacted formaldehyde, urea and the products of reaction were estimated[7].

Unreacted formaldehyde alone was estimated by the sulphite method[9] and sum of free formaldehyde and methylols of urea were estimated by the iodimetric method[10], both modified suitably.

Sulphite method. The reaction mixture (5 ml) was pipetted out into a clean 100 ml conical flask. To this was added 5 drops of thymolphthalein indicator (0.1 g of the indicator per 100 ml ethanol) followed by 5 ml of sodium sulphite solution (1 M). The liberated sodium hydroxide was immediately neutralized with a known excess of dilute hydrochloric acid (0.1 N). The excess acid was back-titrated using standard sodium hydroxide solution. The end-point is the appearance of a faint blue colour. A blank was also done under identical conditions. The amount of alkali liberated, equivalent to the free formaldehyde present, was obtained. Thymolphthalein was found to be a better indicator than the commonly used rosolic acid.
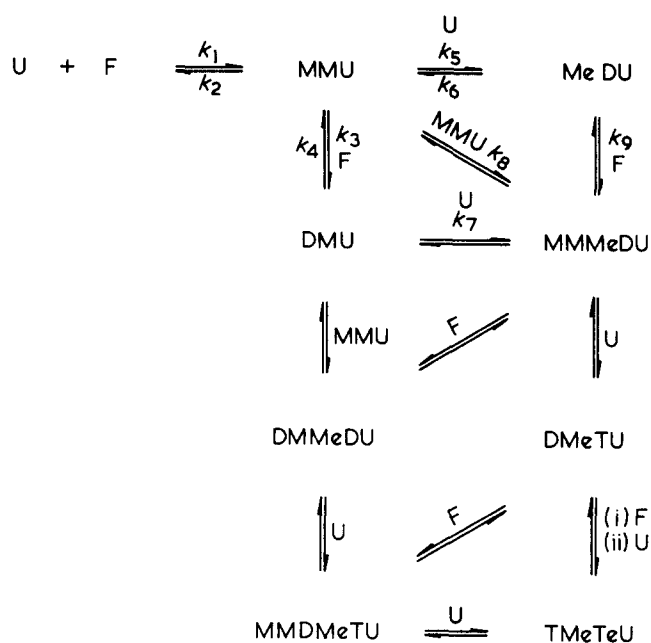
Figure 1 Course of urea–formaldehyde reactions (MMDMeTU = monomethylol dimethylene triurea)

Iodimetric method. The reaction mixture (5 ml) was pipetted into 50 ml of iodine solution (0.1 N) kept in an iodine flask, followed by 10 ml of NaOH solution (2 N). The mixture was kept for 1 h at room temperature. The mixture was acidified with 20 ml of H_2SO_4 solution (2 N) and the liberated iodine was titrated against standard sodium thiosulphate solution (0.05 N) using starch as indicator. A blank was also done. The amount of iodine reacted is equivalent to the formaldehyde present free and bound as methylols.

The methylols and methylene ureas were separated and quantitatively estimated by the t.l.c. method reported earlier[7].

RESULTS AND DISCUSSION

The main reaction steps involved in the U–F reaction are summarized schematically in *Figure 1*. The second-order rate constants and activation energy values for the reactions of urea and its related compounds with formaldehyde are summarized in *Tables 1–3*. Urea functions as a monoacidic base capable of protonation at the oxygen atom. The protonated forms are:
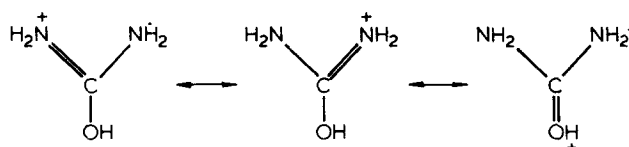
The formation of MMU follows second-order kinetics and the dissociation is first-order. There appears to be general acid and base catalysis.

U–F reaction in neutral medium

In neutral medium the formaldehyde molecule is polarized thus:

The polarized formaldehyde molecule attacks the nucleophilic amide nitrogen of urea:
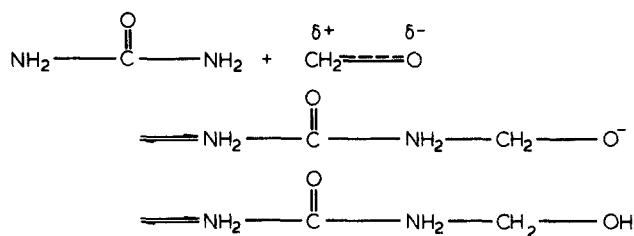
This is followed by a proton transfer giving MMU. The rate was found to be slow due to low activation of the amide nitrogen and the limited polarization of the formaldehyde molecule.

U–F reaction in acid medium

Formaldehyde is made more electrophilic by protonation.
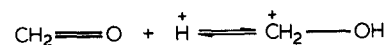
The carbonium ion so formed combines with urea molecule as follows:
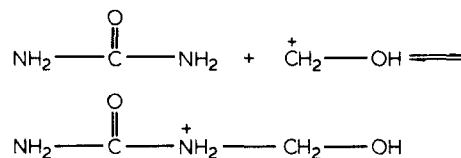
This is followed by the elimination of a proton resulting in the formation of MMU:
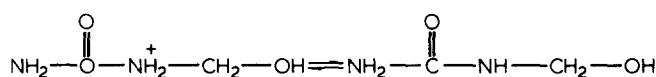
Table 1 Rate constants (k_1) and activation energy (E) for the reactions of urea with formaldehyde (U = 0.25 M, F = 0.25 M)

pH	Temperature (°C)	Rate (second-order) ($\times 10^4$ l mol^{-1} s^{-1})	E (kcal mol^{-1})
3.0	40	8.93	
3.0	50	22.15	17.2
3.0	60	40.64	
4.7	40	2.21	
4.7	50	3.79	11.44
4.7	60	6.71	
7	30	1.13	
7	40	1.94	10.5
7	50	3.20	
7	60	5.37	
9.4	30	3.26	
9.4	40	6.61	16.7
9.4	50	14.61	

Table 2 Rate constants (k_s) and activation energy (E) for the reactions of urea with monomethylol urea (U = 0.25 M, MMU = 0.25 M; *U = 0.40 M, *MMU = 0.1 M)

pH	Temperature (°C)	Rate (second-order) ($\times 10^4$ l mol^{-1} s^{-1})	E (kcal mol^{-1})
4.2	10	0.48	
4.2	20	1.44	18.3
4.2	30	4.04	
3.8	20	4.18	
3.8	30	10.69	
*4.0	20	9.36	
*4.0	30	15.43	
*4.0	40	31.14	
*3.5	20	10.16	
*3.5	30	24.28	
*3.5	40	50.45	

Table 3 Activation energy (E) and entropy of activation ($\Delta S^{\ddagger}$) for the reactions of urea with formaldehyde at various pH values

pH	E (cal mol^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1} at 25°C)
3.0	17160	−18.96
3.5	13070	−33.47
4.7	11440	−40.29
7.0	10500	−43.96
9.4	16700	−22.06
10.5	18300	−12.40

The increase of acid concentration increases the rate of the reaction by favouring the formation of methylol carbonium ion. The rate increases only 1.14 times for a change of pH from 7 to 4.7, at 40°C. But it decreases 4.6 times for the pH change from 7 to 3 at the same temperature. The activation energy also increases with increase of acid concentration (*Table 3*).

U–F reaction in alkaline medium

Under alkaline conditions the basic catalyst may be favouring the reversible removal of a proton from urea:

$$H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH_2 + O\bar{H} \rightleftharpoons H_2N{-}\overset{\overset{O}{\|}}{C}{-}N\bar{H} + H_2O$$
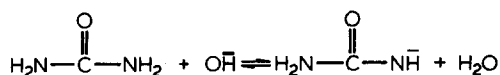
The anion thus formed may be combining with a polarized formaldehyde molecule:

$$H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH^- + \overset{\delta+}{C}H_2{=}\overset{\delta-}{O} \rightleftharpoons H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}O^-$$
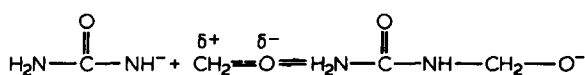
and leads to the formation of MMU by abstraction of a proton:

$$H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}O^- + H_2O \rightleftharpoons H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}OH + OH^-$$
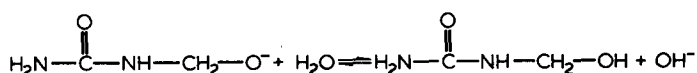
A steep increase in rate was observed in the alkaline medium which may be due to the facile formation of active amide ·anion. Even though the methylol carbonium ion favours the reaction in the acid medium, a similar rapid increase of rate as in the alkaline medium was not observed here. This may be due to the fact that the protonated form of urea is less reactive towards the carbonium ion.

MMU formation in the pH range 10.5–3.5 and temperatures 30°–50°C is shown graphically in *Figure 2*. At all temperatures the rate constants pass through a minimum in the pH range 4.5–8. Below 4.5 and above 8 pH the rate constants increase rapidly, proving thereby catalysis by H_3O^+ and OH^-.

The formation of MMU was doubled by an increase of 10°C and its concentration reached a maximum earlier at a higher temperature and then decreased due to condensation. The rate of formation of MMU from urea and formaldehyde was found to be unaffected by change in concentration of urea and formaldehyde. The rate constant at U:F mole ratio 1:1, 0.25:0.25 and 0.1:0.1 was found to be $(8.4 \pm 0.2) \times 10^{-4}$ l mol^{-1} s^{-1}.

A steep increase in activation energy was observed for the reaction with increase of alkali concentration. The entropy of activation $\Delta S^{\ddagger}$ (*Table 3*) decreased numerically with increase of acid or alkali concentration.

The initial species in the U–F reaction in acid and alkaline media are as shown below:

Figure 2 Reactions of urea and formaldehyde at different pH values (urea = 0.25 M, formaldehyde = 0.25 M): ●, 30°C; ○, 40°C; x, 50°C; +, 60°C

$$H_2N\diagdown_{\underset{\underset{\underline{O}}{|}}{C}}\diagup NH_2 \quad \text{and} \quad \overset{+}{C}H_2\text{—}OH$$

(acid medium)

$$NH_2\text{—}CO\text{—}N\overline{H} \quad \text{and} \quad \overset{\delta+}{C}H_2\overset{\delta-}{=}O$$

(alkaline medium)

The transition states are

$$NH_2\text{—}CO\text{—}\overset{+}{N}H_2\text{—}CH_2OH \quad \text{and} \quad NH_2\text{—}CO\text{—}NH\text{—}CH_2\text{—}\overset{-}{O}$$

respectively in the acid and alkaline media. Inrease of H^+ or OH^- increases the concentration of the initial species and hence leads to a more ordered arrangement in the initial state than in the corresponding transition states. This explains the decreased numerical values of $\Delta S^\ddagger$ with increase in H^+ or OH^-.

Unlike the phenol–formaldehyde reaction products, the urea–formaldehyde reaction products undergo dissociation. Monomethylol urea dissociates to urea and formaldehyde and dimethylol urea dissociates to monomethylol urea and formaldehyde in aqueous solution, in acid, neutral and alkaline conditions. Methylene diurea dissociates to urea and monomethylol urea under acidic conditions. This reversibility of the U–F reaction accounts for the presence of urea, free formaldehyde, methylols of urea, methylene ureas, etc., in U–F reaction mixtures. The results of a detailed investigation of the reversibility of these reactions are to be published elsewhere.

Effect of methylol group on further addition of formaldehyde

Rate of addition of formaldehyde to MMU is lower compared to its reaction with free urea. At pH 7 and 40°C the reactivity of monomethylol urea is only 1/22 of that of one amino nitrogen in urea. (The rate constants are 19.35×10^{-5} and $1.738 \times 10^{-5} \mathrm{l\,mol^{-1}\,s^{-1}}$ for urea and MMU respectively) (*Tables 1* and *2*). At pH 3.5, 4.7 and 10.5 at 30°C the decrease in reactivity was constant (5–6 times). The rates l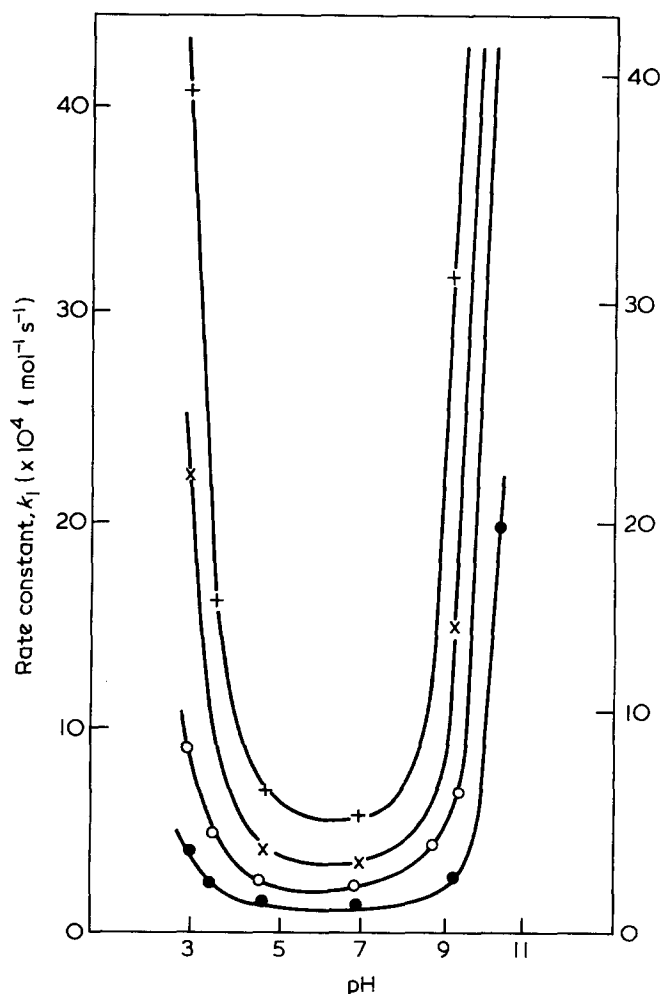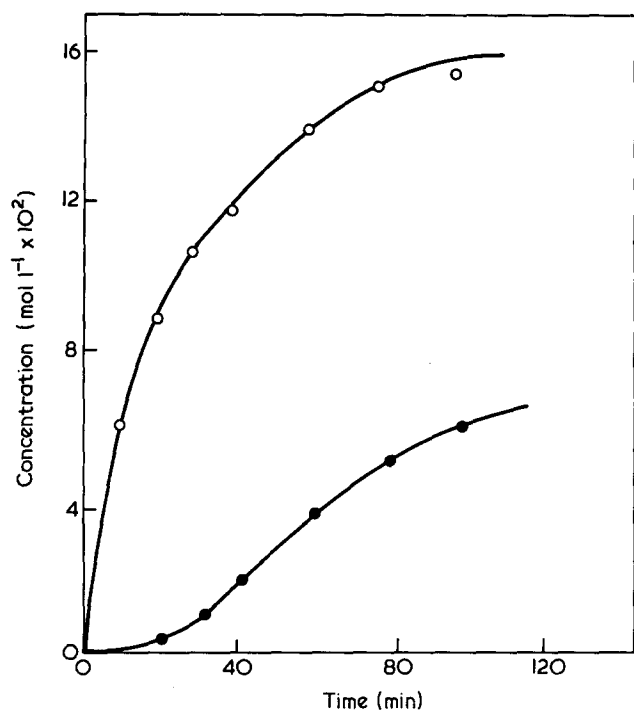owered from 2.5×10^{-4} to 0.44×10^{-4}, 1.5×10^{-4} to 0.3×10^{-4} and 19.5×10^{-4} to $3.43 \times 10^{-4} \mathrm{l\,mol^{-1}\,s^{-1}}$ respectively.

The main reason for the decreased reactivity is the statistical factor, methylol urea having only one reactive position compared to two in the case of urea. Further, on the basis of its apparent similarity with $-CH_2Cl$ group, the methylol group might be expected to be electron-withdrawing and hence deactivating in electrophilic substitution[11]. Sprengling and Lewis[12] found that the methylol phenols have slightly higher dissociation constants compared to phenol, indicating that the $-CH_2-OH$ group is to a slight extent electron-withdrawing, at least in the ground state.

But such an effect is not possible in monomethylol urea. Hence the reduced activity of monomethylol urea may be attributed to the $-I$ effect of the methylol group.

Formation of methylene-bridged compounds and ether linkages

In the presence of acid, the methylol species become protonated, resulting in the formation of a carbonium ion. This readily combines with an amino group with the formation of a methylene bridge:

$$>\!N\text{—}CH_2\text{—}OH \rightleftharpoons >\!N\text{—}CH_2\text{—}\overset{+}{O}H_2 \rightleftharpoons$$
$$\underset{-H^+}{\overset{-H_2O}{\rightleftharpoons}}$$
$$>\!N\text{—}\overset{+}{C}H_2 \quad \underset{|}{\overset{|}{N}}\text{—}H \underset{-H^+}{\rightleftharpoons} >\!N\text{—}CH_2\text{—}N\!<$$

Methylene bridge formation can take place in three different ways: (i) condensation of the methylol compounds with urea; (ii) self-condensation and intercondensation of the methylol ureas; and (iii) formation of higher homologues. These reactions were studied at low temperatures where the dissociation of the methylol ureas are comparatively very slow. The results obtained are discussed below.

Condensation of the mono- and dimethylol ureas with urea. Under similar conditions (pH = 4.2; temperature = 30°C) it is found that the rate of condensation of MMU with urea is greater ($4.04 \times 10^{-4} \mathrm{l\,mol^{-1}\,s^{-1}}$) than that of DMU with urea ($1.7 \times 10^{-4} \mathrm{l\,mol^{-1}\,s^{-1}}$). Since DMU has two reactive groups as compared to one in MMU, the former may be expected to be more reactive. The observed lower reactivity of DMU may be explained as due to the mutual deactivation of the methylol groups in DMU.

Self-condensation and intercondensation of MMU and DMU. Self-condensations were found to be slower (MMU: $1.5 \times 10^{-4} \mathrm{l\,mol^{-1}\,s^{-1}}$; DMU: $0.0178 \times 10^{-4} \mathrm{l\,mol^{-1}\,s^{-1}}$) than the reaction of MMU or DMU with urea (*vide supra*). This is to be expected since on the one hand the methylol ureas have a lesser number of free reactive positions and on the other the methylol group has a deactivating effect on the amino group. The self-condensation of DMU probably results in an ether, the presence of which is not confirmed in the present investigation for lack of standard compounds. The intercondensation of MMU and DMU is complicated by their self-condensation and hence the rates are not determined.

Formation of higher homologues. There are two ways in which higher homologues can form in the urea–formaldehyde reaction: (i) reaction of MeDU with MMU, and (ii) formation of MMMeDU from MeDU and F, followed by its reaction with U.

In a typical reaction of MeDU and MMU it was observed that practically no trimer was obtained and the methylol and formaldehyde (as determined iodimetrically) actually increased with time. Hence under these conditions dissociation was more favoured. On the other hand MeDU was found to react with formaldehyde readily (however the rate of formaldehyde addition to MeDU is much lower than that for the addition of F to U) and the methylol so formed could condense easily with urea. The low reactivity of MeDU towards MMU could be attributed to the lower reactivity of the amide nitrogens as shown below:

$$\underset{H_2N\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH\text{—}CH_2\text{—}NH\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH_2}{}$$

$$\downarrow$$

$$\overset{+}{H_2N}\!\!=\!\!\underset{\underset{O^-}{|}}{C}\text{—}NH\text{—}CH_2\text{—}NH\text{—}\underset{\underset{O^-}{|}}{C}\!\!=\!\!\overset{+}{NH_2}$$

Figure 3 Formation of monomethylol urea and methylene diurea (urea = 1 M, pH = 4, temperature = 30°C): O, monomethylol urea; ●, methylene diurea
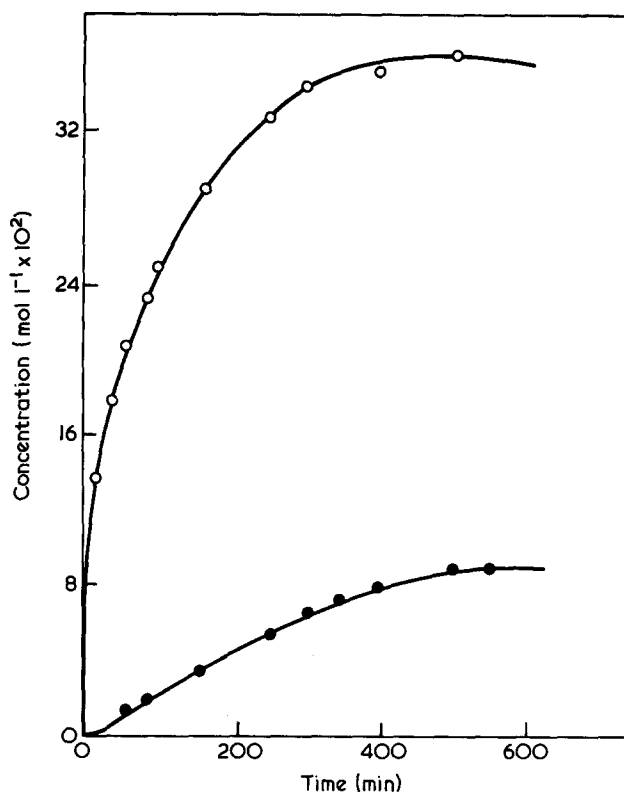

Figure 4 Formation of monomethylol urea and dimethylol urea (urea = 1 M, formaldehyde = 1 M, pH = 9, temperature = 30°C): O, monomethylol urea; ●, dimethylol urea

The higher reactivity of F as compared to MMU compensates for this reduced activity of MeDU and hence the methylols are formed. Thus the reaction of methylols with free urea seems to be the main route for formation of higher homologues in the U–F reaction.

Urea–formaldehyde reactions at high concentrations

Two typical reactions were carried out at pH 4 and 9 using urea and formaldehyde at 1 M each at 30°C. The formation of products is shown graphically in *Figures 3* and *4*. The main products at pH 4 were MMU and MeDU. Traces of DMU could also be seen on the t.l.c. plates. This is in sharp contrast to the reaction at pH 9 where the main products are MMU and DMU. Small quantities of MeDU were also formed. This is in agreement with the general observation that, whereas methylolation is preferred in alkaline medium, methylene bridge formation is the preferred reaction in acidic medium.

ACKNOWLEDGEMENTS

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