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Condensation of Methylolmelamine

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The condensation of methylolmelamine in the range of *ca.* pH 8—1 was investigated. An aqueous-dimethylsulfoxide (DMSO) solution (*ca.* 1 : 2, vol. ratio) was mainly used as the solvent, because it was revealed that the condensate in the latter stage of the condensation is soluble in DMSO solvent, and also that in this solvent methylolmelamine scarcely decomposes into a lower methylolmelamine liberating formaldehyde; then, the condensation mechanism of that methylolmelamine whose composition corresponds approximately to di-, tri-, and hexa-methylolmelamine, was investigated, not only in the early stage but also in the latter stage. It was found that the condensation rates of di- and tri-methylolmelamines (low methylolmelamines) in the early stage show maxima at *ca.* [HCl]/[methylolmelamine]=0.5 (molar ratio), *i. e.*, at *ca.* pH= log$K$, where K is the equilibrium constant between the molecular form of the methylolmelamine and its conjugate acid, and that in hexa-methylolmelamine (high methylolmelamine) the above maximum appears at *ca.* [HCl]/[methylolmelamine]=0.5—1.0 (molar ratio). Also, the above maxima were found to shift toward smaller [HCl]/[methylolmelamine] (molar ratio) values as the condensation proceeded (the latter stage). From these results, a condensation mechanism was proposed for the early stage of the condensation.

Moldings and laminates are prepared by curing methylolmelamine with a composition corresponding approximately to di- or tri-methylolmelamine; an acid catalyst is usually added just prior to the cure because the condensation rate increases remarkably upon the addition of a small amount of an acid[1] (near the neutral range). However, there have been no reports on the condensation of methylolmelamines in a more strong acidic range. For this reason, the condensation of methylolmelamine in the range of *ca.* pH 8—1 was investigated in detail.

It has recently been revealed by the present author[2,3] that dimethylsulfoxide (DMSO) is a good solvent for melamine, methylolmelamine, and the condensate, and that neither the iodometric nor the sulfite method is affected by the presence of a small amount of DMSO.

Moreover, methylolmelamine was found by this study to decompose scarcely into a lower methylolmelamine liberating formaldehyde, in DMSO or even in an aqueous-DMSO solution (*ca.* 1 : 2, vol ratio); consequently, the condensation mechanism of a methylolmelamine with a different number of methylol groups can be investigated by the use of an aqueous-DMSO solution, even in the latter stage of the condensation.

There was another purpose of this study: In the reaction of melamine with formaldehyde, the hydroxymethylation and the condensation proceed almost simultaneously; also, the hydroxymethylation rate shows quite different values with the change in pH values.[4,5] Hence, a hydroxymethylation product prepared in the neutral range (see "Preparation of Methylolmelamine"), *i. e.*, methylolmelamine (monomer), was used as the starting substance for the study of the condensation mechanims.

The present report will summarize in detail our findings on the condensation rate *vs.* the acidity, some properties of the condensate, the rate of

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[1] J. F. Blais, "Amino Resins," Reinhold Publishing Corporation, New York, Champan & Hall Ltd., London (1959), p. 20; K. Koeda, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **60**, 1567 (1957).

[2] K. Sato, This Bulletin, **40**, 724 (1967).

[3] K. Sato, *ibid.*, **40**, 1547 (1967).

[4] M. Okano and Y. Ogata, *J. Am. Chem. Soc.*, **74**, 5728 (1952).

[5] K. Sato, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

decrease in the methylol group *vs.* the acidity, and the change in pH value during the reactions: samples with compositions approximating di-, tri-, and hexa-methylolmelamine were used (for they have different numbers of methylol groups); among these items, we will emphasize the condensation rate *vs.* the acidity. These studies may imply a probable mechanism for the early stage of the condensation. In addition, methylolmelamine was investigated by differential thermal analysis and by thermobalance measurements.

Experimental

Materials. Pure commercial melamine was recrystallized from water. The formaldehyde was the best grade formaline (*ca.* 37 wt%). Pure commercial DMSO was purified by a known method[6]; bp 47°C/3 mmHg.

Preparation[7] of Methylolmelamine. Formaline was added to 126 g (1 mol) of melamine in the formaldehyde/melamine molar ratios of 2, 3, and 8, and the pH was adjusted to 8.0 with 0.1 N sodium hydroxide. This mixture was dissolved by heating it at 70°C, and then heated for an additional 5 min after dissolution; the solution thus formed was quickly poured into a large amount of an ice-cooled methanol and left standing overnight. The precipitate thus formed (methylolmelamine) was collected on a Büchner funnel, washed with methanol, and then dried *in vacuo* (50°C). These products were analyzed by the conventional method[7,8]; the results obtained show that the molar ratios of the combined formaldehyde to melamine are 1.98, 2.68, and 5.65, and that scarcely any condensation takes place in any case, *i. e.*, only the monomer of methylolmelamine is formed since the reaction time is short.

Thus, samples with compositions approximating di-, tri-, and hexa-methylolmelamine were prepared. Henceforth, these will be represented as M1.98F, M2.68F, and M5.65F respectively.

Reaction and Measurement. A definite amount of an aqueous-DMSO solution containing an appropriate amount of M1.98F was prepared. Next, definit amounts of an aqueous solution containing various amounts of hydrochloric acid were prepared. Each solution was then introduced into a thermostat regulated to the operating temperature, and the above solutions were mixed to react them. The initial pH values were controled by [HCl]/[M1.98F] (molar ratio). Aliquots were taken out at appropriate intervals of time and were analyzed by the iodometric and sulfite methods after neutralization, the pH values being measured by means of a glass electrode pH meter; the iodometry was carried out after adding DMSO[3] to the aliquot. The condensation rate, *i. e.*, the rate of the formation of the methylene linkage, was directly computed iodometrically. The results are shown graphically in Fig. 1(1), where the "methylene linkage"/"melamine rest (remainning) in methylolmelamine" molar ratio *vs.* the pH is indicated in connection with the reaction times. The rate of decrease in the methylol group was computed from the difference between the two values obtained by the iodometric and sulfite methods. The results are shown in Fig. 1(2), where the "methylol group"/"melamine rest in methylolmelamine" molar ratio *vs.* the pH is indicated in connection with the reaction times.

Experiments concerning M2.68F and M5.65F were carried out similarly; these results are shown in Figs. 2(1), (2)—4(1), (2).

For comparison, an investigation was also carried out with regard to M1.98F in an aqueous solution instead of an aqueous-DMSO solution. The results are shown in Figs. 5(1) and (2).

Differential Thermal Analysis and Thermobalance Measurement. The investigations were carried out using a 100 mg portions of M2.68F and M5.65F. The temperature was raised at the rate of 5°C/min for the differential thermal analysis, and at the rate of 3°C/min for the thermobalance measurement. For comparison, a 100 mg portion of melamine was also used in these investigations. The results of the differential thermal analysis are shown in Fig. 6, and those of the thermobalance measurement, in Fig. 7.

Results and Discussion

Solvent. Penta- or hexa-methylolmelamine (high methylolmelamine) is almost insoluble in water; therefore, water cannot be used as a solvent in this case. With regard to di- or tri-methylolmelamine (low methylolmelamines) also, water is not suitable as a solvent, because, although these substances are slightly soluble in water, they easily decompose, liberating formaldehyde to become lower methylolmelamines.

However, it became clear from this study that the decomposition of methylolmelamine is almost suppressed in DMSO, even in an aqueous-DMSO solution (*ca.* 1 : 2 vol ratio). For example, an aqueous solution containing 0.040 mol/*l* of M1.98F and of M2.68F were prepared at 50°C, and the formaldehyde thus liberated was determined immediately by the sulfite method. These results indicate that the former decomposes into M1.51F, and the latter, into M1.83F. Then, DMSO solutions containing 0.040 mol/*l* of M1.98F, M2.68F, and M5.65F were similarly tested using the sulfite method. As a result, each of the methylolmelamines was revealed to decompose very little, even after 50 hr (50°C); the same was almost true in the case of aqueous-DMSO solutions (*ca.* 1 : 2, vol ratio) of M1.98F, M2.68F, and M5.65F. The above results suggest a facility of solvation between DMSO and methylolmelamine; such solvation must be associated with the fact that DMSO is a polar solvent and that it dissolves a large amount of methylolmelamine; *e. g.*, the solubilities of M1.98F in water and DMSO are *ca.* 0.9 wt% and 56 wt%[3] respectively at 30°C.

Moreover, when an aqueous-DMSO solution (*ca.* 1 : 2 vol ratio) of methylolmelamine is used,

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[6] C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

[7] T. Kitagawa, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **53**, 181 (1950).

[8] J. J. Levenson, *Ind. Eng. Chem. Anal. Ed.*, **12**, 332 (1940).

no precipitate appears, even in the latter stage of the condensation shown in Figs. 1(1)—4(1), because DMSO is a good solvent for the condensate. However, when an aqueous solution is used instead of the above solution, it soon becomes turbid; then a precipitate is deposited as the condensation proceeds. Therefore, the aliquot was taken out in this case after the solution had been agitated vigorously with a glass rod. Thus, the value obtained using an aqueous solution is not as accurate as that obtained using an aqueous-DMSO solution; in particular, the values of (c) and (d), which correspond to a reaction time of 3.5 hr, shown in Fig. 5 could not be obtained, because the aliquot could not be taken out because the precipitate was deposited at the bottom of the vessel.

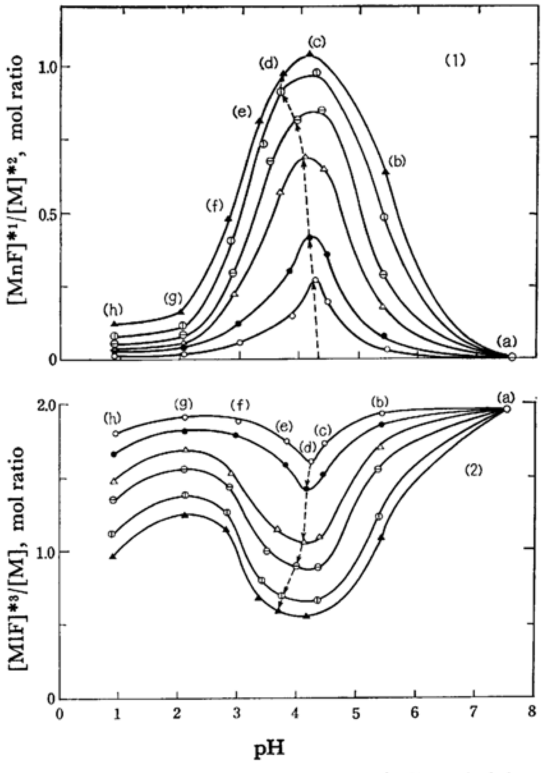

Fig. 1. The constituent change of di-methylolmelamine (M1.98F) *vs.* pH in DMSO-water mixed solution (*ca.* 2 : 1, vol ratio) at 50°C.
(1) Condensation rate *vs.* pH
(2) Decrease rate of methylol group concentration *vs.* pH
-○-: 0.25 -●-: 0.5 -△-: 1.0 -⊖-: 1.5
-⦶-: 2.5 -▲-: 3.5 reaction time (hr)
(a): 0 (b): 0.10 (c): 0.40 (d): 0.50
(e): 0.70 (f): 1.00 (g): 1.80 (h): 11.00
[HCl]/[M1.98F] (mol ratio)
Initial concentration: [M1.98F]=0.0634 (mol/*l*)
*1 [MnF]: Methylene linkage
*2 [M]: Melamine rest in methylolmelamine
*3 [MlF]: Methylol group concentration

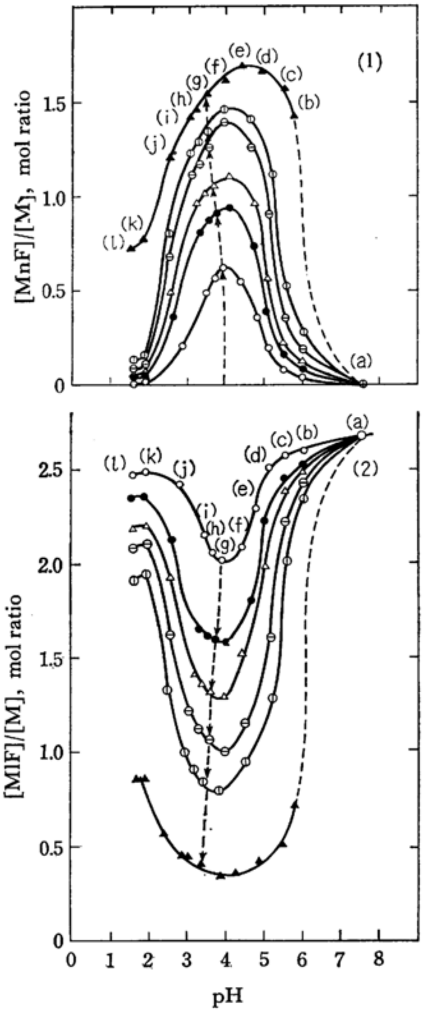

Fig. 2. The constituent change of tri-methylolmelamine (M2.68F) *vs.* pH in DMSO-water mixed solution (*ca.* 2 : 1, vol ratio) at 45°C.
(1) Condensation rate *vs.* pH
(2) Decrease rate of methylol group concentration *vs.* pH
-○-: 0.5 -●-: 1.0 -△-: 1.5 -⊖-: 2.5
-⦶-: 3.5 -▲-: 33.0 reaction time (hr)
(a): 0 (b): 0.03 (c): 0.05 (d): 0.10
(e): 0.20 (f): 0.40 (g): 0.50 (h): 0.60
(i): 0.70 (j): 1.00 (k): 2.00 (l): 3.00
[HCl]/[M2.68F] (mol ratio)
Initial concentration: [M2.68F]=0.0776 (mol/*l*)

Consequently, the advantage of using an aqueous-DMSO solution is that the condensation mechanism of methylolmelamine with different numbers of methylol groups can be investigated not only in the early stage but also in the latter stage.

Relation between the Condensation Rate and the Acidity. The results obtained are shown in Figs. 1(1), 2(1), 3(1), 4(1), and 5(1).

As is well known, the condensation rate of methylolmelamine increases as a solution becomes

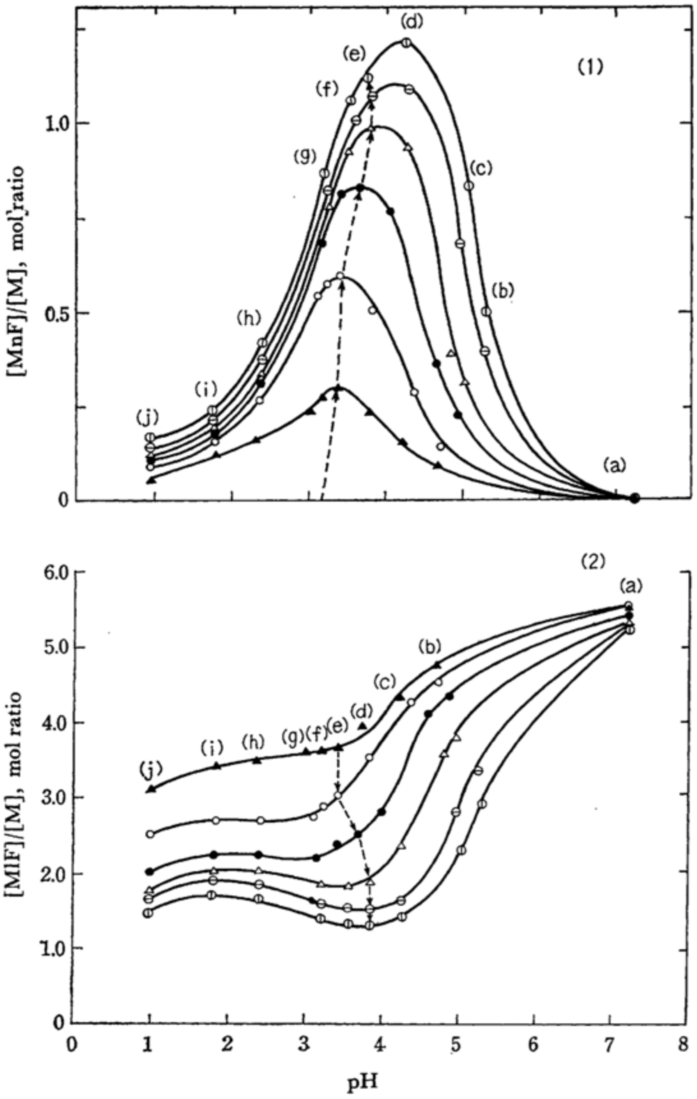

Fig. 3. The constituent change of hexa-methylolmelamine (M5.65F) *vs.* pH in DMSO-water mixed solution (*ca.* 3 : 1, vol ratio) at 65°C.
(1) Condensation rate *vs.* pH
(2) Decrease rate of methylol group concentration *vs.* pH
-▲-: 0.3 -○-: 0.5 -●-: 1.0 -△-: 1.5 -⊖-: 2.5 -⦶-: 3.5 reaction time (hr)
(a): 0 (b): 0.05 (c): 0.10 (d): 0.35 (e): 0.50 (f): 0.70 (g): 1.00
(h): 3.00 (i): 10.00 (j): 50.00 [HCl]/[M5.65F] (mol ratio)
Initial concentration: [M5.65F]=0.0205 (mol/*l*)

more acidic (near the neutral range: *ca.* pH 8[*2]→7).1) However, there have been no reports on the condensation in a range more acidic than this.

It may be found from the above figures that the condensation rates of M1.98F, M2.68F, and M5.65F show a maximum value in each curve. For example, with regard to M1.98F and M2.68F, *i. e.*, low methylolmelamines, the maximum appears at *ca.* [HCl]/[M]=0.5 (molar ratio)[*3] in the early stage, where [M] represents the concentration of the melamine rest in the starting methylolmelamine, and [HCl], that of hydrochloric acid. When an aqueous solution was used

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[*2] Since methylolmelamine is basic, the pH value of a solution containing methylolmelamine is somewhat larger than 7.0.

[*3] In an acidic region, DMSO may form its conjugate acid ($(CH_3)_2SO \rightarrow H^+$), but the additional proton would be remarkably small. In the presence of some hydrochloric acid, the pH value of an aqueous-DMSO solution is somewhat different from that of an aqueous solution. For this reason, the maximum has been discussed in terms of [HCl]/[M] (molar ratio).

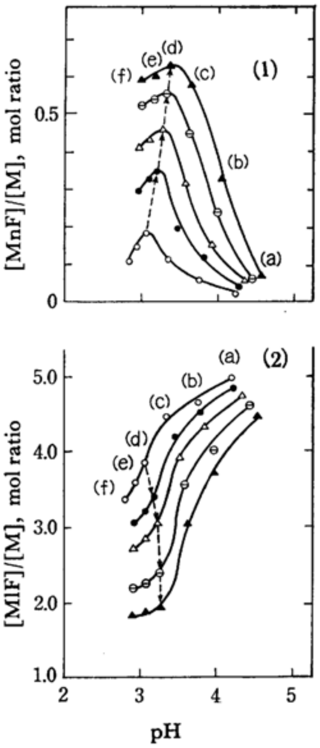

Fig. 4. The constituent change of hexa-methylolmelamine (M5.65F) *vs.* pH in DMSO-water mixed solution (*ca.* 3 : 1, vol ratio) at 40°C.
(1) Condensation rate *vs.* pH
(2) Decrease rate of methylol group concentration *vs.* pH
-○-: 0.5 -●-: 1.0 -△-: 1.5 -⊖-: 2.5
-▲-: 3.5 reaction time (hr)
(a): 0.10 (b): 0.30 (c): 0.50 (d): 1.00
(e): 1.40 (f): 1.80 [HCl]/[M5.65F] (mol ratio)
Initial concentration: [M5.65F]=0.0205 (mol/*l*)

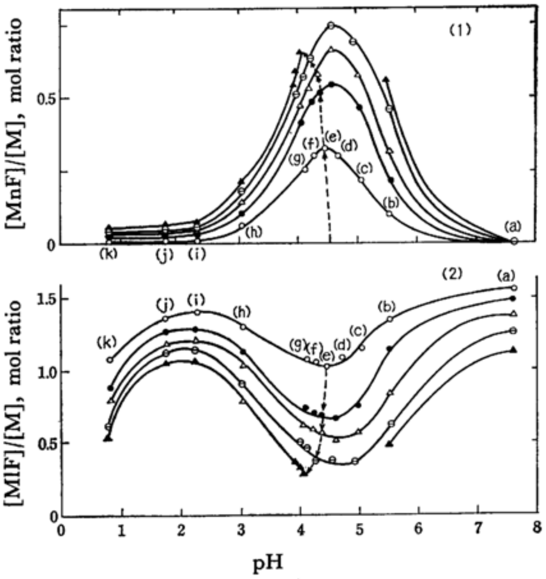

Fig. 5. The constituent change of di-methylolmelamine (Ml.98F) *vs.* pH in aqueous solution at 50°C.
(1) Condensation rate *vs.* pH
(2) Decrease rate of methylol group concentration *vs.* pH
-○-: 0.5 -●-: 1.0 -△-: 1.5 -⊖-: 2.5
-▲-: 3.5 reaction time (hr)
(a): 0 (b): 0.10 (c): 0.30 (d): 0.40
(e): 0.50 (f): 0.60 (g): 0.70 (h): 1.00
(i): 1.50 (j): 2.50 (k): 25.00
[HCl]/[Ml.98F] (mol ratio)
Initial concentration: [Ml.98F]=0.0312 (mol/*l*)

instead of an aqueous-DMSO solution, as has been stated above, no such accurate data can be obtained as in the case of an aqueous-DMSO solution, but the maximum appears at *ca.* [HCl]/[M]=0.5 (molar ratio) (Fig. 5(1)).

Furthermore, the maximum was found to shift toward smaller [HCl]/[M] (molar ratio) values as the condensation proceeds (the latter stage); *e.g.*, as is clear in Fig. 2(1), the maximum shifts from 0.5 to 0.4, and then to 0.2 (molar ratio). The above fact may be explained from the consideration that the melamine rest in the condensate is less basic than that of the starting methylolmelamine (see "Change in pH Value during Reaction" and "Condensation Mechanism for the Early Stage").

Next, the effect of the concentration of methylolmelamine and that of the temperature upon the maximum were studied. Investigations were carried out by adjusting the concentrations of M2.68F to twice the starting concentration shwon in Fig. 2, and also by adjusting the reaction temperature to 60°C and 40°C from the 45°C shown in Fig. 2. These results show that maxima in the early stage appear at *ca.* [HCl]/[M]=0.5 (molar ratio) in all cases, regardless of the concentration of methylolmelamine and the reaction temperature.

High methylolmelamines differ from low methylolmelamines in the following behavior. In M5.65F, a high methylolmelamine, maxima in the early stage appear at *ca.* [HCl]/[M]=0.5 and 1.0 (mol ratio) at 65°C and 45°C respectively, as Figs. 3(1) and 4(1) show. The maximum of a high methylolmelamine, thus, shifts toward smaller [HCl]/[M] (molar ratio) values, and it approaches that of a low methylolmelamine, *i.e.*, [HCl]/[M]=0.5 (molar ratio), with an elevation in temperature. These results will be discussed below in connection with the condensation mechanism (see "Condensation Mechanism for the Early Stage").

Some Properties of the Condensate. According to Eqs. (3) and (4) (*cf.* "Condensation Mechanism for the Early Stage"), the "methylene linkage"/"melamine rest in methylolmelamine" ratio of the dimer is 0.5 (molar ratio). Kohler *et al.*⁹⁾ stated that the above value of the molded product of the methylolmelamine prepared under the usual molding conditions is *ca.* 1.2 (molar ratio) and that it does not dissolve in solvents. From Figs. 1 (1) and 2 (1), it was found that the value of the condensate in the latter stage is *ca.* 1.2—1.6 (molar ratio), and also that this condensate is easily soluble in an aqueous-DMSO solution.

Thus, the above value of the condensate in the latter stage is almost the same or somewhat larger than that of the molded product; also, melamine resin is one of the thermosetting resins.

Therefore, this condensate (in the latter stage) may be predicted to show a three-dimensional structure with a remarkably large molecular weight, and to be insoluble in any solvent. However, the molecular weight of this condensate has been estimated by this research to be not as large as had been predicted, since the above condensate is soluble in an aqueous-DMSO solution.

Relation between the Rate of Decrease in the Methylol Groups in Methylolmelamine and the Acidity. The results obtained are shown in Figs. 1(2), 2(2), 3(2), 4(2), and 5(2).

First, it may be inferred that the methylol group is decreased by the formation of the methylene linkage and by the liberation of formaldehyde through the decomposition, which is mainly due to an acid.

Concerning M1.98F and M2.68F, Figs. 1(1), (2) and 2(1), (2) show that the maximum in the rate of decrease in the methylol group, *i. e.,* the minimum in the methylol group (present) *vs.* the pH, almost coincides with the maximum in the condensation rate; that is to say, it appears at *ca.* [HCl]/[M]=0.5 (molar ratio) in the early stage and shifts toward smaller [HCl]/[M] values as the condensation proceeds. Furthermore, regarding the early stage, from the above figures, it can be seen that the decrease in the methylol group is roughly the same as the increase in the methylene linkage formed in the range of *ca.* pH 7—3; therefore, the methylol group has been confirmed to be consumed mainly by the condensation within this pH range; however, within *ca.* pH 1—2, the decrease in the methylol group is considerably larger than the increase in the methylene linkage; this confirms that the methylol group is decreased by the decomposition due to a large amount of acid in this pH range.

On the other hand, as for M5.65F, the above mentioned minimum can scarcely be observed, and the decrease in the methylol group in the early stage is remarkably larger than the increase in the methylene linkage, even in a weak acidic range (Figs. 3(1), (2) and 4(1), (2)); this fact suggests that high methylolmelamines are unstable and easily liberate formaldehyde, even in the presence of a small amount of an acid.

Change in pH Value during Reaction. With regard to M1.98F and M2.68F, the pH values of the solution gradually shift toward smaller pH values as the reactions proceed, as Figs. 1(1), 2 (1) and 5(1) show, particularly at [HCl]/[M]= 0.5 (molar ratio). Thus, the change in pH value is observed, in particular, when the condensation rate is large. The melamine rest in the condensate is surely less basic than that of methylolmelamine; this effect accounts for the above fact.

On the contrary, with regard to M5.65F, the pH values were found to shift toward larger pH values (Figs. 3(1) and 4(1)). This fact may be explained as follows: During the course of reactions, high methylolmelamines easily decompose into lower methylolmelamines, liberating formaldehyde, as has been described above. Hence, the basicity of the solution increases as the decomposition proceeds, because the basicity increases in the order of M1.98F>M2.68F≫M5.65F (based on their neutralization curves). The observed change in the pH value is mainly affected by the above effect, only slightly by the opposing effect of the decrease in the basicity as the result of the formation of the condensate.

Differential Thermal Analysis and Thermobalance Measurement. As is shown in Fig. 6 (differential thermal analysis), the endothermic peaks, somewhat flattened, were observed at *ca.* 150°C in M2.68F and M5.65F.

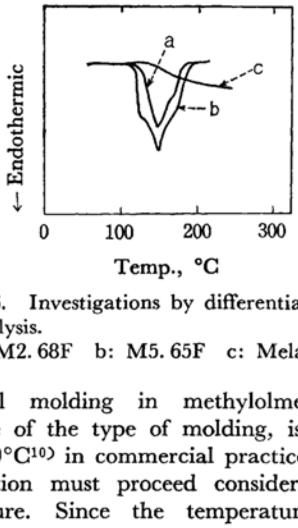

Fig. 6. Investigations by differential thermal analysis.
a: M2. 68F b: M5. 65F c: Melamine

General molding in methylolmelamine, irrespective of the type of molding, is carried out at *ca.* 150°C¹⁰⁾ in commercial practice; hence, the condensation must proceed considerably at this temperature. Since the temperature of endothermic peak closely coincides with that of the molding, this peak may be explicable from the considerations that the condensation proceeds upon

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9) A. Gam, G. Widmer and W. Fisch, *Helv. Chem. Acta,* **24**, 302E (1941); R. Kohler, *Kolloid. Z.,* **103**, No. 2, 138 (1943); H. P. Wohnsiedler, *Ind. Eng. Chem.,* **45**, 2307 (1953).

10) J. F. Blais, "Amino Resins," Reinhold Publishing Corporation, New York, Champan & Hall Ltd., London (1959), p. 77.

the discharge of a large amount of water (according to Eqs. (3) and (4), 1 mol of water is discharged for 1 mol of each methylene linkage), and that the heat of vaporization of water is large.*4

Next, Fig. 7 (thermobalance) shows the reduction in the weight of methylolmelamine that was observed during the rise in the temperature. This reduction may result from the liberation of formaldehyde by the thermal decomposition of methylolmelamine, and that of water by the condensation of methylolmelamine. Also, a more striking reduction in weight was observed in M5.65F than in M2.68F. This result may be explained from the thermal unstability of M5.65F, which easily liberates formaldehyde.

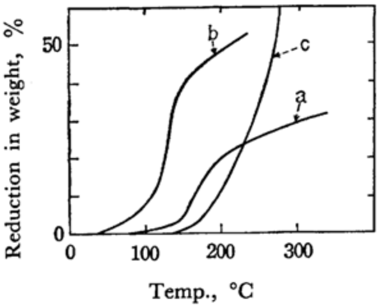


Fig. 7. Investigations by thermo-balance.
a: M2. 68F b: M5. 65F c: Melamine

Besides, melamine sublimes[12] easily. The observed endothermic behavior (Fig. 6(c)) and reduction in weight (Fig. 7(c)) may be due to this sublimation.

Condensation Mechanism for the Early Stage. Since the curve showing the condensation rate *vs.* the acidity for methylolmelamine resembles that of an acid-catalyzed semicarbazone formation,[13] and since a C–N linkage is formed in both reactions, a similarity in mechanism may be suggested.

Methylolmelamine and methylolurea are both amino resins. The condensation rate of methylolurea[14] increases with an increase in the acidity, but, contrarily, that of methylolmelamine passes through a maximum. This different behavior in the condensation rate *vs.* the acidity suggests a difference in their condensation mechanisms; it may be explained in brief in terms of the large difference in their basicities.

Let us discuss the condensation mechanisms of low and high methylolmelamines for the early stage.

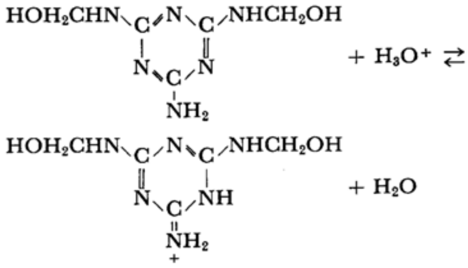
(1) Di- and Tri-methylolmelamine. Although low methylolmelamines such as di- and trimethylolmelamine are slightly less basic[15,16] (mono-acidic)[17] than melamine, these low methylolmelamines, unlike methylolurea, have sufficient basicity to combine with an equivalent amount of hydrochloric acid to form the conjugate acid. The relation between the molecular form of methylolmelamine, MCH_2OH, and its conjugate acid, $H\overset{+}{M}CH_2OH$, is shown in Eq. (1):

$$MCH_2OH + H_3O^+ \overset{K}{\rightleftarrows} H\overset{+}{M}CH_2OH + H_2O \qquad (1)$$

$$K = \frac{[H\overset{+}{M}CH_2OH]}{[MCH_2OH][H_3O^+]} \qquad (1')$$

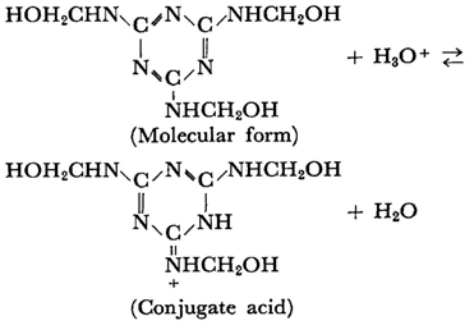
The structure of the conjugate acid has been demonstrated by Dixon *et al.*[15-18] on the basis of the ultraviolet absorption spectra (Eqs. (1a) and (1b)):

Di-methylolmelamine:



(1a)

Tri-methylolmelamine:



(1b)

Therefore, the condensation takes place between them, and Eq. (2) may be derived:

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*4 In the case of hexa-methylolmelamine-hexamethylether,[11] scarcely no endothermic peak was observed at *ca.* 150°C (or even in the range of *ca.* 30—200°C). This result may be due to the fact that this condensation occurs with the liberation of methanol, as is well known, and that the heat of the vaporization of methanol is markedly small.

[11] R. N. Housekeeper, U. S. Pat. 2998411 (1961).

[12] "Beilstein Handbuch der Organishen Chemie," XXVI (1937), p. 246.

[13] B. M. Anderson and W. P. Jenks, *J. Am. Chem. Soc.*, **82**, 1773 (1960); R. Wolfenden and W. P. Jenks, *ibid.*, **83**, 2763 (1961); I. D. Fiarman and J. D. Gettler, *ibid.*, **84**, 961 (1962).

[14] S. Takahashi, *Kobunshi Kagaku (Chem. High Polymers Japan)*, **9**, 50 (1952) and others.

[15] J. K. Dixon, N. T. Woodberry and G. W. Costa, *J. Am. Chem. Soc.*, **69**, 599 (1947).

[16] G. W. Costa, R. C. Hirt and D. J. Salley, *J. Chem. Phys.*, **18**, 434 (1950).

[17] R. C. Hirt and R. G. Schmitt, *Spectrochem. Acta*, **12**, 127 (1958).

[18] E. N. Boitsov, *Opt. Spectry.*, **9**, 26 (1960); *ibid.*, **12**, 108 (1962); *ibid.*, **13**, 151 (1962).

	MCH_2OH	$H\overset{+}{M}CH_2OH$
MCH_2OH	k_1	k_2
$H\overset{+}{M}CH_2OH$	k_2	k_3

$$\left.\begin{aligned}\text{Rate} &= k_1[MCH_2OH]^2\\ &\qquad\text{(molecular form, molecular form)}\\ &\qquad\qquad\text{1st term}\\ &+ k_2[MCH_2OH][H\overset{+}{M}CH_2OH]\\ &\qquad\text{(molecular form, conjugate acid)}\\ &\qquad\qquad\text{2nd term}\\ &+ k_3[H\overset{+}{M}CH_2OH]^2\\ &\qquad\text{(conjugate acid, conjugate acid)}\\ &\qquad\qquad\text{3rd term}\end{aligned}\right\}\quad(2)$$

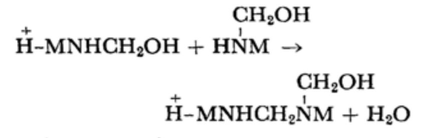
where k_1, k_2, and k_3 are the respective rate constants of the elementary reaction in Eq. (2).

The condensation without an acid is evidently a reaction between the molecular forms themselves, *i. e.*, the first term of Eq. (2). This reaction is markedly slow because the condensation without an acid does not proceed even after a long time has elapsed, as is clear from (a) of Figs. 1(1), 2(1) and 5(1).

The condensation may occur by an attack of the electrophilic carbon of the amino-methylol group on the nitrogen of the amino group or on that of the amino-methylol group of methylolmelamine. In view of this, the carbon of the amino-methylol group of the conjugate acid is markedly more electrophilic, that is to say, conspicuously more reactive, than that of the molecular form of methylolmelamine; also, the amount of the conjugate acid (reactive) increases with an increase in the acidity. The enhancement of the rate with an increase in the acidity in the range of $[HCl]/[M] < 0.5$ (molar ratio) can be explained by this mechanism. This is expressed in Eqs. (3) and (4):

$$\overset{+}{H}\text{-}MNHCH_2OH + H_2NM \rightarrow \overset{+}{H}\text{-}MNHCH_2NHM + H_2O \qquad (3)$$

(the formation of the *methylene bisamide linkage*)



$$\overset{+}{H}\text{-}MNHCH_2OH + H\overset{CH_2OH}{N}M \rightarrow \overset{+}{H}\text{-}MNHCH_2\overset{CH_2OH}{N}M + H_2O \qquad (4)$$

(the formation of the *methylol methylene bisamide linkage*)

However, this effect is counteracted by the increasing removal of the molecular forms of methylolmelamines by the formation of the conjugate acid in the range of $[HCl]/[M] > 0.5$ (molar ratio). The result of these opposing factors obviously is that a maximum appears at *ca.* $[HCl]/[M]=0.5$ (molar ratio); this 0.5 (molar ratio) value corresponds to $pH=\log K$[*5] where K is an equilibrium constant between the molecular form of methylolmelamine and its conjugate acid (see Eq. (1')).

In other words, the maximum can be explained from Eq. (2) as follows: According to the above electronic theory, k_2 is markedly larger than k_1 or k_3. (k_1 shows the smallest value because the smallest condensation rate is observed without an acid, as is shown in Fig. 1(1), 2(1) and 5(1).) Thus, k_2 is larger than k_1, and k_3 is smaller than k_2, thus accounting for the increase in the rate in the range of $[HCl]/[M] < 0.5$ (molar ratio), and the decrease in the rate in the range of $[HCl]/[M] > 0.5$ (molar ratio). Also, the $[MCH_2OH][H\overset{+}{M}CH_2OH]$ (concentration product) of the second term in Eq. (2) shows a maximum at $[MCH_2OH]=[H\overset{+}{M}CH_2OH]$, as is clear from Eq. (1').[*6] Consequently, a maximum in the rate appears at this point. In view of this, it may be considered that the main reaction in the condensation among the three reactions of Eq. (2) in the range of $0 < [HCl]/[M] < 1.0$ (molar ratio) is that between the molecular form of methylolmelamine and its conjugate acid (the second term).

In this case, methylolmelamine is converted into its conjugate acid by the addition of the proton in an acidic region, as has been stated above (*cf.* Eqs. (1), (1a) and (1b)); hence, the proton is scarcely added to methylolmelamine to form carbonium ion (Eq. (5)). Therefore, the carbonium ion, $M\overset{+}{C}H_2$, must play a minor part in the condensation, unlike methylolurea.[*7] On the assumptions that the carbonium ion is rapidly formed, *i. e.*, that the

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[*5] As is well known, the K (or the base constant of methylolmelamine, K_b) is obtained from the pH value of the solution at [HCl]/[methylolmelamine]= 0.5 (molar ratio). The pK_b[15)] values of M1.99 F and M3.00F are 9.5 and 10.1 (25°C) respectively; hence, the K is amount to $10^{4.5}$ and $10^{3.9}$ respectively. Therefore, the pH value of the observed maximum agreed fairly well with that computed from the pK_b of the literature.

[*6] From Eq. (1'), the following relation can be derived between pH and $H\overset{+}{M}CH_2OH$ (or MCH_2OH):

$$pH = \log K - \log\frac{\alpha}{1-\alpha}$$

$$([H\overset{+}{M}CH_2OH] = \alpha,\ [MCH_2OH]=1-\alpha)$$

[*7] For example, the condensation of mono-methylolurea in an acidic range[19)] is as follows:

$$H_2NCONHCH_2OH + H_3O^+ \rightleftarrows H_2NCONHCH_2\overset{+}{O}H_2 + H_2O \rightleftarrows H_2NCONH\overset{+}{C}H_2 + 2H_2O$$

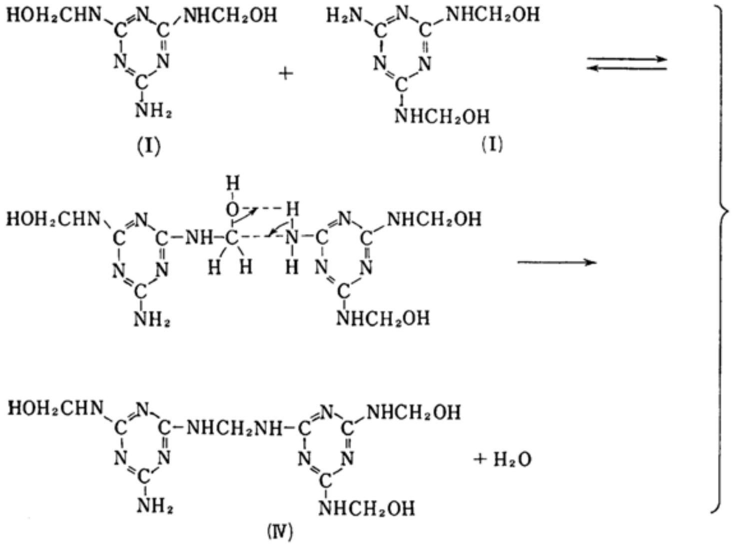
$$H_2NCONH\overset{+}{C}H_2 + H_2NCONHCH_2OH \rightarrow H_2NCONHCH_2NHCONHCH_2OH + H^+$$

19) G. Smeth, *J. Poly. Sci.*, **8**, 371 (1952); L. E. Smythe, *J. Am. Chem. Soc.*, **75**, 574 (1953) and others.

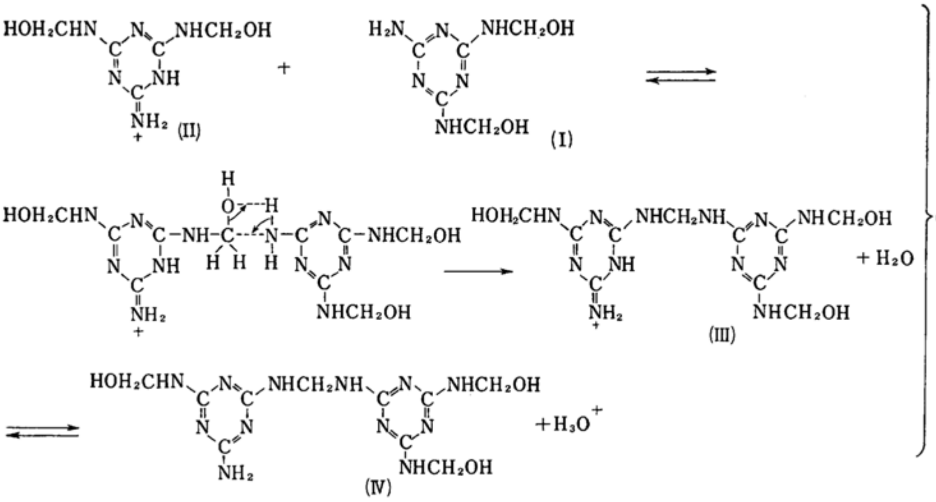
reaction of Eq. (5) is fast, and that the succeeding reaction of the carbonium ion with the molecular form of methylolmelamine (Eq. (6)) is the rate-determining step, the observed maximum may be explained on the basis of this mechanism because the carbonium ion is proportional to the conjugated acid formed (Eq. (1)) at the same pH values, as is clear from the relationship between Eqs. (1) and (5):

$$MCH_2OH + H_3O^+ \rightleftarrows MCH_2\overset{+}{O}H_2 + H_2O \rightleftarrows M\overset{+}{C}H_2 + 2H_2O \quad (5)$$

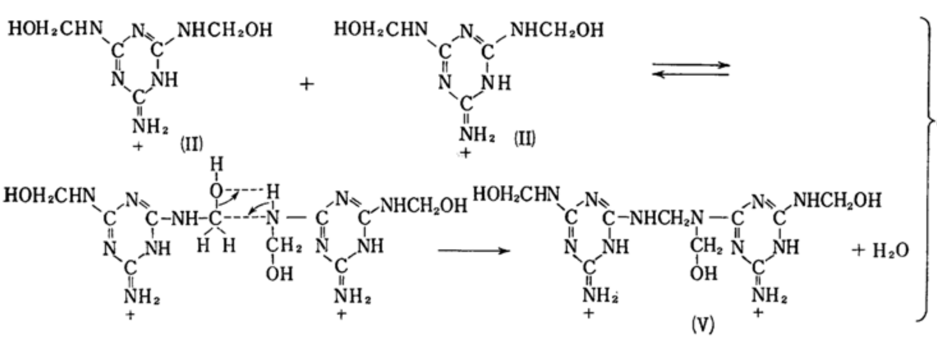
$$M\overset{+}{C}H_2 + MCH_2OH \rightarrow \overset{+}{M}CH_2MCH_2OH \quad (6)$$



(7)



(8)



(9)

However, it is not clear whether or not these assumptions are reasonable. On the other hand, *if the conjugate acid itself reacts as an active species,* the observed maximum can readily be accounted for without any assumption, as has been indicated above.

Furthermore, the main reaction for the condensation among the three reactions of Eq. (2) in the range of [HCl]/[M]$>$1.0 (molar ratio) may be considered to be that between the conjugate acids of methylolmelamine themselves, *i. e.,* the third term of Eq. (2), because the concentration of the molecular form of methylolmelamine is markedly small (methylolmelamine turns almost completely into its conjugate acid) and the observed rate (Figs. 1(1), 2(1) and 5(1)) is considerably larger than that of a reaction between the molecular form of methylolmelamine and its conjugate acid, both concentrations being computed from the base constant[15] of methylolmelamine. (That is, if the main reaction in this range is the second term of Eq. (2), the rate must be considerably smaller than the observed one; the same is true for the first term of Eq. (2). Consequently, the main reaction in this range is neither the first term nor the second term of Eq. (2).)

Previously[20] it has been speculated that the condensation of methylolmelamine in such a strong acidic range takes place between the conjugate acids themselves; but there has been no experimental evidence for this. Nevertheless, the present findings may support this speculation. In a strongly acidic range, reactions between conjugate acids themselves have often been reported.[21]

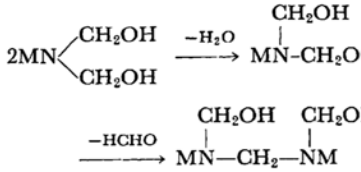
Next, in view of the above, let us propose some structural mechanisms of the reaction between the molecular forms (I) themselves, the conjugate acid (II) and the molecular form, and the conjugate acids themselves to form the dimer in the early stage. Those mechanisms are illustrated in relation to di-methylolmelamine in Eqs. (7), (8), and (9) respectively.

In Eq. (8), with the formation of the dimer with the conjugate acid form (III), this dimer converts into its molecular form (IV: triazine with the conjugate double bond) with the release of the proton, because the melamine rest of the dimer is less basic than that of the starting methylolmelamine; this probably takes place to a major extent with the molecular form of methylolmelamine and its coexisting conjugate acid ($0<$[HCl]/[M]<1.0 (molar ratio)). Hence, the proton thus released combines with ane quvalent amount of the molecular form of methylolmelamine to form its conjugate acid (reactive). The fact that the maximum shifts toward smaller [HCl]/[M] values as the condensation proceeds is thus obviously accounted for. Also, in the case of methylolmelamine, small changes in the acidity have a greater effect on the condensation rate than in the case of methylolurea (near the neutral region)[22]; this fact, which is well known from experience, may be explained by this mechanism.

With the further growth of the condensate, additional protons are released as the basicity decreases, so that in the case of the trimer a smaller proportion would exist in the charged form, *i. e.,* in the conjugate acid form, than in that of the dimer. (In Eq. (7), the release of the proton does not take place.)

On the other hand, the reaction of Eq. (9) takes place to a major extent in the range of [HCl]/[M]$>$1.0 (molar ratio), as has been stated above; hence, more hydrochloric acid than methylolmelamine is present in this range. Therefore, the release of the proton in the dimer with the conjugate acid form (V) seems to be markedly smaller than that in the reaction of Eq. (8) in this range. However, since the melamine rest of the condensate in the latter stage is markedly less basic, this condensate may easily release the proton more than in the case of the dimer.

(2) Hexa-methylolmelamine. Hexa-methylolmelamine has the terminal group $-(\mathrm{CH_2OH})_2$. Hence, it is assumed that a dimethylene ether linkage, $-\mathrm{CH_2OCH_2}-$, is formed with the liberation of water, and then this linkage, completely or partially or not all, is converted into a methylene linkage with the liberating formaldehyde during the course of the condensation. This is shown in Eq. (10):



$$2\mathrm{MN}\begin{matrix}\diagup\mathrm{CH_2OH}\\ \diagdown\mathrm{CH_2OH}\end{matrix} \xrightarrow{-\mathrm{H_2O}} \mathrm{M}\overset{\overset{\mathrm{CH_2OH}}{|}}{\mathrm{N}}\text{-}\mathrm{CH_2OCH_2}\text{-}\overset{\overset{\mathrm{CH_2OH}}{|}}{\mathrm{N}}\mathrm{M} \xrightarrow{-\mathrm{HCHO}} \mathrm{M}\overset{\overset{\mathrm{CH_2OH}}{|}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\overset{\mathrm{CH_2OH}}{|}}{\mathrm{N}}\mathrm{M} \tag{10}$$

The reaction of Eq. (10) may play a minor part in the condensation under the conditions of Figs. (3) and (4), because no dimethylene ether linkage could be found by the conventional analytical method[23] during the course of the reactions; what is more, when the rate of the formation of the methylene linkage of M2.68F was compared with that of M5.65F under the same conditions (The investigation was carried out in the medium of an aqueous-DMSO solution without an acid.), the

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20) H. P. Wohnsiedler, *Ind. Eng. Chem.,* **44**, 2679 (1952); J. F. Blais, "Amino Resins," Reinhold Publishing Corporation, New York, Champan & Hall Ltd., London (1959), p. 21.

21) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Hold and Company, Inc., New York (1959), p. 432 and others.

22) J. F. Blais, "Amino Resins," Reinhold Publishing Corporation, New York, Champan & Hall Ltd., London (1959), p. 20.

23) K. Tanimoto, M. Nemoto and T. Akita, *Kobunshi Kagaku (Chem. High Polymers Japan)*, **13**, 288 (1956).

rate of M5.65F was confirmed to be negligibly smaller than that of M2.68F.

Contrarily, in the polycondensation reaction of melamine-formaldehyde, Gam *et al.*[24] have attached particular importance to the dimethylene ether linkage and have assigned a minor role to the methylene linkage as a condensate—forming linkage. However, as has been demonstrated above, the reaction forming a dimethylene ether linkage is slow; this linkage would be formed if the temperature were higher and the solution more concentrated than in the present experiments.

From this evidence, the condensation mechanism of hexa-methylolmelamine may be considered to be that hexa-methylolmelamine first decomposes into a lower methylolmelamine such as tri- or tetra-methylolmelamine in the presence of an acid, and that then the condensation proceeds by the same mechanism as in the case of a low methylolmelamine. The observed results can be explained by this mechanism. The decomposition of hexa-methylolmelamine at a high temperature proceeds even in the presence of a small amount of an acid. Therefore, as the temperature is raised, the maximum shifts toward smaller [HCl]/[M] values and approaches to *ca.* [HCl]/[M]=0.5 (molar ratio), as has been stated above. On the other hand, with a lowering of the temperature, the maximum shifts toward larger [HCl]/[M] values, because the decomposition of hexa-methylolmelamine proceeds slowly and more acid is necessary for its decomposition with a lowering of the temperature.

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24) A. Gam, G. Widmer and W. Fisch, *Brit. Plastics.*, **14**, 508 (1943).