NOTES

Condensation of a Methylolmelamine (with a Low Degree of Methylolation) in Acidic Media

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Moldings and laminates are prepared by curing a methylolmelamine whose composition corresponds nearly to di- or tri-methylolmelamine (with low degrees of methylolation); an acid catalyst is usually added before this cure because the condensation rate increases conspicuously upon the addition of a small amount of an acid.[1,2] However, there have been no reports on the condensation rate in strongly acidic media.

For this reason, the condensation rate *vs.* the pH was investigated in the media of *ca.* pH 2—8; the latter condensation stage was also studied.[3] The above methylolmelamine was prepared and analyzed by the usual method[4] (M 2.68 F[*2]). It was confirmed by the use of the sulfite method that the methylolmelamine decomposes easily in water, but that it scarcely decomposes in dimethylsulfoxide (DMSO[3]) or even in an aqueous-DMSO solution (*ca.* 1 : 2, vol. ratio); consequently, an aqueous-DMSO solution was used as the solvent.

Figure 1 shows the "formation of methylene linkage"/"initial methylolmelamine" (molar ratio) *vs.* the pH; in this case the iodometric[3] and sulfite methods were used. As is well known, the condensation rate increases with the increase in acidity (*ca.* pH 8→7).[1,2] Figure 1 shows that the maximum appearing in the early stage corresponds to the $[H^+]/[\text{initial methylolmelamine}] = A \doteqdot 0.5$ (molar ratio).

The condensation without acid is a reaction of the molecular forms[*2] of the methylolmelamines themselves (Eq. (1)). The condensation mechanism is considered to be an attack of the electrophilic carbon of the amino-methylol group on the nitrogen of the amino or amino-methylol group of a methylolmelamine; this mechanism may be similar to that of an acid-catalyzed semicarbazone formation[5] in terms of the formation of the C–N bond. Moreover, the above methylolmelamine has sufficient basicity[6] to combine with an equivalent amount of hydrochloric acid to form a conjugate acid[*3,6]; in addition, the carbon of the amino-methylol group of a conjugate acid is

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

2) K. Koeda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **60**, 1567 (1957).

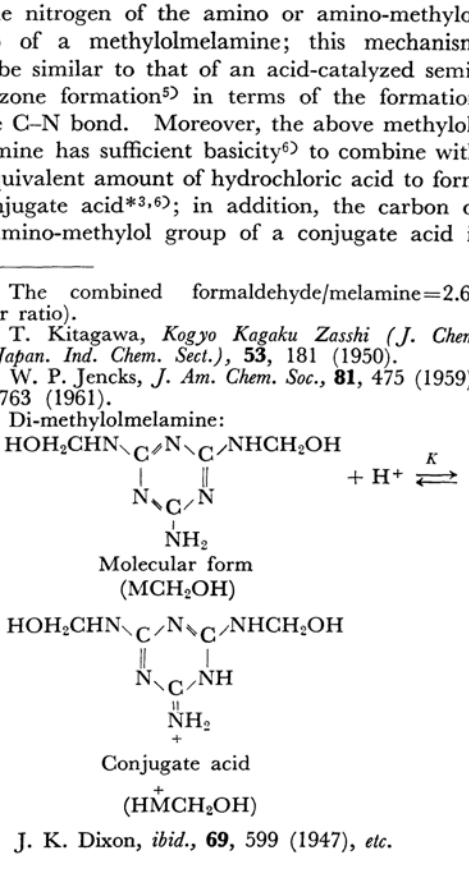
3) K. Sato, This Bulletin, **40**, 1547 (1967).

[*2] The combined formaldehyde/melamine=2.68 (molar ratio).

4) T. Kitagawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan. Ind. Chem. Sect.)*, **53**, 181 (1950).

5) W. P. Jencks, *J. Am. Chem. Soc.*, **81**, 475 (1959); **83**, 2763 (1961).

[*3] Di-methylolmelamine:



Molecular form

(MCH_2OH)

Conjugate acid

$(H\overset{+}{M}CH_2OH)$

6) J. K. Dixon, *ibid.*, **69**, 599 (1947), *etc.*

more electrophilic (more reactive) than that of a molecular form of a methylolmelamine. This effect accounts for the increase in the rate with the increase in the acidity ($A<0.5$ (molar ratio)). This effect is counteracted by the increasing removal of the molecular forms of methylolmelamines by the formation of a conjugate acid in the region of $A>0.5$ (molar ratio). Because of these opposing factors, the curve shows its maximum at $A=0.5$ (molar ratio), *i. e.*, $[H^+]=1/K$, where K*[3,6] is the equilibrium constant between the molecular form and the conjugate acid. Hence, it may be considered that the main condensation in the region of $0<A<1.0$ (molar ratio) is a reaction between the conjugate acid and the molecular form of methylolmelamine (Eq. (2)), since the curve shows its maximum at nearly the same concentration in both substances.

Also, the maximum shifts toward the smaller A values as the condensation progresses, because the basicity of the condensate is smaller than that of the methylolmelamine.

Besides, it may be considered that the main condensation in the region of a $A>1.0$ (molar ratio) is a reaction of the conjugate acids of the methylolmelamines themselves (Eq. (3)), because the concentration of the molecular forms of methylolmelamines is markedly small (the methylolmelamines become conjugate acid almost completely); the observed rate is considerably larger than that of the reaction between the conjugate acid and the molecular forms of methylolmelamines, both whose concentrations are calculated from the base constant[6] of the methylolmelamines; this mechanism may be similar to that of semicarbazone formation in strongly acidic media.[5]

$$\text{Rate} = k_1[\text{MCH}_2\text{OH}]^2 \qquad (1)$$

(molecular form, molecular form)

$$+\ k_2[\text{MCH}_2\text{OH}][\text{H}\overset{+}{\text{M}}\text{CH}_2\text{OH}] \qquad (2)$$

(molecular form, conjugate acid)

$$+\ k_3[\text{H}\overset{+}{\text{M}}\text{CH}_2\text{OH}]^2 \qquad (3)$$

(conjugate acid, conjugate acid)

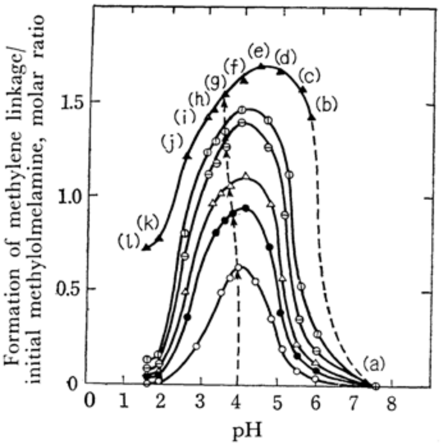


Fig. 1. Formation of methylene linkage/initial methylolmelamine (molar ratio) *vs.* pH in aqueous-DMSO solution (*ca.* 1 : 2, vol. ratio) at 45°C.

-○-: 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] (molar ratio)

Initial concn. of methylolmelamine:
[M2.68F]=0.0776 (mol/*l*).