Studies on Melamine Resin. VII. Kinetics of the Acid-Catalyzed Condensation of Di- and Trimethylolmelamine*

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ABSTRACT: Initial-stage kinetics for the condensation of di- and trimethylolmelamine (M2F and M3F respectively) have been studied in an aqueous dimethylsufoxide media with pH *ca.* 1—9. The main results were as follows.

(1) Regardless of pH, the initial rate was given by $R_0 = k[MnF]^2$ ($n = 2$ or 3) and k is the overall rate constant. The values of k in the pH range of *ca.* 1—9 were obtained.

(2) The observed curves (k *vs.* pH, log k *vs.* pH, and k *vs.* [H$^+$]) were compared with the corresponding calculated curves based on the rate equation. Consequently, in the presence of the acid, it was revealed that for an $S \equiv$ [hydrochloric acid]$_0$/[M2F]$_0$ or [M3F]$_0$ ratio less than 1.0 (pH *ca.* 2—7) the main reaction at the early stage of the condensation is the reaction between the methylolmelamine molecule and the conjugate acid; furthermore for $S > 1.0$—1.2 (pH < *ca.* 2) the main condensation would be the reaction between the conjugate acid themselves.

(3) At equal S, the k for M3F is remarkably larger than that for M2F. This is opposite to the rates of mono- and dimethylolurea. The mechanism was interpreted.

KEY WORDS   Methylolmelamine / Melamine Resin / Condensation / Methylene Linkage / Amino Resin / Kinetics / Acid Catalyst /

As is well-known, urea and melamine (M) resins are the most prominent members of amino resins. There have been a number of kinetic studies[1a—e] on the condensation (the formation of methylene linkages) of methylolurea. On the other hand, condensation of methylolmelamine has been studied by Kitagawa,[2] Wohnsiedler,[3] Koeda,[4] and Yoshimi, *et al.*,[5] and recently by Sato[6a,b] who reported in a previous work using an aqueous dimethylsulfoxide (DMSO) media. However, studies on kinetics of the condensation of methylolmelamine have not yet been reported. For this reason, condensations of di- and trimethylolmelamine (M2F and M3F respectively) were kinetically studied in detail at the early stages, using an aqueous-DMSO media in the pH range of *ca.* 1—9.

The present report deals with the important relationship between the condensation rate and the acidity of the solution, since the acidity relates to some probable mechanism at the early stage of the condensation.

In this paper, [ ] denotes the concentration, [ ]$_0$, the initial concentration, and S, the molar ratio of [hydrochloric acid]$_0$/[M1.97F]$_0$ or [M2.95F]$_0$.

EXPERIMENTAL

Materials

The method used in the purification of M and DMSO has been described in a previous paper.[6b]

Preparation of M1.97F and M2.95F[3]

The present method[3] differs from that reported previously.[4,6b]

Preparation of M1.97F. A mixture of 1600 ml (*ca.* 22 mol) of commercial formaline (F) (*ca.* 37 wt%) and 800 ml of water was adjusted at pH 9.0—9.5 with 0.1-*N* sodium hydroxide, and heated to 70°C; then, 1.26 kg (10 mol) of M was added with stirring, and reaction temperature was kept at 70°C until the M was almost dis-

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solved (*ca.* 20 min). The turbid solution thus obtained was decanted to remove the small amount of insoluble substance, quenched with ice water, and left standing overnight. The precipitate produced was washed with methanol and ether, and dried *in vacuo*. Yield was 1.40 kg.

Preparation of M2.95F. The method was almost the same as that of M1.97F: 2300 ml (*ca.* 31 moles) of commercial F, 600 ml of water and 1.26 kg (10 mol) of M were used. Yield was 1.81 kg. These yields were remarkably better than those reported previously.[4,6b]

Results of the analysis[2,7] show that the molar ratios of the combined F to M were 1.97 and 2.95, and that weight per cents of water were 0.78 and 2.20 respectively. The compositions of the sample were thus approximately M2F and M3F. They will be described as M1.97F and M2.95F.

A Typical Procedure for the Rate Measurements

All investigations were carried out with 35°C as the reaction temperature, at a constant volume ratio of DMSO/H_2O.

Initially, 4.66 g (0.025 mol) of M1.97F or 5.49 g (0.025 mol) of M2.95F was dissolved to 250 ml by using an aqueous DMSO solution (the volume ratio, 1/4). On the other hand, a mixture of 30 ml of DMSO and an appropriate amount of hydrochloric acid was diluted to 50 ml using distilled water; thus, the volume ratio of DMSO/H_2O was made almost the same as that of the M1.97F or M2.95F solution, since dilution of DMSO with water is considerably exothermic. Then, the two solutions were respectively kept in a thermostat regulated at 35°C, followed by mixing with each other (Table I, no. 1—24 for M1.97F, and Table II, no. 32—52 for M2.95F).

Aliquots were analyzed by the iodometric and the sulfite methods, the pH being measured by a glass-electrode pH-meter, as previously reported.[6b,8]

An Estimation of the Initial Rate

The methylene linkage formed was evaluated as previously[6b] reported. Figure 1 shows some typical examples of the concentration of methylene linkage formed *vs.* time. The initial rate R_0 was computed from the slope of the curve of methylene linkage *vs.* time at time zero.
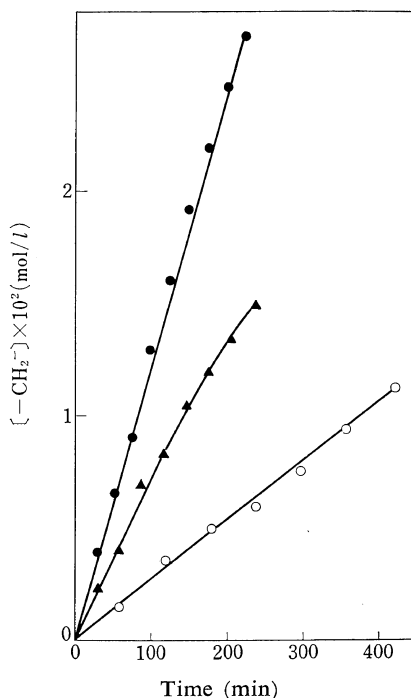

Figure 1. The methylene linkage formed *vs.* reaction time: ○, Table I exptl no. 4; ●, no. 7; ▲, no. 16.

RESULTS AND DISCUSSION

Reaction Order and the Calculation of k

The rate was measured at various concentration of M1.97F and pH 5.96, 4.75, 4.20, 3.04, and 2.07 respectively. As Figure 2a shows, the plots of log R_0 *vs.* log $[M1.97F]_0$ gave straight lines and the slopes (tan α) were 2.0 regardless of the pH. Accordingly, the reaction was of second order. The same was true for M2.95F, as shown in Figure 2b. It follows that

$$R_0 = k[MnF]^2, \qquad n = 1.97 \text{ and } 2.95 \qquad (1)$$

where k denotes the overall rate constant.

The values of k for M1.97F were calculated by the use of eq 1, and are shown in Table I together with the acidity of the solution (S, 0—6.901; pH, *ca.* 1—9), and those for M2.95F, in Table II (S, 0—6.129; pH, *ca.* 1—9). In these Tables, no. 25—31 and no. 53—62 show respectively the values which corresponded to more concentrated M1.97F and M2.95F, since their rate was slow at pH < *ca.* 3.

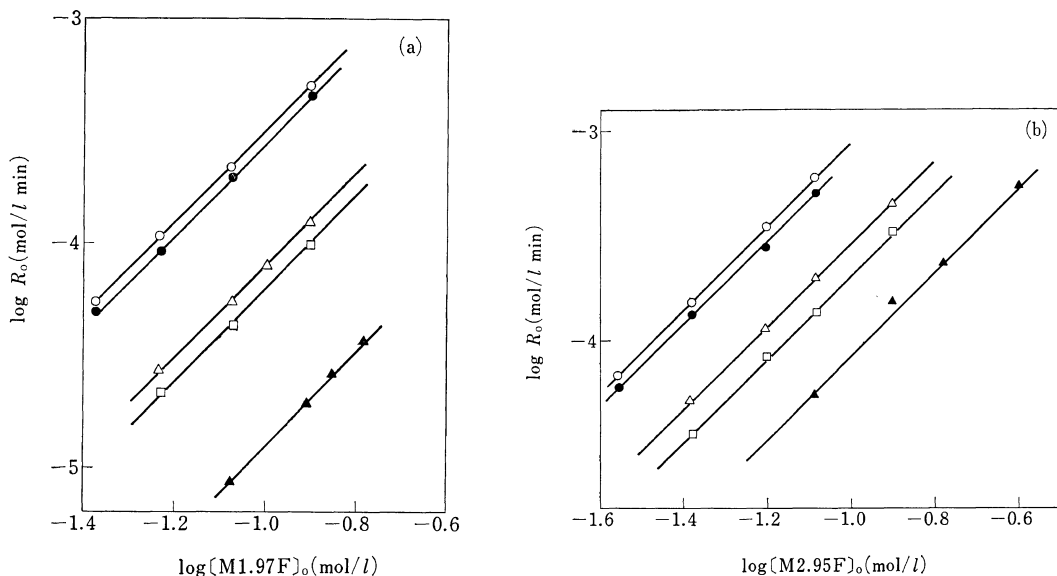**Figure 2.** The relationship between $\log R_0$ and $\log[\text{M1.97F}]_0$ or $\log[\text{M2.95F}]_0$: (a) for M1.97F; □, pH 5.96; ●, pH 4.75; ○, pH 4.20; △, pH 3.04; ▲, pH 2.07; (b) for M2.95F; □, pH 5.38; ○, pH 4.15; ●, pH 3.72; △, pH 2.84; ▲, pH 2.10.

Table I. The value of k for M1.97F at 35°C (The effect of acidity)

Exptl[a] no.	[HCl]₀/ [M1.97F]₀, molar ratio	pH	[H⁺],[b] mol/l	k, 1/mol min
1	0.000	8.62	2.40×10^{-9}	0.00
2	0.006	7.37	4.27×10^{-8}	1.21×10^{-4}
3	0.021	6.76	1.74×10^{-7}	1.50×10^{-3}
4	0.051	6.34	4.57×10^{-7}	3.67×10^{-3}
5	0.095	6.00	1.00×10^{-6}	6.25×10^{-3}
6	0.193	5.60	2.51×10^{-6}	1.28×10^{-2}
7	0.292	5.29	5.13×10^{-6}	1.77×10^{-2}
8	0.393	5.01	9.78×10^{-6}	2.32×10^{-2}
9	0.491	4.73	1.86×10^{-5}	2.83×10^{-2}
10	0.583	4.44	3.63×10^{-5}	3.23×10^{-2}
11	0.595	4.42	3.80×10^{-5}	3.16×10^{-2}
12	0.684	4.15	7.08×10^{-5}	2.99×10^{-2}
13	0.783	3.84	1.45×10^{-4}	2.55×10^{-2}
14	0.839	3.56	2.76×10^{-4}	1.77×10^{-2}
15	0.889	3.43	3.72×10^{-4}	1.39×10^{-2}
16	0.955	3.12	7.59×10^{-4}	9.54×10^{-3}
17	0.982	3.06	8.71×10^{-4}	7.80×10^{-3}
18	1.080	2.82	1.51×10^{-3}	4.88×10^{-3}
19	1.191	2.66	2.19×10^{-3}	3.56×10^{-3}
20	1.489	2.29	5.13×10^{-3}	2.01×10^{-3}
21	1.990	1.99	1.02×10^{-2}	1.15×10^{-3}
22	2.971	1.70	2.00×10^{-2}	7.80×10^{-4}
23	4.909	1.45	3.55×10^{-2}	7.41×10^{-4}
24	6.901	1.22	6.03×10^{-2}	7.01×10^{-4}
25	0.986	2.69	2.40×10^{-3}	4.98×10^{-3}
26	1.081	2.34	4.57×10^{-3}	2.53×10^{-3}
27	1.179	2.13	7.41×10^{-3}	1.84×10^{-3}
28	1.270	1.97	1.07×10^{-2}	1.54×10^{-3}
29	1.479	1.75	1.78×10^{-2}	1.25×10^{-3}
30	2.011	1.48	3.31×10^{-2}	9.20×10^{-4}
31	3.030	1.12	7.59×10^{-2}	1.06×10^{-3}

[a] For exptl no. 1—24, [M1.97F]₀, 8.38×10^{-2} mol/l; for exptl no. 25—31, [M1.97F]₀, 2.514×10^{-1} mol/l.
[b] Computed from the pH.

Table II. The value of k for M2.95F at 35°C (The effect of acidity)

Exptl[a] no.	[HCl]₀/ [M2.95F]₀, molar ratio	pH	[H⁺], mol/l	k, 1/mol min
32	0.000	8.79	1.62×10^{-9}	0.00
33	0.023	6.23	5.90×10^{-7}	3.48×10^{-3}
34	0.034	5.97	1.07×10^{-6}	5.66×10^{-3}
35	0.053	5.72	1.91×10^{-6}	9.87×10^{-3}
36	0.103	5.34	4.58×10^{-6}	1.92×10^{-2}
37	0.203	4.90	1.26×10^{-5}	4.17×10^{-2}
38	0.302	4.64	2.29×10^{-5}	6.31×10^{-2}
39	0.404	4.36	4.37×10^{-5}	7.42×10^{-2}
40	0.505	4.11	7.77×10^{-5}	8.06×10^{-2}
41	0.548	3.97	1.07×10^{-4}	8.23×10^{-2}
42	0.609	3.90	1.26×10^{-4}	7.98×10^{-2}
43	0.706	3.64	2.29×10^{-4}	7.10×10^{-2}
44	0.801	3.37	4.26×10^{-4}	6.11×10^{-2}
45	0.909	3.13	7.41×10^{-4}	4.86×10^{-2}
46	1.000	2.91	1.23×10^{-3}	3.38×10^{-2}
47	1.121	2.71	1.95×10^{-3}	2.32×10^{-2}
48	1.329	2.48	3.31×10^{-3}	1.74×10^{-2}
49	1.523	2.29	5.14×10^{-3}	1.20×10^{-2}
50	2.008	2.05	8.92×10^{-3}	7.40×10^{-3}
51	2.990	1.74	1.82×10^{-2}	4.21×10^{-3}
52	6.129	1.33	4.68×10^{-2}	2.03×10^{-3}
53	0.868	2.86	1.38×10^{-3}	3.29×10^{-2}
54	0.932	2.68	2.09×10^{-3}	2.33×10^{-2}
55	0.979	2.55	2.82×10^{-3}	2.16×10^{-2}
56	1.056	2.33	4.68×10^{-3}	1.41×10^{-2}
57	1.152	2.16	6.92×10^{-3}	1.15×10^{-2}
58	1.281	1.99	1.02×10^{-2}	9.34×10^{-3}
59	1.479	1.82	1.51×10^{-2}	6.02×10^{-3}
60	1.675	1.68	2.09×10^{-2}	4.31×10^{-3}
61	2.000	1.55	2.82×10^{-2}	3.63×10^{-3}
62	2.959	1.22	6.03×10^{-2}	2.03×10^{-3}

[a] For exptl no. 32—52, [M2.95F]₀, 8.30×10^{-2} mol/l; for exptl no. 53—62, [M2.95F]₀, 2.490×10^{-1} mol/l.

Observed Curves

By the use of the values in Table I for M1.97F and Table II for M2.95F, the observed curves (k vs. pH, $\log k$ vs. pH, and k vs. $[H^+]$) are obtained, which are shown in Figures 3, 4, and 5, respectively.

Earlier it had been found by Sato,[9] one of the authors that the condensation rate of M2F, M3F, and M6F passes through a maximum. Several years later,[10] a similar maximum has been confirmed for a study of the condensation of hydroxymethylated 2-methoxy-4, 6-diamino-s-triazine by Tashiro, et al.

As the above Figures show, not only maximum but also inflection points are found; e.g., the curves (k vs. pH) show one maximum and two inflection points (Figure 3), and the curves (k vs. $[H^+]$) show one maximum and one inflection point (Figure 5). Their values are listed in Table IV.

Rate Equation

Unlike urea and methylolurea, M1.97F and
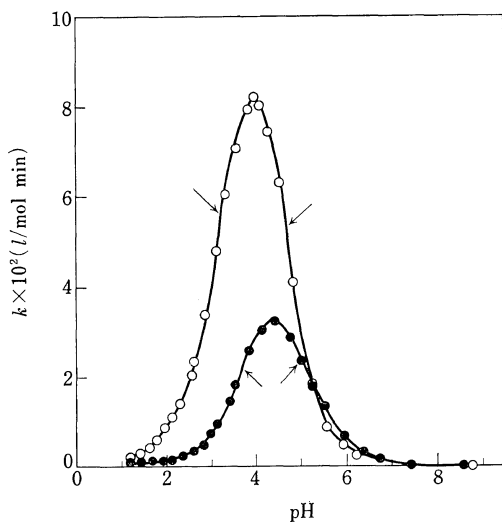
Figure 3. Observed curve (k vs. pH) at 35°C: →, inflection points. ●; for M1.97F [from right, Table I exptl no. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20 (in above cases, $[M1.97F]_0$, 8.38×10^{-2} mol/l) 27, 28, 29, 30, and 31 ($[M1.97F]_0$, 2.514×10^{-1} mol/l)]; ○, for M2.95F [from right, Table II exptl no. 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45 ($[M2.95F]_0$, 8.30×10^{-2} mol/l), 53, 54, 55, 56, 57, 58, 59, 60, 61, and 62 ($[M2.95F]_0$, 2.490×10^{-1} mol/l)].
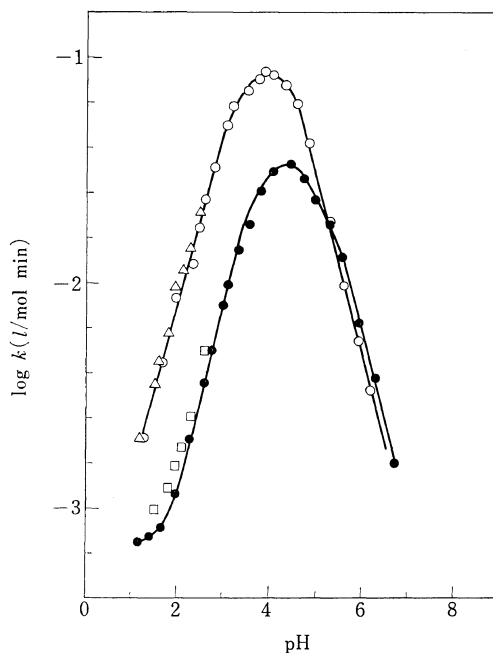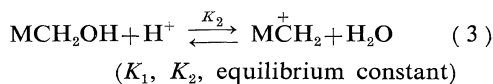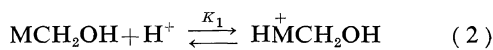

Figure 4. Observed curve ($\log k$ vs. pH) at 35°C: ●, for M1.97F [from right, Table I exptl no. 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, and 24 ($[M1.97F]_0$, 8.38×10^{-2} mol/l); □, 25, 26, 27, 28, 29 and 30 ($[M1.97F]_0$, 2.514×10^{-1} mol/l); the slope, -0.87 at $[H^+] \ll K_1^{-1}$; 0.85 at $[H^+] \gg K_1^{-1}$ (pH > ca. 2)]; ○, for M2.95F [from right, Table II exptl no. 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, and 52 ($[M2.95F]_0$, 8.30×10^{-2} mol/l); △: 55, 56, 57, 58, 59, 60, 61, and 62 ($[M2.95F]_0$, 2.490×10^{-1} mol/l); the slope, -0.82 at $[H^+] \ll K_1^{-1}$; 0.75 at $[H^+] \gg K_1^{-1}$ (pH > ca. 2)].

M2.95F as well as M have sufficient basicities.[11] This fact made the rate equation complex.

As has been stated previously,[6b] in an acidic media, the methylolmelamine molecule MCH_2OH is in equilibrium with the conjugate acid $H\overset{+}{M}CH_2OH$, and the carbonium ion $M\overset{+}{C}H_2$.[12]

$$MCH_2OH + H^+ \underset{\overrightarrow{}}{\overset{K_1}{\rightleftharpoons}} H\overset{+}{M}CH_2OH \qquad (2)$$

$$MCH_2OH + H^+ \underset{\overrightarrow{}}{\overset{K_2}{\rightleftharpoons}} M\overset{+}{C}H_2 + H_2O \qquad (3)$$

(K_1, K_2, equilibrium constant)

The condensation at the early stage may proceed among these species (Table III). Therefore, the rate is given by eq 4, where k_1, k_2, k_3, k_4, k_5, and k_6 are shown in Table III. Presumably eq 4
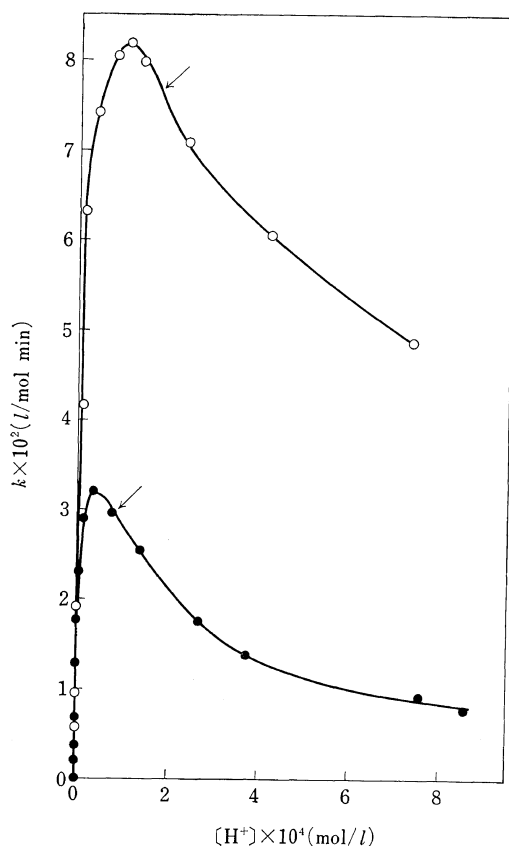
Figure 5. Observed curve (k vs. $[H^+]$) at 35°C: →, inflection points; ●: for M1.97F [from left, Table I exptl no. 1, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, and 17 ($[M1.97F]_0$, 8.30×10^{-2} mol/l)]; ○: for M2.95F [from left, Table II exptl no. 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, and 45 ($[M2.95F]_0$, 2.490×10^{-1} mol/l)].

(*cf. Condensation Mechanism*) would be the rate-determining step, because there is a maximum

Table III. The rate constants of the elementary reaction for the condensation

	MCH_2OH	$\overset{+}{H}MCH_2OH$	$M\overset{+}{C}H_2$
MCH_2OH	k_1	k_2	k_3
$\overset{+}{H}MCH_2OH$	k_2	k_4	k_5
$H\overset{+}{C}H_2$	k_3	k_5	k_6

in the condensation rate with changing acidity, and also the reaction order is second order in the concentration of M1.97F or M2.95F. If the reactions of eq 2 and 3 which occur before those of eq 4 were rate-determining, the above results would not be obtained.

From the equilibrium between $\overset{+}{H}MCH_2OH$ and $M\overset{+}{C}H_2$ (*cf.* eq 2 and 3; $MCH_2OH=$intermediate), eq 8 and 8′ can be derived. By the use of k_2' and k_4' shown in eq 8 (or k_3' and k_6' shown in eq 8′), eq 4 can be reduced to eq 5. This concept is nothing but "ambiguities in kinetics."[13] By the use of K_1, K_2, and eq 9, each portion of eq 10 is given, where "a" denotes the initial concentration (mol/l) of M1.97F or M2.95F, "x", the concentration (mol/l) of methylene linkage formed after t min, and "$a-2x$," the concentration (mol/l) of M1.97F or M2.95F after t min. Because this is the early stage of the condensation only dimer formation needs to be discussed here. By the application of eq 10, eq 5 can be led to eq 6. From the comparison between eq 6 and 7, eq 11 is given. Evidently K_2 is small, whereas K_1^{11} is markedly large ($K_1 \gg K_2$). Hence, eq 11 can be reduced to eq 12.

$$\text{Rate}=\frac{dx}{dt}=k_1[MCH_2OH]^2+k_2[MCH_2OH][\overset{+}{H}MCH_2OH]+k_3[MCH_2OH][M\overset{+}{C}H_2]$$

$$+k_4[\overset{+}{H}MCH_2OH]^2+k_5[\overset{+}{H}MCH_2OH][M\overset{+}{C}H_2]+k_6[M\overset{+}{C}H_2]^2 \tag{4}$$

$$=k_1[MCH_2OH]^2+k_2'[MCH_2OH][\overset{+}{H}MCH_2OH](\text{or } k_3'[MCH_2OH][M\overset{+}{C}H_2])$$

$$+k_4'[\overset{+}{H}MCH_2OH]^2(\text{or } k_6'[M\overset{+}{C}H_2]^2) \tag{5}$$

$$=\frac{k_1+k_2'K_1[H^+](\text{or } k_3'K_2[H^+])+k_4'(K_1[H^+])^2(\text{or } k_6'(K_2[H^+])^2)}{\{1+(K_1+K_2)[H^+]\}^2}(a-2x)^2 \tag{6}$$

$$=k(a-2x)^2 \tag{7}$$

$$k_2' = k_2 + k_3 \frac{K_2}{K_1}$$

$$k_4' = k_4 + k_5 \frac{K_2}{K_1} + k_6 \left(\frac{K_2}{K_1}\right)^2 \qquad (8)$$

$$k_3' = k_3 + k_2 \frac{K_1}{K_2}$$

$$k_6' = k_6 + k_5 \frac{K_1}{K_2} + k_4 \left(\frac{K_1}{K_2}\right)^2 \qquad (8)'$$

$$[MCH_2OH] + [\overset{+}{H}MCH_2OH] + [\overset{+}{M}CH_2] = a - 2x \qquad (9)$$

$$[MCH_2OH] = \frac{a - 2x}{1 + (K_1 + K_2)[H^+]}$$

$$[\overset{+}{H}MCH_2OH] = \frac{K_1[H^+](a - 2x)}{1 + (K_1 + K_2)[H^+]} \qquad (10)$$

$$[\overset{+}{M}CH_2] = \frac{K_2[H^+](a - 2x)}{1 + (K_1 + K_2)[H^+]}$$

$$k = \frac{k_1 + k_2'K_1[H^+] + k_4'(K_1[H^+])^2}{\{1 + (K_1 + K_2)[H^+]\}^2} \qquad (11)$$

$$\doteqdot \frac{k_1 + k_2'K_1[H^+] + k_4'(K_1[H^+])^2}{\{1 + K_1[H^+]\}^2} \qquad (12)$$

Calculated Curves

Calculated curves corresponding to the above observed ones are described below, where the calculated ones are based on the rate equation given by eq 12.

Equation 12 is divided in three terms involving k_1, k_2', and k_4' (cf. eq 5). They are represented as A, B, and C respectively:

$$A = \frac{k_1}{(1 + K_1[H^+])^2} \qquad (13)$$

$$B = \frac{k_2'K_1[H^+]}{(1 + K_1[H^+])^2} \qquad (14)$$

$$C = \frac{k_4'(K_1[H^+])^2}{(1 + K_1[H^+])^2} \qquad (15)$$

From eq 13, 14, and 15, calculated curves for M1.97F are graphically shown, where K_1 of M1.97F* is regarded as $10^{4.5}$ (M1.99F; pK_b, 9.5

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* To 20 ml of an aqueous DMSO solution (the volume ratio: 1/4) containing 0.0838 mol/l of M1.97F, 0.1-N hydrochloric acid was added at 35°C. When S was 0.5, the pH was 4.5. As a result, K_1 for M1.97F would be $10^{4.5}$ since the proton would hardly add to DMSO to form the conjugate acid.[6] This value agrees with that calculated from the pK_b of the literature[11] (aqueous solution).

at 25°C),[11] viz., the calculated curves (A, B and C vs. pH) are shown in Figure 6, those (log A, log B and log C vs. pH) in Figure 7, and those (A, B, and C vs. [H+]) in Figure 8.
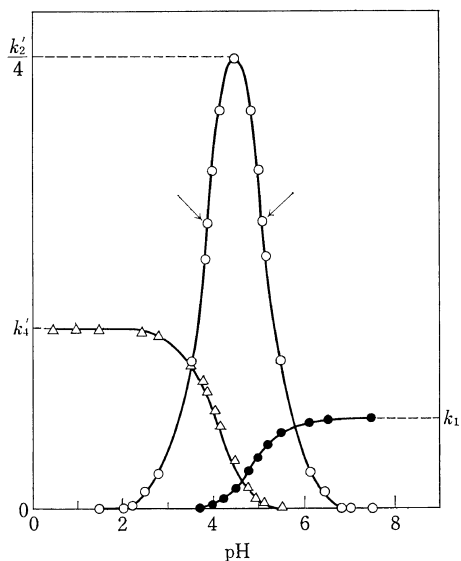

Figure 6. Calculated curves (A, B, and C vs. pH): ●, A; ○, B; △, C; →, inflection point.

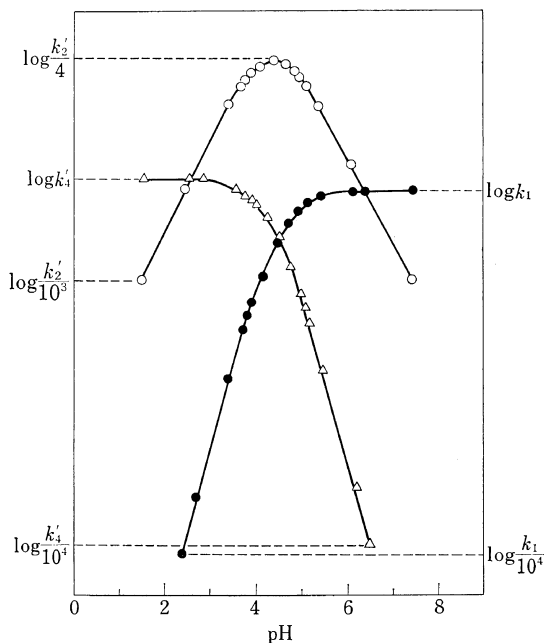**Figure 7.** Calculated curves (log A, log B, and log C vs. pH): ●, log A; ○, log B; △, log C: the slope of (log B vs. pH), −1.0 at [H+]≪K_1^{-1}; 1.0 at [H+]≫K_1^{-1}.
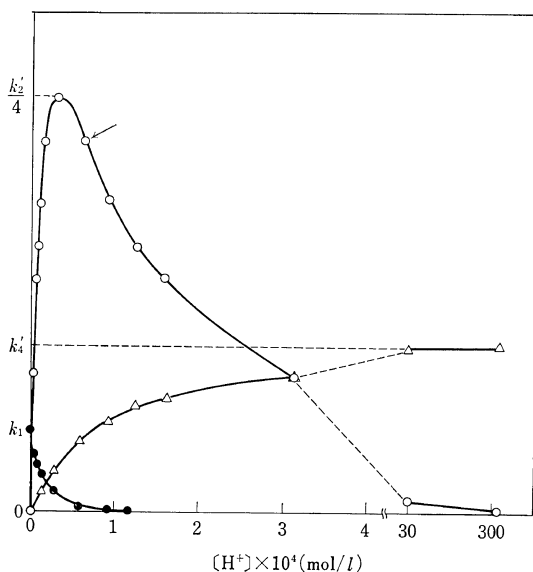
Figure 8. Calculated curves (A, B, and C vs. [H$^+$]): ●, A; ○, B; △, log C; →, inflection point.

Condensation Mechanism at the Early Stage

From the comparison of the above observed curves (k vs. pH, log k vs. pH, and k vs. [H$^+$]) with the corresponding calculated ones (A, B, and C vs. pH; log A, log B, and log C vs. pH; and A, B, and C vs. [H$^+$]) respectively, it can be easily estimated which of the reactions k_1, k_2' or k_4', is the main reaction; as eq 5 shows, the k_1 reaction is the reaction between two MCH$_2$OH molecules, the k_2' reaction, the reaction of MCH$_2$OH with HṀCH$_2$OH, and the k_4' reaction, the reaction of two HṀCH$_2$OH molecules.

The condensation mechanism in the presence of acid (pH < ca. 7; S > 0) was described as follows.

Range of $0 < S < 1.0$ (pH ca. 2—7). In this pH range, the observed curves do not coincide with the corresponding calculated ones A and C. (Figure 3 for M1.97F corresponds to A and C in Figure 6; Figure 4 for M1.97F, to log A and log C in Figure 7; Figure 5 for M1.97F, to A and C in Figure 8): First, if the main reaction in this pH range is assumed to be the k_1 reaction, the k (the observed curves) should decrease with increasing acidity. Second, if the main reaction is assumed to be the k_4' reaction, the k (the observed curves) should increase with increasing

acidity and remain constant at $S > 1.0$—1.2 (pH < ca. 2). But, these assumptions do not coincide with the relationship between k and acidity in the observed curves.

Hence, neither of them is the main reaction. Also, the observed curve (e.g., Figure 3 for M1.97F) and the only remaining calculated curve B (e.g., Figure 6) are similar to each other. For these reasons, the remaining k_2' reaction may be the main one.

In view of this, B denoting the k_2' reaction was investigated in detail.

First, as to the following three curves, the maximum and inflection points are respectively computed.

Curve (B vs. pH)
maximum point (I),[*] pH = log K_1 ;
inflection points (II),[*]

$$pH = \log \frac{K_1}{2 \pm \sqrt{3}}$$

Curve (log B vs. pH)
maximum point (III),[*] pH = log K_1 ;
inflection point (IV),[*] does not exist
(convex curve)

Curve (B vs. [H$^+$])
maximum point (V),[*] [H$^+$] = K_1^{-1} ;
inflection point (VI),[*] [H$^+$] = 2K_1^{-1}

$$(16)$$

By the use of eq 16, maximum and inflection points are computed and shown in Table IV, where K_1 is regarded as $10^{4.5}$ for M1.97F.[11] The

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[*] (I) $\dfrac{dB}{dpH} = \dfrac{dB}{d[H^+]} \cdot \dfrac{d[H^+]}{dpH} = 0$

(II) $\dfrac{d^2B}{dpH^2} = \dfrac{d}{dpH}\left(\dfrac{dB}{d[H^+]} \cdot \dfrac{d[H^+]}{dpH}\right) = 0$

(III) $\dfrac{d \log B}{dpH} = \dfrac{d \log B}{d[H^+]} \cdot \dfrac{d[H^+]}{dpH} = 0$

(IV) $\dfrac{d^2 \log B}{dpH^2} = \dfrac{d}{dpH}\left(\dfrac{d \log B}{d[H^+]} \cdot \dfrac{d[H^+]}{dpH}\right) = 0$

(V) $\dfrac{dB}{d[H^+]} = 0$

(VI) $\dfrac{d^2B}{d[H^+]^2} = 0$

Where, e.g., (II) is given as follows

$$\frac{d^2B}{dpH^2} = \frac{(2.3)^2 k_2' K_1[H^+](K_1^2[H^+]^2 - 4K_1[H^+] + 1)}{(K_1[H^+] + 1)^4}$$

Table IV. Maximum and inflection points

Curve	Methylolmel- amine	Maximum point		Inflection point	
		Calculated	Observed	Calculated	Observed
B vs. pH	M1.97F	4.5	4.4[a]	3.9 and 5.1	3.7 and 5.0[a]
	M2.95F	4.1	4.0[a]	3.5 and 4.6	3.2 and 4.7[a]
log *B* vs. pH	M1.97F	4.5	4.4[b]	Not exist	Not exist[b]
	M2.95F	4.1	4.1[b]	Not exist	Not exist[b]
B vs. $[H^+]$[d]	M1.97F	3.2×10^{-5}	3.6×10^{-5}[c]	6.3×10^{-5}	7.1×10^{-5}[c]
	M2.95F	7.9×10^{-5}	1.1×10^{-4}[c]	1.6×10^{-4}	1.7×10^{-4}[c]

[a] Figure 3 at pH *ca.* 2—7.

[b] Figure 4 at pH *ca.* 2—7.

[c] Figure 5 at pH *ca.* 2—7.

[d] $[H^+]$, mol/*l*.

calculated curves for M2.95F show the similar form to those of M1.97F, though they were omitted in this paper. Hence, the same was also true for M2.97F, as Figures 3, 4, and 5 for M2.95F show. Thus, the results for M2.95F are shown in Table IV together with those of M1.97F, where K_1 of M2.95F is regarded as $10^{4.1}$ (M2.97F; pK_b, 9.9 at 25°C).[11]

Table IV demonstrates the coincidence of the observed values with the calculated ones for both of maximum and inflection points;* it is seen that the above values are affected by the difference between the pK_b of M1.97F and that of M2.95F, *e.g.*, the observed maximum for M1.97F appears at pH 4.4, but that for M2.95F, at pH 4.0.

Second, from eq 14, log *B* is given by:

$$[H^+] \ll K_1^{-1}: \quad \log B \doteqdot -pH + \log k_2' + \log K_1 \quad (17)$$

$$[H^+] \gg K_1^{-1}: \quad \log B \doteqdot pH + \log k_2' - \log K_1 \quad (18)$$

From eq 17 and eq 18, the slope, d log *B*/d pH is given to be

---

* Instead of *B*, when the *k* shown by eq 12 is used, *e.g.*, the maximum point $dk/d[H^+]=0$, and the inflection point $d^2k/d[H^+]^2=0$ are given.

Curve (*k* vs. $[H^+]$)

$$\text{maximum point, } [H^+] = \frac{k_2' - 2k_1}{K_1(k_2' - 2k_4')} \doteqdot \frac{1}{K_1};$$

$$\text{inflection point, } [H^+] = \frac{3k_1 - 2k_2' + k_4'}{K_1(2k_4' - k_2')} \doteqdot \frac{2}{K_1}$$

By the use of $k_1 = 0$, and $k_4' = 0$ ($k_2' \gg k_1$ and k_4', *cf.*, next section), these are approximately reduced to those for the curve (*B* vs. $[H^+]$) given by eq 16, respectively.

$$[H^+] \ll K_1^{-1}, \quad \frac{d \log B}{d pH} = -1.0 \quad (19)$$

$$[H^+] \gg K_1^{-1}, \quad \frac{d \log B}{d pH} = 1.0 \quad (20)$$

Thus, the curves (log *B* vs. pH) should be linear, and their slopes should be $|1.0|$, at $[H^+] \ll K_1^{-1}$ and $[H^+] \gg K_1^{-1}$. With regard to M1.97F and M2.95F, Figure 4 shows the straight lines, and their slopes are nearly $|1.0|$, in the range of $[H^+] \ll K_1^{-1}$ and $[H^+] \gg K_1^{-1}$ with pH *ca.* 2—7 (somewhat smaller than $|1.0|$).

Such numerous kinetic evidences stated above strongly support that the main reaction in this pH range is the k_2' reaction.

Range of S > 1.0—1.2 (pH < ca. 2). Since M1.97F and M2.95F have sufficient basicities[11] to combine with an equivalent amount of hydrochloric acid to form $H\overset{+}{M}CH_2OH$, the concentration of MCH_2OH at S > 1.0—1.2 is extremely small.

In this pH range (S > 1.0—1.2; pH < *ca.* 2), the observed curves (*e.g.*, Figure 3) do not coincide with the corresponding calculated one *B* (*e.g.*, Figure 6); *i.e.*, if the main reaction in this pH range is the k_2' reaction as in the range of 0 < S < 1.0, *k* of the observed curves in this pH range (Figure 3) should be considerably smaller. Accordingly, the k_2' reaction would not be the main reaction. Similarly, the k_1 reaction is not the main one. Hence, the only one remaining, the k_4' reaction would be the main reaction, as speculated by Sato.[6a,b]

While the calculated curve *C* remains constant

at pH < *ca.* 2 (Figures 6 and 7), the k of the observed one decreases slightly and the k of M2.95F decreases more markedly with increasing acidity than that of M1.97F (Figure 3). This discrepancy would be interpreted as follows. In this study, the decomposition of M1.97F and M2.95F was considerably supressed by the use of an aqueous DMSO media; this result has been stated in a previous paper.[6b] But, from this study, it was revealed by using the sulfite method that the decomposition rate of M1.97F and M2.95F increase somewhat with increasing acidity, and also the decomposition rate of M2.95F is faster than that of M1.97F, in this pH range.* This data is similar to that of di- and trimethylolacetoguanamine.[14] Furthermore, as is found in the next section, the condensation rate of M2.95F is remarkably larger than that of M1.97F at the same S. As a result, with increasing acidity, the k of M2.95F would decrease more markedly than that of M1.97F even though the k_4' reaction is the main reaction. Thus, this discrepancy can be explained.

In a previous paper by Sato,[6a,b] the k_4' reaction at $S > 1.0$—1.2 has been estimated for the condensation of methylolmelamine. The condensation of methylolacetoguanamine has recently been studied at pH 3—7 by Uragami, *et al.*,[15] but the similar k_4' reaction is not estimated in this pH range. However, the similar k_4' reaction has been confirmed at pH 1.2 in the study of the condensation of hydroxymethylated 2-methoxy-4,6-diamino-s-triazine by Tashiro;[16] thus this consideration has been supported by Tashiro.

In addition, on the basis of the electronic theory, the above consideration may be acceptable: Surely k_2' is markedly larger than k_1 and k_4'.[6b] But, at pH < *ca.* 2, the k_4' reaction would be the main reaction, because the concentration of MCH_2OH, which is the active species for both k_1 and k_2' reactions (see eq 5), is extremely small at pH < *ca.* 2.

Comparison between the Condensation Rate of M1.97F and M2.95F

Previously, the condensation rate between mono- and dimethylolurea has been compared

at "the same pH" of the media (pH 4.0) by De Jong, *et al.*[1e] Hence, the same comparison was made between the k of M1.97F and the k of M2.95F. As shown in Figure 3, at the same pH < *ca.* 5, the k of M2.95F is remarkably larger than the k of M1.97F, notwithstanding, they are nearly equal to each other at pH > *ca.* 5.

But for methylolmelamine, the above comparison is unsuitable, because the pK_b of M1.97F differs considerably from that of M2.95F,[11] not similar to those of mono- and dimethylolurea.

Obviously, the molar ratios of $[\overset{+}{H}MCH_2OH]_0/[MCH_2OH]_0$ for M1.97F are respectively the same as those for M2.95F, so far as S is the same for each. Therefore, the comparison of k at "the same S" would be suitable in this case; the k of M2.95F—k of M1.97F ratio at the same S means the k_2' of M2.95F—k_2' of M1.97F ratio at $0 < S < 1.0$ since the main reaction in this range is the k_2' reaction (also see eq 5), and the k_4' of M2.95F—k_4' of M1.97F ratio at $S > 1.0$—1.2 since the main reaction in this range seems to be the k_4' reaction (also see eq 5). This comparison is shown in Figure 9.

As shown in Figure 9, at the same S, the k of M2.95F is remarkably larger than that of M1.97F in any acidity. Also, at the same S, the k of M2.95F—k of M1.97F ratios at $S > 1.0$—1.2 are more larger than those at $0 < S < 1.0$. In detail, at $0 < S < 1.0$, the k of M2.95F is nearly three times larger than that of M1.97F, *i.e.*, the k_2' of M2.95F—k_2' of M1.97F ratios keep nearly constant at 3 to 1 in this range. Contrarily, at $S > 1.0$—1.2, the k of M2.95F is nearly six times larger than that of M1.97F, *i.e.*, the k_4' of M2.95F—k_4' of M1.97F ratios keep nearly constant at 6 to 1 in this range. This finding suggests the difference between the condensation mechanism in the range of $0 < S < 1.0$ and that in $S > 1.0$—1.2 for M1.97F and M2.95F.

De Jong, *et al.*,[1e] have reported that the condensation rate of monomethylolurea is greatly larger than that of dimethylolurea. From this, they stated that the reaction of eq 21 is greatly faster than that of eq 22, *viz.*, the N of the amino group is greatly reactive (nucleophilic) than the N of the aminomethylol group. Therefore, the result obtained for M1.95F and M2.95F is "apparently" opposite to the case of mono-
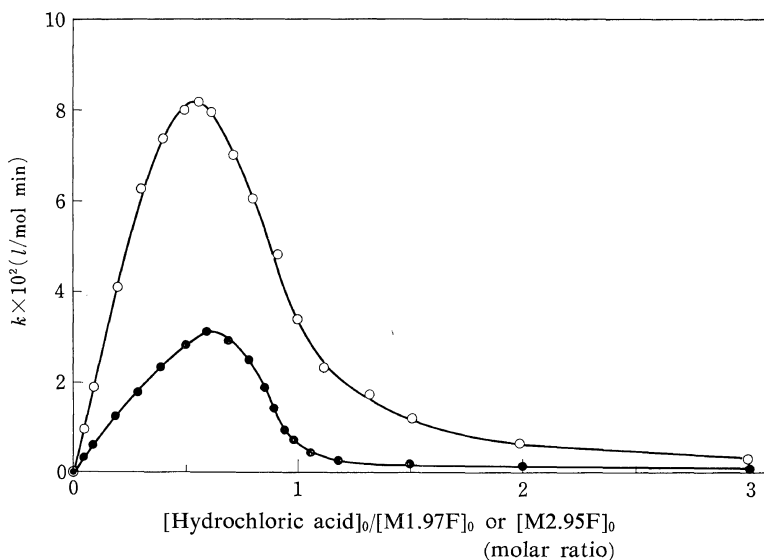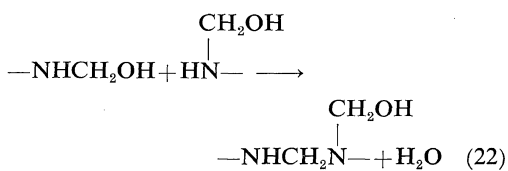
Figure 9. Comparison between the k of M1.97F and k of M2.95F at the same S and 35°C: ●, for M1.97F [from left, Table I exptl no. 1, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, and 22 ([M1.97F]$_0$, 8.38×10^{-2} mol/l)]; ○, for M2.95F [from left, Table II exptl no. 32, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, and 51 ([M2.95F]$_0$, 8.30×10^{-2} mol/l)].

and dimethylolurea, since M2.95F has scarcely amino group.

$$-NHCH_2OH + H_2N- \longrightarrow$$
$$-NHCH_2NH- + H_2O \quad (21)$$

$$\begin{array}{c} CH_2OH \\ | \\ -NHCH_2OH + HN- \longrightarrow \end{array}$$

$$\begin{array}{c} CH_2OH \\ | \\ -NHCH_2N- + H_2O \quad (22) \end{array}$$

This finding can be interpreted as follows. The k_2' and k_4' reaction schemes for M2F would be formulated in eq 23 and 24, respectively; those for M3F, in eq 25 and 26, respectively, where the structure of the conjugate acid of methylolmelamine has been used as given by Dixon, *et al.*[11]
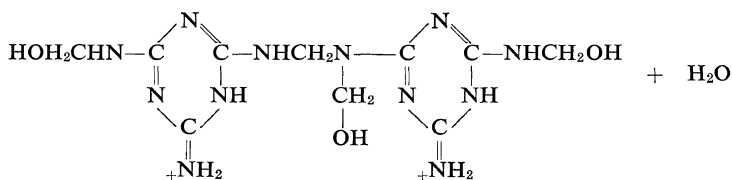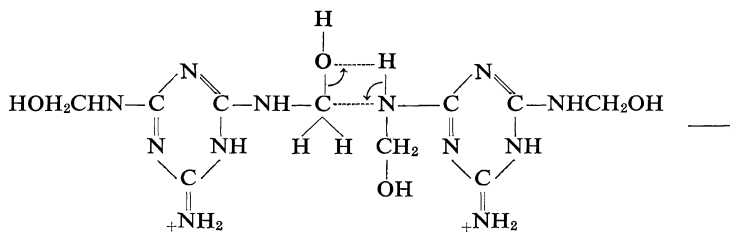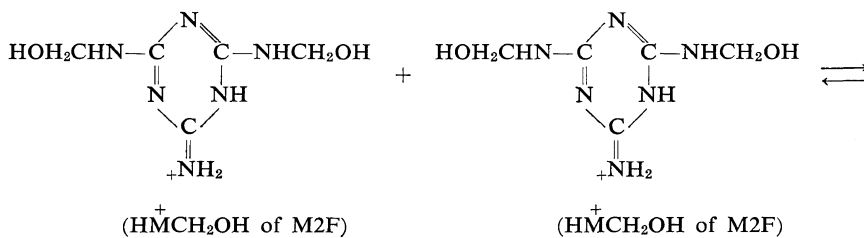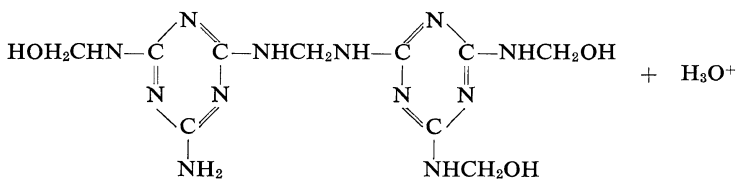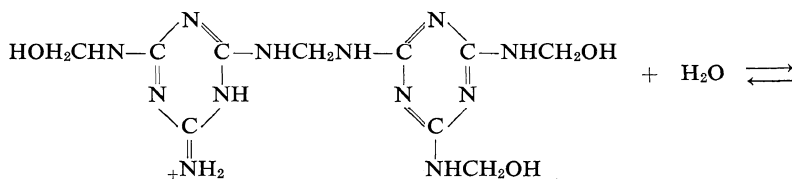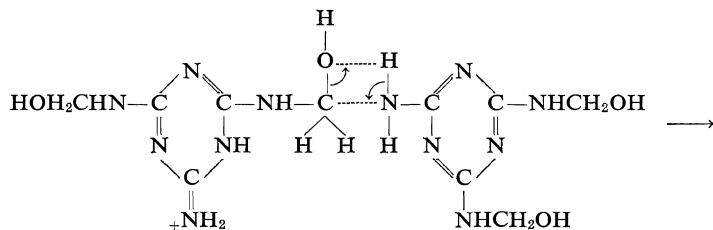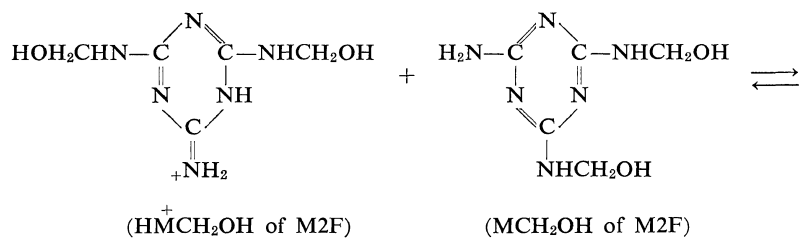
Range of $0 < S < 1.0$. The main reaction in this range is the k_2' reaction. Accordingly, the k_2' reaction schemes between M2F and M3F were compared.

With regard to M2F, as eq 23 formulates, the condensation of the k_2' reaction would proceed mainly between "the C of the methylol group apart from the N" in $H\overset{+}{M}CH_2OH$ and "the N of the amino group" in MCH_2OH. However,

with regard to M3F, as eq 25 formulates, the condensation of the k_2' reaction would proceed mainly between "the C of the methylol group neighboring the $\overset{+}{N}$" in $H\overset{+}{M}CH_2OH$ and "the N of the aminomethylol group" in MCH_2OH.

The condensation rate would be faster, with increase of the electrophilic effect of the C of the methylol group and/or the nucleophilic effect of the N of the amino group or aminomethylol group. In this case, the above C in $H\overset{+}{M}CH_2OH$ for M3F more markedly shows electrophilic effects, *i.e.*, more marked reactivity than the above C in $H\overset{+}{M}CH_2OH$ for M2F. On the other hand, the above N of the aminomethylol group in MCH_2OH for M3F would show less nucleophilic effect, *i.e.*, less reactivity than the above N of the amino group in MCH_2OH for M2F, and similar to those of methylolurea.[1e] Therefore, these effects are opposite each other for the condensation of the k_2' reaction of M3F. Since "the effect of the C" is larger than "the effect of the N" on the rate, it is interpreted that in this range the k of M2.95F shows larger values than k of M1.97F at the same S.

The effect of the N would be discussed in detail as follows. With regard to hydroxymeth-

$$\text{HOH}_2\text{CHN}-\text{C}\underset{\underset{\text{C}}{\overset{\text{N}}{\underset{\underset{+\text{NH}_2}{\|}}{\text{N}}}}{\overset{\text{N}}{=}}\text{C}-\text{NHCH}_2\text{OH} \quad + \quad \text{H}_2\text{N}-\text{C}\underset{\underset{\text{C}}{\overset{\text{N}}{\text{N}}}}{\overset{\text{N}}{=}}\text{C}-\text{NHCH}_2\text{OH} \quad \rightleftharpoons$$

(H$\overset{+}{\text{M}}$CH$_2$OH of M2F)   (MCH$_2$OH of M2F)

(23)

$$\text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NH}-\text{C}\cdots\text{N}-\text{C}=\text{C}-\text{NHCH}_2\text{OH}$$

$$\text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NHCH}_2\text{NH}-\text{C}=\text{C}-\text{NHCH}_2\text{OH} \quad + \text{H}_2\text{O} \rightleftharpoons$$

$$\text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NHCH}_2\text{NH}-\text{C}=\text{C}-\text{NHCH}_2\text{OH} \quad + \text{H}_3\text{O}^+$$

$$\text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NHCH}_2\text{OH} \quad + \quad \text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NHCH}_2\text{OH} \quad \rightleftharpoons$$

(H$\overset{+}{\text{M}}$CH$_2$OH of M2F)   (H$\overset{+}{\text{M}}$CH$_2$OH of M2F)

(24)

$$\text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NH}-\text{C}\cdots\text{N}-\text{C}=\text{C}-\text{NHCH}_2\text{OH}$$

$$\text{HOH}_2\text{CHN}-\text{C}=\text{C}-\text{NHCH}_2\text{N}-\text{C}=\text{C}-\text{NHCH}_2\text{OH} \quad + \text{H}_2\text{O}$$

$$HOH_2CHN-\overset{N}{\underset{\underset{NHCH_2OH}{C}}{\overset{N}{C}}}\overset{+}{C}=NHCH_2OH \quad + \quad HOH_2CHN-\overset{N}{\underset{\underset{NHCH_2OH}{C}}{\overset{N}{C}}}C-NHCH_2OH \quad \rightleftharpoons$$

(HṀCH_2OH of M3F) \qquad\qquad (MCH_2OH of M3F)

$$\longrightarrow \qquad (25)$$

$$+ \ H_2O \ \rightleftharpoons$$

$$+ \ H_3O^+$$

$$HOH_2CHN-\overset{N}{\underset{\underset{NHCH_2OH}{C}}{\overset{N}{C}}}\overset{+}{C}=NHCH_2OH \quad + \quad HOH_2CHN-\overset{N}{\underset{\underset{+NHCH_2OH}{C}}{\overset{N}{C}}}C-NHCH_2OH \quad \rightleftharpoons$$

(HṀCH_2OH of M3F) \qquad\qquad (HṀCH_2OH of M3F)

$$\longrightarrow \qquad (26)$$

$$+ \ H_2O$$

ylation, the functionality of M has been observed to be 6 against F, but the functionality of urea, only 2.4[17]. Similarly, it has been indicated that M[12,18] easily reacts with F to form M3F, in addition, to form M6F in the concentrated F media, whereas urea[17,19] readily forms dimethylolurea but forms tetramethylolurea with marked difficulty. These results suggest that the N of the aminomethylol group in methylolurea would be greatly less nucleophilic than the N of the amino group in urea. However, the N of the aminomethylol group in MCH_2OH of methylolmelamine would not be markedly less nucleophilic than the N of the amino group in M[17], presumably due to the difference in the characteristics of the basicity between urea and M as has been speculated previously.[3,20]

With regard to condensation, the same would be also true, since the rate constant of dimethylolurea is less than one—two thousandth[1e] of that of monomethylolurea at 35°C and pH 4.0.

If the N of the aminomethylol group in MCH_2OH for M3F shows significantly less nucleophilic effect than the N of the amino group in MCH_2OH for M2F, the above result on the k of M2.95F—k of M1.97F ratio would not be obtained, because the effect of the N may be larger than that of the C in this case. (Thus, the condensation of methylolmelamine would be proceeded not only by the reaction of eq 21 to a major extent, but also by that of eq 22. For this reason, unlike methylolurea,[1e] it is complex to consider the reactivity of the respective functional group; hence, it has not been discussed in this paper.)

Range of S > 1.0—1.2. The k_4' reaction scheme of M2F was compared with that of M3F, since k_4' reaction would be the main reaction in this range.

As to M2F, as eq 24 formulates, the condensation of the k_4' reaction would proceed mainly between "the C of the methylol group apart from the $\overset{+}{N}$" in $H\overset{+}{M}CH_2OH$ and "the N of the aminomethylol group" in $H\overset{+}{M}CH_2OH$. But, for M3F, as eq 26 formulates, the condensation of the k_4' reaction would proceed mainly between "the C of the methylol group neighboring the $\overset{+}{N}$" in $H\overset{+}{M}CH_2OH$ and "the N of the aminomethylol group" in $H\overset{+}{M}CH_2OH$. Thus, the

above C in $H\overset{+}{M}CH_2OH$ for M2F and that for M3F react with "the N of the same aminomethylol group" in the respective $H\overset{+}{M}CH_2OH$, unlike the case of $0 < S < 1.0$. Hence, the effects of the N would be negligible. As indicated, the above C in $H\overset{+}{M}CH_2OH$ of M3F is more reactive than the above C in $H\overset{+}{M}CH_2OH$ of M2F, as is the case in the range $0 < S < 1.0$. Consequently, it is considered that in the $S > 1.0$—1.2 range the k of M2.95F—k of M1.95F ratios at the same S show larger values than those in the range of $0 < S < 1.0$.

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