TABLE V

ABSOLUTE VERDET CONSTANTS OF BENZENE

Temp., t, °C.	Density	λ = 589 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$	λ = 578 mμ $V \times 10_2$	$V/d \times 10^2$	$V/d \cdot M$	λ = 546 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$	λ = 436 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$
5	0.89474	3.0412	3.3990	2.6550	3.1759	3.5495	2.7725	3.6295	4.0565	3.1685	6.3568	7.1046	5.5494
10	.88935	3.0175	3.3929	2.6502	3.1512	3.5433	2.7677	3.6013	4.0494	3.1630	6.3069	7.0916	5.5392
15	.88397	2.9940	3.3870	2.6456	3.1266	3.5370	2.7627	3.5731	4.0421	3.1573	6.2571	7.0784	5.5289
20	.87859	2.9705	3.3810	2.6409	3.1020	3.5306	2.7577	3.5449	4.0348	3.1516	6.2073	7.0651	5.5185
25	.87321	2.9470	3.3749	2.6361	3.0773	3.5241	2.7527	3.5167	4.0273	3.1457	6.1574	7.0514	5.5078
30	.86782	2.9235	3.3688	2.6314	3.0527	3.5177	2.7477	3.4886	4.0199	3.1399	6.1076	7.0379	5.4973
40	.85706	2.8765	3.3562	2.6215	3.0035	3.5044	2.7373	3.4321	4.0045	3.1279	6.0079	7.0099	5.4754
50	.84629	2.8296	3.3435	2.6116	2.9542	3.4908	2.7267	3.3757	3.9888	3.1156	5.9083	6.9814	5.4532
60	.83552	2.7826	3.3304	2.6014	2.9049	3.4767	2.7156	3.3193	3.9727	3.1031	5.8086	6.9521	5.4303

less than those for any previous Verdet constants.

It is seen from the data in Table IV that the dispersion for benzene is not constant but decreases slightly with temperature. This behavior is similar to that found previously for the magnetic rotatory dispersion of water above 25°.[13]

The results in Table V show that the molecular Verdet constants, MV/d, decrease with temperature over the entire range. Richardson[14] has suggested that the origin of the temperature dependence of the normal Faraday effect might be in the thermal opposition to the precessional motion of finite magnetic moments, thus, to a mean paramagnetic polarization. These results, therefore, might be interpreted in terms of a slight paramagnetic polarization in the case of benzene. It is of interest to note that the temperature coefficient at 436 mμ is approximately twice that at 589 mμ. Further extensions of theory would have to account for this behavior.

STORRS, CONNECTICUT

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(13) Chas. E. Waring and Robert L. Custer, THIS JOURNAL, **74**, 2506 (1952).

(14) S. S. Richardson, *Proc. Roy. Soc.* (*London*), **31**, 232 (1916).

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Kinetics of the Condensation of Melamine with Formaldehyde

BY MASAYA OKANO AND YOSHIRO OGATA

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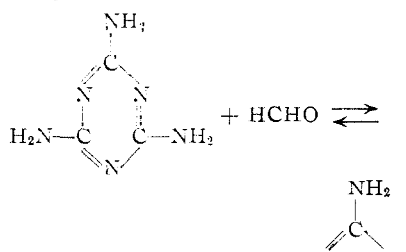
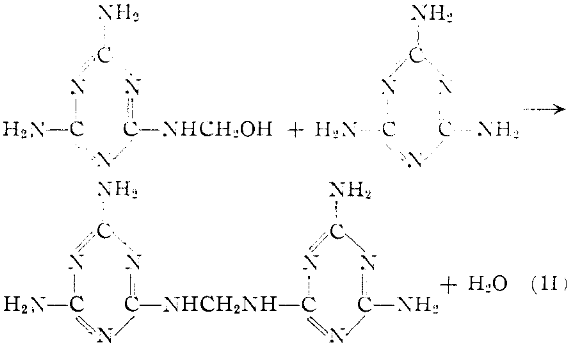
The rates of the condensation of melamine with formaldehyde in aqueous media in the pH's varying from 3 to 10.6 have been estimated at 35, 40 and 70° by employing both iodometric and sulfite methods. The primary product of the condensation, methylolmelamine, was found to consume iodine like formaldehyde itself, and therefore the result of the iodometric method indicates the amount of formaldehyde together with that of methylol group present, while the sulfite method estimates solely formaldehyde unreacted. From the data obtained by these two methods, the rates of the formation of methylolmelamine, *e.g.*, (I), and methylene-bonded melamines, *e.g.*, (II), were determined. There were found evidences that only the formation of methylol compounds occurs at 35–40° except in acidic solution and that the reaction is reversible all through the pH range, its forward rate being proportional to either [melamine] [formaldehyde], [melamine] [conjugate acid of formaldehyde], or [conjugate base of melamine] [formaldehyde] according to the pH's of the media. The rate of the irreversible condensation of methylolmelamine with melamine in neutral and acidic media at 70°, where the hydroxymethylation (I) is very rapid, is determined by the condensation step of conjugate acids of methylolmelamines with melamine, the rate being expressed as [melamine]^2 [formaldehyde]. The rate equations based on the reaction mechanisms which are suggested from these results satisfied the relationship between pH and the rate constant experimentally found.

It has been pointed out that the nature and structure of the melamine–formaldehyde condensate are considerably varied with reaction conditions, especially molar ratio of reactants, pH and temperature of the solution.[1] There seems to be no decisive kinetic evidence for this condensation mechanism, although the primary process may be presumed from the similar reactions such as those of urea–formaldehyde and aniline–formaldehyde.[2]



(I)



(II)

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(1) T. S. Hodgins, *et al.*, *Ind. Eng. Chem.*, **33**, 769 (1941).

(2) T. S. Hodgins and A. F. Hovey, *ibid.*, **30**, 1021 (1938); K. Frey, *Helv. Chim. Acta*, **18**, 491 (1935).

The present report summarizes our results on the melamine–formaldehyde condensation studied from the kinetic standpoint, placing emphasis upon the important relation between *p*H and the rate, which implies some probable mechanisms for the early stages of the condensation.

Experimental

Materials.—Nippon Carbide Ind. Co. best grade melamine was recrystallized from water, m.p. 353° (cor., block). The formaldehyde was the best grade. It was also confirmed that impurities in the formaldehyde used, *e.g.*, formic acid or methanol, did not affect the estimation of the reaction rate at least in their small quantities.

A Typical Procedure for the Rate Measurements.—In an erlenmeyer flask or a flask equipped with a reflux condenser for the higher temperature experiments, 2.5226 g. (0.02 mole) of the melamine was dissolved in distilled water, added with appropriate amount of dilute hydrochloric acid or sodium hydroxide, diluted to 180 cc., and dipped in a thermostat regulated to the operating temperature. Into this solution was poured 20 cc. of 1.00 *M* aqueous formaldehyde solution, maintaining the same temperature, by using a calibrated pipet. A twenty-cc. aliquot of the mixed solution was pipetted out at known intervals of time and estimated by the sulfite method and a 5-cc. aliquot by iodometry.[3] In the sulfite method, the aliquot was run into 25 cc. of 0.5 *N* sodium sulfite solution and the produced sodium hydroxide was immediately titrated with 0.1 *N* hydrochloric acid by using rosolic acid as an indicator. When an acidic or alkaline reaction medium was employed, it was necessary to add previously to the sulfite solution an appropriate amount of acid or alkali for the neutralization. In the iodometry, the aliquot was poured into *ca.* 10 cc. of 0.5 *N* sodium hydroxide, added 25 cc. of 0.05 *N* iodine solution, then 7–8 cc. of 1 *N* hydrochloric acid after five minutes, and thereafter titrated with 0.05 *N* sodium thiosulfate.

The Reaction Products Criterion and Blank Tests. (A) **Trimethylolmelamine.**—Since this substance was soluble and could not be isolated from such a dilute aqueous solution as that used for rate measurement, it was synthesized by the usual method,[4] in which 1 mole of melamine was stirred with 3 moles of 35% formaldehyde of *p*H 8.0 at 70° until the dissolution was complete, heated for additional five minutes, cooled readily, filtered, washed with methanol and then dried *in vacuo*. This crude product, contaminated with a small amount of melamine, higher condensate and formaldehyde was difficult to purify; it was dissolved in warm water, filtered and evaluated with both sulfite and iodometric analyses. The results indicated that the sulfite method measures solely the formaldehyde present, whereas the iodometry can estimate not only formaldehyde but methylol group present mainly as trimethylolmelamine[5] in this case. It was also confirmed that even a larger excess of formaldehyde, *e.g.*, 2.0 *M* formaldehyde per 0.1 *M* melamine, does not increase the number of methylol group per one melamine molecule more than three, at least under the conditions similar to those of kinetic experiment (at 40 and 70° in neutral media); therefore, the most hydroxymethylated state is surely trimethylolmelamine.[6]

(B) **Methylene-bonded Melamine.**—Even a dilute solution as used in the rate measurement emulsified after *ca.* 20 minutes at 70° and *p*H about 5. After allowing to stand over three hours at the temperature to complete precipitation, the resinous product was filtered and dried under reduced pressure. The product forms white amorphous powder, insoluble in water, alcohol and benzene but soluble in strong acids and phenol, just as the aniline–formaldehyde condensate, and softened at about 300° with decomposition. This substance was dissolved in aqueous acid and tested with two analytical methods, of which the sulfite method was utterly insensible to it, but the iodometry revealed the presence of some unattacked methylol groups in the molecule.

Experimental Results and Calculations.—The rate of hydroxymethylation (I) may be calculated from the difference of two values obtained by sulfite and iodometric methods; however, it was recognized that in the *p*H range above 6 or below 4 no methylene bridge formation but the hydroxymethylation was possible at the temperature (35 and 40°). The hydroxymethylation is reversible and resembles that of urea.[7] Since trimethylolmelamine may easily be obtained as a main product, it appears probable that there is hardly difference in the rates between the hydroxymethylations of melamine, mono- and dimethylolmelamines. Consequently, the rate of the consumption of formaldehyde v_A may be expressed as

$$v_A = k(3m - x)(f - x) - k'x \qquad (1)$$

Here, *k* and *k'* are the forward and reverse rate constants, respectively, *m* and *f* the initial concentrations (moles/l.) of melamine and formaldehyde, respectively, and *x* the consumed concentration of formaldehyde after *t* seconds. The integration of the equation leads to

$$\left.\begin{aligned} k &= \frac{x_e}{(3mf - x_e^2)t} \ln \frac{(3mf - x_e x)x_e}{(x_e - x)3mf} \\ k' &= \frac{(3m - x_e)(f - x_e)}{x_e}\, k \end{aligned}\right\} \qquad (2)$$

where x_e is the *x* at equilibrium state, which may be determined graphically by plotting the conversion percentage *vs.* time. Table I(a) lists the rate constants *k* and *k'* with

TABLE I

THE RATE CONSTANTS OF HYDROXYMETHYLATION AND THE FORMATION OF METHYLENE BRIDGE: THE EFFECT OF THE MOLAR RATIO OF REACTANTS

(a) Hydroxymethylation

	Initial concn.				
Temp., °C.	*M* Melamine (*m*)	*M* Formaldehyde (*f*)	*p*H	$k_{av} \times 10^4$ (l.·mole⁻¹ sec.⁻¹)[a]	$k'_{av} \times 10^4$ (sec.⁻¹)
40.0 ± 0.1	0.100	0.050–0.300	7.7	2.14 ± 0.03	0.43
40.0 ± .1	0.050–0.125	0.100	7.7	2.11 ± .04	.46
40.0 ± .1	.050– .150	.100	3.8	0.72 ± .01	.76
35.0 ± .1	.035– .065	.100	10.2	6.2 ± .1	.56

(b) The formation of methylene bridge

				$k''_{av} \times 10^3$ (l.²·mole⁻²·sec.⁻¹)[a]
70.0 ± 0.2	0.100	0.050–0.300	4.9	2.67 ± 0.04

[a] Figures following ± mean probable errors.

TABLE II

THE RATE CONSTANTS OF HYDROXYMETHYLATION OF MELAMINE: THE EFFECT OF *p*H

(a) Alkaline media at temp. 35.0 ± 0.1° Initial concn.: melamine, 0.05 *M*; formaldehyde, 0.10 *M*		(b) Neutral and acidic media at temp. 40.0 ± 0.1° Initial concn.: melamine, 0.10 *M*; formaldehyde, 0.10 *M*	
*p*H	$k \times 10^4$ (l.·mole⁻¹·sec.⁻¹)[a]	*p*H	$k \times 10^4$ (l.·mole⁻¹·sec.⁻¹)[a]
7.6	1.62 ± 0.01	7.7	2.14 ± 0.03
9.0	1.89 ± .02	5.8	2.13 ± .02
9.5	2.54 ± .03	5.3	1.94 ± .03
10.0	3.76 ± .04	4.9	1.35 ± .02
10.2	6.3 ± .1	3.8	0.72 ± .01
10.4	8.9 ± .2	3.0	0.74 ± .01
10.5	11.7 ± .2		
10.6	14.1 ± .2		

[a] Figures following ± mean probable errors.

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(3) J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, pp. 256.

(4) *E.g.*, (a) J. K. Dixon, N. T. Woodberry and G. W. Costa, THIS JOURNAL, **69**, 599 (1947); (b) C. Kitagawa, *J. Chem. Soc. Japan*, **53**, 181 (1950).

(5) Hexamethylolmelamine is also known. However, it was impossible to isolate this material beside trimethylolmelamine under these conditions. It would be formed only at higher temperature and concentration.

(6) It was observed that in the sulfite method standing for a longer time or estimation of aqueous methylolmelamines in alkaline medium remarkably increased the titer of hydrochloric acid, while in the iodometric method the titer held constancy. These phenomena seem to indicate that alkali, which is either originally present or produced by the reaction of sulfite, accelerates the decomposition of methylolmelamines into melamine and formaldehyde (*cf.* equation 9).

(7) G. A. Crowe, Jr., and C. C. Lynch, THIS JOURNAL, **70**, 3795 (1948).

varying molar ratio of reactants. Table II shows the effect of pH on the value of k with a constant molar ratio.

On the other hand, **the rate of methylene bridge formation** (II) may be directly evaluated iodometrically. In order to simplify the analysis of the rate equation, the rate was measured at 70°, where the hydroxymethylation was so rapid that the reaction mixture soon reached to a mobile equilibrium. Since a reaction between aminomethylol and amino group is rate-determining, the rate v_B may be given, as that in the aniline-formaldehyde condensation,[8] in a form

$$v_B = k''(3m - z - 2y)^2(f - z - y) \qquad (3)$$

Here, k'' is the rate constant, y the concentration (moles/l.) of formaldehyde consumed for the methylene bridge formation after t seconds, z the concentration of formaldehyde consumed for the hydroxymethylation. As described above, z may be determined from the difference in two analytical methods; this value became a constant soon after starting the reaction and tends to decrease slightly with the procession of the condensation, but the decrease was negligibly small during the rate measurement.[9] The rate constant k'' may be calculated by integrating equation (3) as follows

$$k'' = \frac{1}{(3m - 2f + z)^2 t}\left\{\ln \frac{(f - z)(3m - z - 2y)}{(3m - z)(f - z - y)} - \frac{(3m - 2f + z)2y}{(3m - z)(3m - z - 2y)}\right\} \qquad (4)$$

These k'' values with various molar ratios at a constant pH are shown in Table I(b), which proves the adequacy of equation (3). Although it would surely be desirable to list also the data with varying concentrations of melamine, the change of the concentration of basic melamine in weakly acidic solution brought about a considerable change in pH, which also influenced the reaction rate to a larger extent as described below, and hence this experiment was abandoned. The values of k'' tabulated were calculated from the data with less than 35% conversion of formaldehyde. They hold fairly good constancy within this range, but tend to decrease as the condensation proceeds over and it becomes apparently more accurate to replace the term $(3m - z - 2y)$ in equation (3) by $(3m - z - 5y)$. It thus appears that there is very small range in which $(3m - z - 3y)$ or $(3m - z - 4y)$ may be applied; these facts would be accounted for by assuming that the three amino groups in a melamine molecule have the same reactivity for methylol group at early stages of the condensation in a dilute solution, but as the reaction proceeds the reactivity falls rapidly by the production of sterically hindered amino groups in the condensate.

The effect of pH on the rate was roughly measured by comparing the reaction ratio after definite time, because the solution soon became turbid or the reaction velocity was slow. The pH values listed in these tables were measured at 25° by means of a glass electrode.

TABLE III

THE COMPARISON OF THE RATES OF THE FORMATION OF METHYLENE BRIDGE: THE EFFECT OF pH AT TEMP. 70 ± 1°

Initial concn.: melamine, 0.10 M; formaldehyde, 0.10 M

	Conversion, %[a]			Conversion, %[a]	
pH	After 15 min.	After 30 min.	pH	After 30 min.	After 60 min.
5.8	15	26	4.3	13	19
5.5	17	30	3.8	5	9
5.2	21	37			
4.9	11	20			

[a] These values show the amount of consumed formaldehyde which is measured iodometrically, *i.e.*, the conversion percentage of formaldehyde into $-CH_2-$ bridge.

Discussion of Results

There seem to be three probable mechanisms as to the formation of methylolmelamines corresponding to the pH's of reaction media, *i.e.*, the reaction of the conjugate base of melamine with formaldehyde, that of melamine with formaldehyde and that of melamine with the conjugate acid of formaldehyde (*cf.* equations 6, 15 and 12).

Like the urea-formaldehyde condensation,[10] **the hydroxymethylation in alkaline media** appears to involve an attack of nitrogen anion of melamine on the carbonyl carbon of formaldehyde. This mechanism will lead to the rate equation previously described. The mechanism involves the stages

$$MH + OH^- \rightleftarrows M^- + H_2O \text{ (fast)} \qquad (5)$$

$$M^- + HCHO \rightleftarrows MCH_2O^- \text{ (slow)} \qquad (6)$$

$$MCH_2O^- + H_2O \rightleftarrows MCH_2OH + OH^- \text{ (fast)} \qquad (7)$$

where MH is a molecule of melamine, M^- an anion of melamine. Equilibrium (5) is probable because melamine is able to form metallic salts[1] and furthermore the solution of it in dilute aqueous alkali shows pH which is consistent with this equilibrium (K_A = *ca.* 10^{-12}). It has been known from polarographic investigations[10,11] that the degree of hydration of formaldehyde, *i.e.*, the equilibrium constant of equation $HCHO + H_2O \rightleftarrows CH_2(OH)_2$, is much influenced by pH, especially in the alkaline medium. But there seem to be no available data on the hydration degree in such a high concentration of aqueous formaldehyde as those in our experiments and also our attempt to obtain these data was unsuccessful. The following rate equation may thus be obtained by assuming that there is no shift in the equilibrium above, the equation holding at least in the relatively narrow pH range,

$$\begin{aligned} dx/dt &= k_6[M^-][CH_2O] - k_{-6}[MCH_2O^-] \\ &= \frac{k_6(3m - x)(f - x)}{\left\{\dfrac{[H_2O]}{K_5[OH^-]} + 1\right\}} - \frac{k_{-6}x}{\left\{1 + \dfrac{K_7[H_2O]}{[OH^-]}\right\}} \\ &= k(3m - x)(f - x) - k'x \end{aligned} \qquad (8)$$

where K_5 and K_7 are the equilibrium constants of equations (5) and (7), respectively, k_6 and k_{-6} are the forward and reverse rate constants of equation (6), respectively. Although no accurate values of K_5 and K_7 are available, it would be reasonable to suppose that K_5 is a small value, whereas K_7 is large. Therefore, in the alkaline range where $[OH^-]$ is 10^{-3}–10^{-6}, $[H_2O] \gg K_5[OH^-]$ and $[OH^-] \ll K_7[H_2O]$, and hence k and k' should be related to $[OH^-]$ in expressions

$$k = k_6K_5[OH^-]/[H_2O] \text{ and } k' = k_{-6}[OH^-]/K_7[H_2O] \qquad (9)$$

The values $k/[OH^-]$ were calculated from data at pH 10.0–10.6 in Table II (a) to be 3.8, 4.0, 3.6, 3.8 and 3.5, holding constancy, which supports this mechanism.

In the hydroxymethylation in acidic media, the rate-determining step is surely an attack of the conjugate acid of formaldehyde on the nitrogen of melamine and such a mechanism, *i.e.*

$$MH + H_3O^+ \rightleftarrows MH_2^+ + H_2O \text{ (fast)} \qquad (10)$$

$$HCHO + H_3O^+ \rightleftarrows \overset{+}{C}H_2OH + H_2O \text{ (fast)} \qquad (11)$$

$$MH + \overset{+}{C}H_2OH \rightleftarrows MCH_2OH + H^+ \text{ (slow)} \qquad (12)$$

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(8) Y. Ogata, M. Okano and M. Sugawara, THIS JOURNAL, **73**, 1715 (1951).

(9) This would be attributed to the fact that amino groups in the condensate of lower molecular weight are as easily hydroxymethylated as those in melamine itself.

(10) G. A. Crowe, Jr., and C. C. Lynch, THIS JOURNAL, **71**, 3731 (1949).

(11) K. Vesely and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 313 (1947).

readily leads to a rate equation, where MH_2^+ is a conjugate acid of melamine

$$\begin{aligned} dx/dt &= k_{12}[MH][\overset{+}{C}H_2OH] - k_{-12}[MCH_2OH][H_3O^+] \\ &= \frac{k_{12}\,(3m - x)(f - x)}{\left\{1 + \frac{K_{10}[H_3O^+]}{[H_2O]}\right\}\left\{\frac{[H_2O]}{K_{11}[H_3O^+]} + 1\right\}} - k_{-12} \times [H_3O^+] \\ &= k\,(3m - x)(f - x) - k'x \qquad (13) \end{aligned}$$

Here, K's represent the equilibrium constants of subscripted equations and k_{12} and k_{-12} are the rate constants of forward and reverse reactions of equation (12), respectively. The observed value of K_{11} is very small (0.9×10^{-4} at 23°)[12] and hence $[H_2O] \gg K_{11}[H_3O^+]$ when $[H_3O^+]$ is smaller than 10^{-3}. Consequently, a relation[13]

$$k = \frac{k_{12}K_{11}[H_3O^+]}{[H_2O] + K_{10}[H_3O^+]} \qquad (14)$$

holds under these conditions. The value of K_{10} in this equation has been measured to be 5.5×10^6 at 25°.[14] Therefore, as expected from equation (14), k should increase linearly as $[H_3O^+]$ increases, if $[H_3O^+] <$ *ca.* 10^{-6}. But if $[H_3O^+] >$ *ca.* 10^{-4}, k should become a constant independent of $[H_3O^+]$. This expectation is satisfied with data at *p*H 3.0–3.8 in Table II(b) whereas the data at *p*H > *ca.* 4.5 do not. This phenomenon may suggest that the reaction between neutral molecules of formaldehyde and melamine ($C{=}O + H_2N \rightarrow$) become important as stated just below.

The hydroxymethylation reaction between neutral molecules in the range of *p*H smaller than 7 is evidently represented by the following steps and rate equation.

$$MH + H_3O^+ \rightleftarrows MH_2^+ + H_2O \text{ (fast)} \qquad (10)$$

$$MH + HCHO \rightleftarrows MCH_2OH \quad \text{(slow)} \qquad (15)$$

$$\begin{aligned} dx/dt &= k_{15}[MH][HCHO] - k_{-15}[MCH_2OH] \\ &= \frac{k_{15}(3m - x)(f - x)}{\left\{1 + \frac{K_{10}[H_3O^+]}{[H_2O]}\right\}} - k_{-15}x \\ &= k\,(3m - x)(f - x) - k'x \qquad (16) \end{aligned}$$

where k_{15} and k_{-15} are the forward and reverse rate constants of step (15). Consequently,

$$k = \frac{k_{15}[H_2O]}{[H_2O] + K_{10}[H_3O^+]} \qquad (17a)$$

The relationship requires that k is nearly constant, if $[H_3O^+] <$ *ca.* 10^{-6}, that k is inversely proportional to $[H_3O^+]$, if $[H_3O^+] >$ *ca.* 10^{-4}, and that k decreases gradually with $[H_3O^+]$ in the neighborhood of $[H_3O^+] = 10^{-5}$ where both first and second terms in the denominator of equation (17a) are not negligible. The data at *p*H *ca.* 5–6 in Table II (b) agree with this deduction.

Also this mechanism seems to be applied with slightly alkaline media. In these cases, the degree of hydration of formaldehyde should be taken in account, while $[H_3O^+]$ in equation (10) is very small. The relationship

$$k = \frac{k_{15}}{1 + K[H_2O]} \qquad (17b)$$

may thus be derived easily. Here, K is the equilibrium constant of the hydration of formaldehyde. The results at *p*H *ca.* 7–10 in Table II (a) seem to satisfy this equation quantitatively because of the well-known decrease of K with $[OH^-]$.

The methylene bridge formation reaction between melamine molecules would proceed by way of a rate-determining attack of the conjugate acid of methylolmelamine (probably in its dehydrated form) on free melamine, because there is a considerable difference in reaction rates with varying *p*H's from *ca.* 4 to 6. Since the reaction was conducted at higher temperature so that equation (15) becomes mobile, the steps and rate equation should be expressed as

$$MCH_2OH + H_3O^+ \rightleftarrows M\overset{+}{C}H_2 + 2H_2O \text{ (fast)} \qquad (18)$$

$$M\overset{+}{C}H_2 + MH \longrightarrow MCH_2M + H^+ \quad \text{(slow)} \qquad (19)$$

$$\begin{aligned} dy/dt &= k_{19}[M\overset{+}{C}H_2][MH] \\ &= k_{19}K_{15}K_{18}[MH]^2[HCHO][H_3O^+]/[H_2O]^2 \\ &= \frac{k_{19}K_{15}K_{18}\,(3m - z - 2y)^2(f - z - y)[H_3O^+]}{\left\{1 + \frac{K_{10}[H_3O^+]}{[H_2O]}\right\}^2 [H_2O]^2} \\ &= k''(3m - z - 2y)^2(f - z - y) \qquad (20) \end{aligned}$$

$$k'' = \frac{C[H_3O^+]}{\{[H_2O] + K_{10}[H_3O^+]\}^2} \; (C\text{: a constant}) \qquad (21)$$

Here, k_{19} is the rate constant of rate-determining step (19). From equation (21), a maximum value of k'' can easily be obtained at the *p*H where $dk''/d[H_3O^+] = 0$ or $[H_3O^+] = [H_2O]/K_{10} = 10^{-5}$, which agrees with the data shown in Table III.

The formation of ether linkage $-CH_2-O-CH_2-$ may be less probable, since the rate equation derived from this mechanism would be second order with respect to formaldehyde and to melamine, and first order to oxonium ion concentration, which does not accord with the experimental data. Perhaps this reaction will be much slower, and its occurrence would be observed in a higher temperature and a more concentrated solution.

Acknowledgments.—The authors wish to thank Prof. T. Nishi for his assistance in *p*H measurements and to Prof. S. Yoshizawa for his advice in polarographic experiments.

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[12] M. Wadano, C. Trogus and K. Hess, *Ber.*, **67**, 174 (1934), $K_B = 1.62 \times 10^{-20}$.

[13] The same rate equation will also be derived from reaction (12′) instead of reaction (12).

$$MH_2^+ + CH_2O \rightleftarrows HMCH_2OH^+ \qquad (12')$$

This appears to involve a cationic attack of N^+ on a positive center of carbonyl ($C^+{-}O^-$) carbon, but it seems less probable than that of $HOCH_2^+$ on N based on the electronic theory. Perhaps such attack will only be possible on a negative oxygen of carbonyl. [*Cf.* the formation of semicarbazone (THIS JOURNAL, **54**, 2881 (1932); **56**, 1962 (1934)) and the reaction of nitrile with formaldehyde (*ibid.*, **73**, 1028 (1951)).] Even if it would be possible, the rate constant of (12′) would be much smaller than that of (12). Readers might feel that reaction (12′) might occur since free $-NH_2$'s remaining could react even after being added a proton to a melamine molecule. But it is not right, because the concentration ($3m - x$) in our rate equation does not mean that of melamine, but that of amino group.

[14] J. R. Dudley, *ibid.*, **73**, 3007 (1951). $K_B = 1.0 \times 10^{-9}$. The difference in K_B values of melamine and methylolmelamines would be small. For instance, the value $1.0 \times 10^{-9.3}$ was given to dimethylolmelamine (see ref. 4a).