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The Initial Stage of the Reaction of Melamine with Formaldehyde

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ABSTRACT

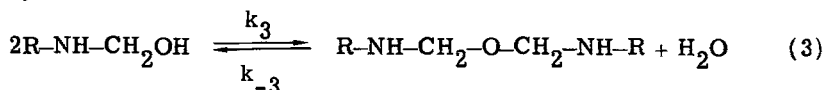
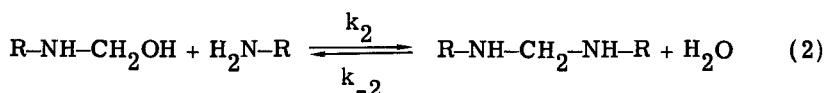
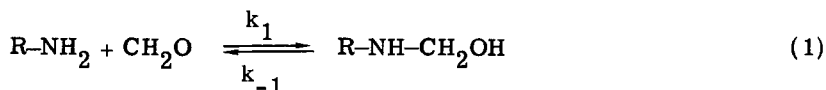
The concentration-time relationships of the individual active species in the oligocondensation stage of the reaction of melamine with formaldehyde have been investigated, mainly by electrochemical methods. Based on the reaction equations, a kinetic model of the overall reaction was established and the rate constants were calculated by numerical methods. The results suggest the hydroxy-methylamines are converted to methylene and dimethylene ether bridged compounds by acid- and base-catalyzed reactions, respectively. At pH 7-10 the formation of methylene bridges by base-catalyzed scission of dimethylene ether bridges may occur.

INTRODUCTION

The reaction of melamine with formaldehyde and the partial oligocondensation of primarily formed hydroxymethylene compounds are essential initial stages in the preparation of resins of great commercial importance, for instance, in moldings, particle boards, and laminates.

Because of this commercial importance, numerous investigations on the kinetics and mechanism of the synthesis of melamine resins have been performed. However, hydroxymethylation or methylation and the formation of methylene bridges have not been investigated together. Hydroxymethylation as the first stage has been studied in highly diluted solution without taking into account the consecutive reactions [1-6]. Investigations of oligocondensation based on determining methylene bridge formation were carried out with nonuniform hydroxymethylmelamines by using aqueous/organic solvents in order to avoid de- and transmethylation [7-9].

Reactions (1) to (3) proceed consecutively or concurrently. Immediately after the start of hydroxymethylation (1), oligocondensation resulting in the formation of methylene bridges (2) and dimethylene ether bridges (3) is found to occur and depends on the pH value and the temperature of reaction.



where R = melamine residue.

The kinetics of dimethylene ether bridge formation have not been investigated.

The first attempts to investigate hydroxymethylation and oligocondensation simultaneously were described by Okano and Ogata [5]. From the present point of view, however, the suggestion that no dimethylene ether bridges are formed and the total content of formaldehyde in the acid precipitate can be ascribed exclusively to methylene bridges can no longer be considered valid. The description of the complex reaction requires selective analytical techniques relating to the individual steps.

More detailed investigations on the analysis of melamine resins proved polarography to be an appropriate tool for determining free formaldehyde and formaldehyde bound in N-hydroxymethyl groups (1) and methylene bridges (2) [10, 11]. In contrast to current analytical methods, polarography offers many advantages with respect to speed and selectivity.

The formaldehyde bound in dimethylene ethers (3) can be determined selectively only by ^{13}C -NMR [12-14]. However, because of the separation and preparation of samples involving prolonged accumulation times, NMR spectroscopy proved unsuitable for repeated measurements in this case. The ether formaldehyde determined by oxidation [10] corresponds to the total of the formaldehyde bound in dimethylene ether bridges, oligoacetals, and oligooxymethylenes.

In our investigations the combination of analytical techniques with mathematical modeling opened a way for investigating the course of the reaction of melamine with formaldehyde up to the formation of oligomers including the formation of ether bridges that were not detectable selectively.

EXPERIMENTAL

The hydroxymethylation of melamine and the oligocondensation of the methylolmelamines formed were performed within the ranges of pH value, reaction temperatures, molar ratio of melamine and formaldehydes, and concentrations indicated in Table 1.

Solutions of melamine and formaldehyde were mixed at the reaction temperature, the moment of mixing being taken as $t = 0$ of the hydroxymethylation and oligocondensation processes. In experiments at a formaldehyde concentration of 1.0 mol/L, melamine was found to dissolve incompletely in water on heating, but admixing of formaline resulted in dissolution of the remainder within the first minute of the reaction. The temperature was kept constant within the limits of ± 1 K and the pH value was adjusted continuously (± 0.1 pH unit). After reaction times of 0.5, 1, 3, 5, 7.5, 10, 15, 20, 30, 40, and 60 min, samples were recovered and immediately placed into the buffer solutions used for polarographic analysis in order to ensure that no further noticeable reaction occurred in the samples recovered. At low pH values and high reaction temperature, some samples became turbid at reaction times of less than 1 h. These experiments were finished when turbidity occurred.

Changes in concentration of free formaldehyde as well as of formaldehyde bound in hydroxymethylene groups and methylene bridges were determined by the polarographic methods described in Refs. 10 and 11. The experiments at formaldehyde concentrations of 0.1 mol/L were performed with standard buffer solutions (according to Michaelis) at the corresponding pH values in a polarographic double cell devised in our laboratory (Fig. 1) which allows the simultaneous and continuous

TABLE 1. Experimental Conditions

Temperature ($^{\circ}\text{C}$)	50	70	80
pH value	7	8	9
Molar ratio (F/M)	1.0	2.0	3.0
Initial concentration (F), mol/L	1.0	0.1 ^a	

^aPreliminary experiments.

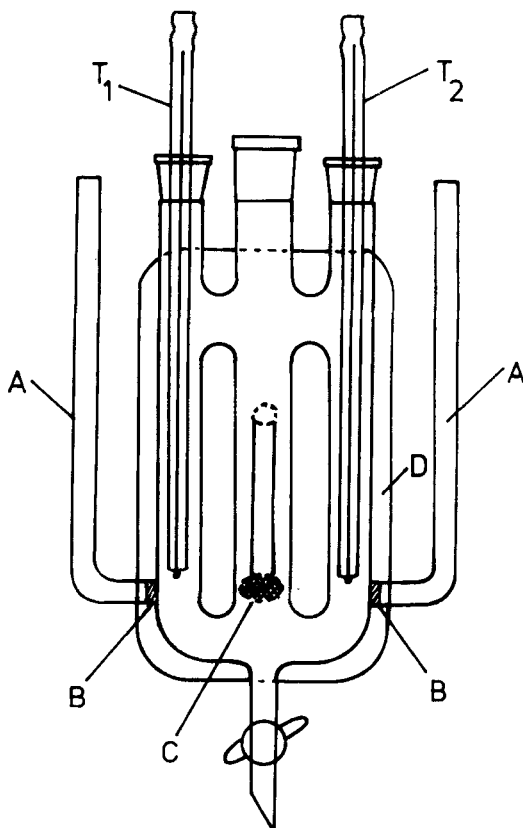


FIG. 1. Polarographic cell for measuring two polarographically active components continuously. A = SC electrodes, B = diaphragm, C = feeding tube for inert gas with a G4 frit as the large pump, T_1 and T_2 = mercury dropping electrodes, D = double jacket for temperature control.

determination of changes in concentration of free formaldehyde and formaldehyde bound in methylene bridges. The determination of methylol groups was carried out discontinuously, as in the experiments with 1 M solutions.

The measurements were conducted with a dc-ac polarograph GWP 673 (Center for Scientific Instruments of the Academy of Sciences, GDR) and a polarograph OH-105 (Radelkis, Budapest).

KINETIC MODEL

The mathematical modeling of the overall reaction was based on the following system of differential equations:

$$d[-H]/dt = -k_1[-H][CH_2O] - k_2[-H][-CH_2OH] + k_{-1}[-CH_2OH] \quad (4)$$

$$d[CH_2O]/dt = -k_1[-H][CH_2O] + k_{-1}[-CH_2OH] \quad (5)$$

$$d[-CH_2OH]/dt = k_1[-H][CH_2O] - k_2[-H][-CH_2OH] - k_{-1}[-CH_2OH] - k_3[-CH_2OH]^2 + k_{-3}[-CH_2-O-CH_2-][H_2O] \quad (6)$$

$$d[-CH_2-]/dt = k_2[-H][-CH_2OH] \quad (7)$$

$$d[-CH_2-O-CH_2-]/dt = k_3[-CH_2OH]^2 - k_{-3}[-CH_2OCH_2-][H_2O] \quad (8)$$

under the initial conditions

$$[-H](0) = [-H]_0 = 6[\text{melamine}]_0 \quad (9)$$

$$[CH_2O](0) = [CH_2O]_0 \quad (10)$$

$$[-CH_2OH](0) = 0 \quad (11)$$

$$[-CH_2-](0) = 0 \quad (12)$$

$$[-CH_2-O-CH_2-](0) = 0 \quad (13)$$

Because of the low concentration and intensive mixing, the system was considered to be kinetically controlled. In agreement with Gordon [1] and Sato [9], the calculations were based on a functionality value of 6 for melamine. The desactivation effect of the second step of hydroxymethylation of the amino groups of melamine, amounting

to about 40% [1], was not taken into account since at low molar ratios the primary hydrogen atoms of the amino groups are preferentially substituted [2].

The constants in Eqs. (4) to (8) were determined by minimizing the deviations of the calculated values $[\text{CH}_2\text{O}](t_1)$, $[-\text{CH}_2\text{OH}](t_1)$, $[-\text{CH}_2-](t_1)$, $[-\text{CH}_2\text{-O-CH}_2-](t_1)$, and $[-\text{H}](t_1)$ from the experimental values of concentration, respectively, and the value of $[-\text{H}]_t$ estimated by Eq. (14). Minimizing of the deviations was based on the method proposed by Rosenbrock [15]. Approximation of the initial value problem expressed by Eqs. (4) to (8) was achieved by the Crank-Nicolson method using nonlinear algebraic equations.

$$[-\text{H}]_t = 6[\text{melamine}]_0 - ([\text{CH}_2\text{O}]_0 - [\text{CH}_2\text{O}]_t) - [-\text{CH}_2-]_t \quad (14)$$

RESULTS AND DISCUSSION

Selected numerical values of the rate constants are presented in Table 2. The concentration-time relationships calculated with these constants were found to be almost identical with the experimental plots, as shown in Fig. 2. The adequacy of the model is further supported by the considerable agreement between the values of the rate constant (k_2) of methylene bridge formation calculated from initial rate data and the values obtained by the model (Table 3). Therefore, the constants of the ether reaction as calculated by the model (k_2 and k_{-3}) can be considered reliable.

Hydroxymethylation

The constants of hydroxymethylation obtained in our investigations were found to be about 5 times higher than those reported in the literature. This can be explained by the current consideration of hydroxymethylation as an individual reaction and neglecting the consecutive reactions. Thus, the determined equilibrium constants prove somewhat lower than the values indicated in the literature (Table 4). The hydroxymethylation of urea and melamine proceeds according to the general mechanism of acid-base catalysis [16-19]. Thus k_1 becomes a composed quantity.

$$k_1 = k_0 + k_{\text{HO}^+}[\text{H}_3\text{O}^+] + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{HA}}[\text{HA}] + k_{\text{A}^-}[\text{A}^-] + k_{\text{p}}[\text{HA}][\text{A}^-] \quad (15)$$

TABLE 2. Numerical Rate Constants of Hydroxymethylation and Oligocondensation ($c_0 = 1.0$ mol/L formaldehyde)

Reaction conditions		Rate constants ($k_n \times 10^3$)					
F/M	pH	T, °C	$k_1, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	k_{-1}, s^{-1}	$k_2, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_3, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_{-3}, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
1.0	7	50	0.436	0.123	0.012	22.9	0.200
	8		0.371	0.105	0.009	17.8	0.251
	9		0.524	0.114	0.002	20.9	0.363
3.0	7	50	1.29	0.398	0.052	2.88	0.068
	8		1.58	0.398	0.012	2.51	0.186
	9		1.82	0.369	0.002	5.37	0.209
1.0	7	70	1.03	0.405	0.066	44.7	0.287
	8		0.776	0.225	0.017	30.3	0.409
	9		1.2	0.270	0.004	38.9	0.696
3.0	7	70	3.71	1.28	0.125	5.49	0.1
	8		4.16	1.2	0.065	4.27	0.275
	9		5.01	0.948	0.032	8.91	0.661

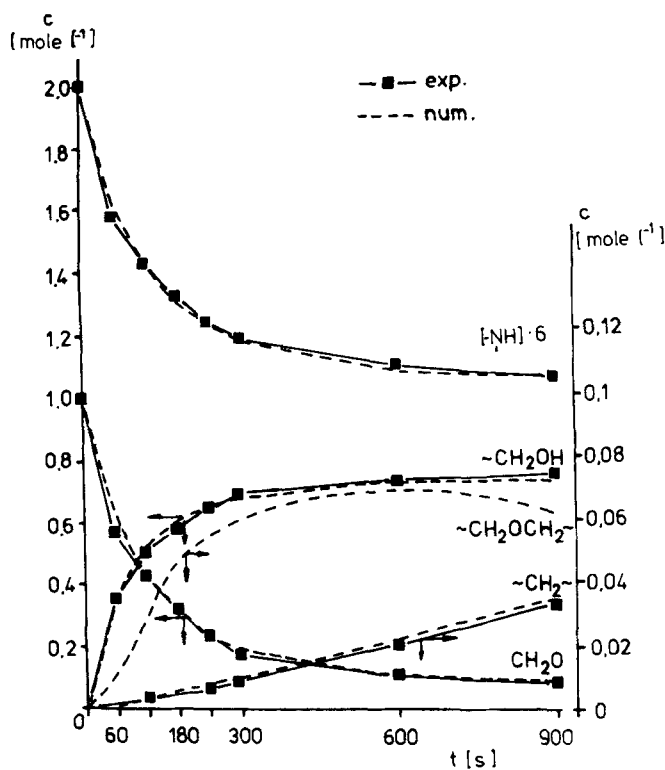


FIG. 2. Calculated and experimental concentration-time relationships. $c_{F_0} = 1.0$ mol/L, $F/M = 1.0$, 70°C , pH 8.

The rate constant of the noncatalyzed reaction (k_0) cannot be determined. The terms $k_{HA}[HA]$ and $k_A[A^-]$ involve all species (e.g., melamine, formaldehyde, their different steps of dissociation, and also salts). The term $k_p[HA][A^-]$ accounts for the buffer system (borate buffer). As suggested by the data on the hydroxymethylation kinetics of urea and urea derivatives [3], the catalyses of protons ($k_{H_3O^+}$) and hydroxy ions (k_{OH^-}) are the most important in hydroxymethylation.

The effect of general acid-base catalysis on k_1 is expressed by the minimum of this constant in the region near pH 7 (Fig. 3). At the molar ratio $F/M = 3.0$, the value of k_1 is found to be 3 to 5 times

TABLE 3. Rate Constants of Methylene Bridge Formation ($c_0 = 1.0$ mol/L formaldehyde)

F/M	T, °C	pH	$k_2^+ \times 10^3,^a$ L·mol ⁻¹ ·s ⁻¹	$k_2 \times 10^3,$ L·mol ⁻¹ ·s ⁻¹
2.0	80	7	0.11	0.099
		8	0.04	0.033
		9	0.0059	0.0055
1.0	80	7	0.079	0.083
		8	0.035	0.03
		9	0.0061	0.0092

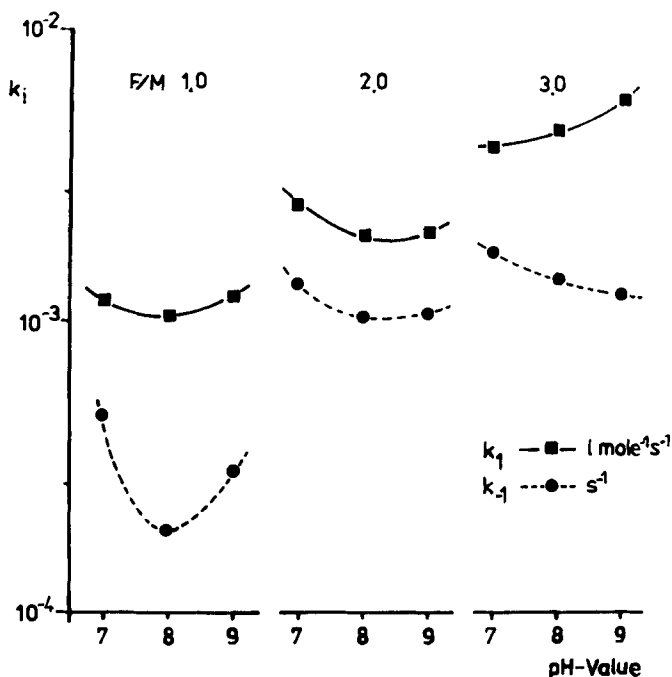
^aDetermined graphically.FIG. 3. Dependence of the constants of hydroxymethylation (k_1) and dehydroxymethylation (k_{-1}) on the pH value and F/M molar ratio. $c_{F_0} = 1.0$ mol/L, 80°C.

TABLE 4. Rate and Equilibrium Constants of Hydroxymethylation in Dilute Solutions

	Molar ratio F/M	pH value	T, °C	K_1^a mol/L	$k_1 \times 10^4$ L·mol ⁻¹ ·s ⁻¹
Okano and Ogata [5]	2.0	9.0	35	-	1.89
	1.0	7.7	40	0.21	2.14
Sato and Ouchi [6]	2.5	8.0	40	-	0.92
	3.0	9.5	55	0.324	7.1
Gordon et al. [1]	3.0	8.6	45	0.273	1.78
	3.0	9.0	50	0.21	18.2
Experiments of the authors	2.0	9.0	50	0.21	8.1

^aEquilibrium constant of demethylation ($K = k_{-1}/k_1$).

higher than at $F/M = 1$. This can be explained by Eq. (5): by increasing the concentrations $[HA]$ and $[A^-]$, the additional effect of the corresponding terms results in an increase of k_1 . Likewise, the demethylation constant k_{-1} increases with an increasing amount of formaldehyde and, independently of the pH value, passes a distinct minimum at the molar ratio 1 of melamine and formaldehyde. At higher values of this molar ratio the dependence of the demethylation on the pH value seems to be weak (Fig. 3). The equilibrium constant K_1 amounts to about 2 to 4 L/mol (Table 4).

Oligocondensation

Oligocondensation starts immediately after formation of the initial hydroxymethyl groups. Thus, Reactions (1) to (3) proceed as parallel, consecutive, and competitive reactions. All these reactions are equilibrium reactions, the methylene group formation being considered irreversible in the model discussed (Eq. 7). The formation of bridge structures occurs by individual steps which are also subjected to general and specific acid and base catalysis (analogous to Eq. 15). The dependence of the individual numerical rate constants on the reaction conditions suggests the following relationships.

The rate constant of methylene bridge formation (k_2) distinctly depends on the pH value. The value of k_2 increases as the pH value decreases and is found to be higher at a molar ratio of 3 than at a molar ratio of 1. This result suggests a mechanism with protons playing a predominant part (Fig. 4). The rate constant of ether bridge formation (k_3) passes a minimum at pH 8 but proves to be about one order of magnitude higher at a molar ratio of 1 than at a molar ratio of 3. Here, an opposite behavior with respect to k_1 , k_{-1} , and k_2 is observed (Fig. 5). The rate constant of ether cleavage (k_{-3}) increases with increasing pH value and is, at a first approximation, independent of the molar ratio. Particularly with respect to the ether reaction, the molar ratio for formaldehyde/melamine of 2.0 combined with pH 8 provides an unstable region of the reaction.

The activation parameters of the overall Reactions (1) to (3) are comparatively high (Table 5). The high values of the entropy of activation were observed with experiments performed in buffer solutions. Comparative measurements in unbuffered aqueous solutions resulted in values that were about 50 to 80 $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ lower, the energy of activation being almost unaffected (Table 5). These results suggest that the buffer participates immediately in the rate-determining step of the reaction. However, even in unbuffered solutions the salt concentration was steadily increased by continuous control of the pH value.

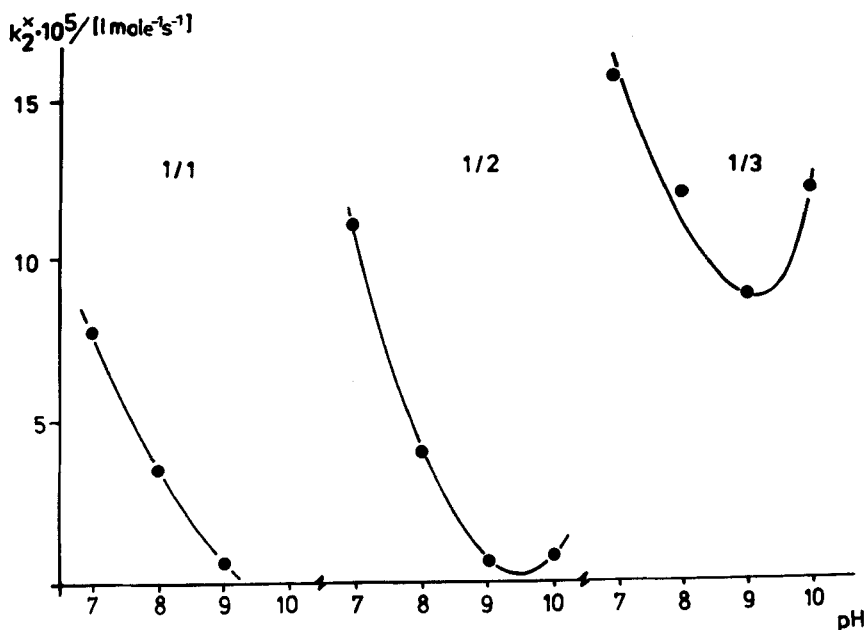


FIG. 4. Dependence of the constant of methylene bridge formation (k_2) on the pH value. $c_{F_0} = 1.0 \text{ mol/L}$, 80°C .

TABLE 5. Activation Parameter of the Melamine-Formaldehyde Reaction ($c_{F_0} = 1.0 \text{ mol/L}$, $F/M = 2.0$, $\text{pH } 8$)^a

Reaction	E, kJ/mol		$-S^\ddagger$, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1b}$	
	Buffered	Unbuffered	Buffered	Unbuffered
Methylation	40	41	200	120
Demethylation	46	49	150	100
Methylene bridge formation	76	73	100 ^c	85
Dimethylene ether bridge formation	27	-	210	125 ^d
Dimethylene ether bridge scission	28	-	230	145 ^d

^aThe values shown are average values.

^bRelated to 70°C .

^cStrong dependence on molar ratio and pH value.

^dCalculated from the activation energy of the catalyzed reaction.

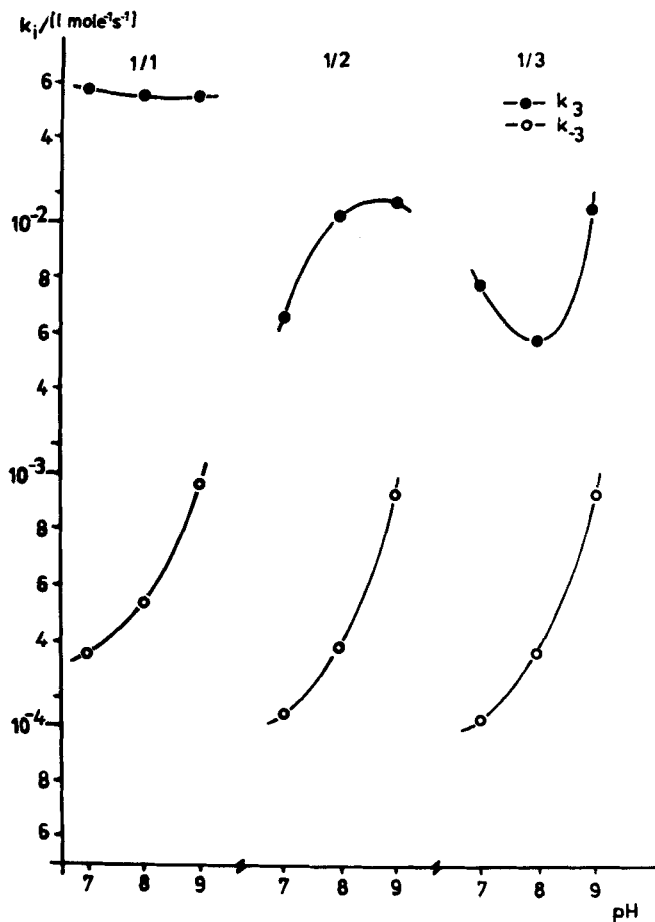
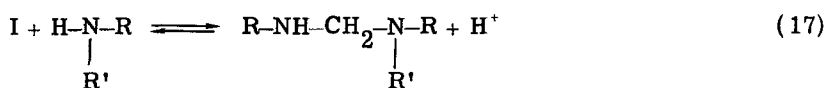
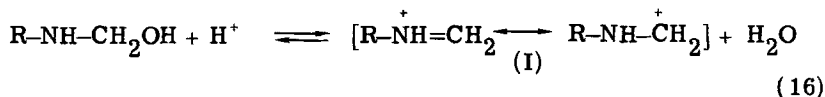


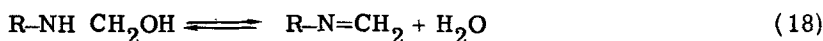
FIG. 5. Dependence of the constants of ether bridge formation (k_3) and cleavage (k_{-3}) on the pH value at different F/M molar ratios. $c_{F_0} = 1.0 \text{ mol/L}$, 80°C .

The rate constant of methylene bridge cleavage (as determined with methylene diurea), amounting to about $10^{-8} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, are seen to be 2 to 4 orders of magnitude lower than the rate constants of methylene bridge formation (k_2). Despite their slow formation, methylene bridges can be detected in the oligocondensate. Ether bridges are formed faster, but are also more quickly subjected to cleavage.

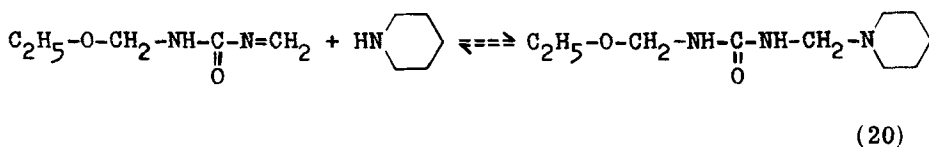
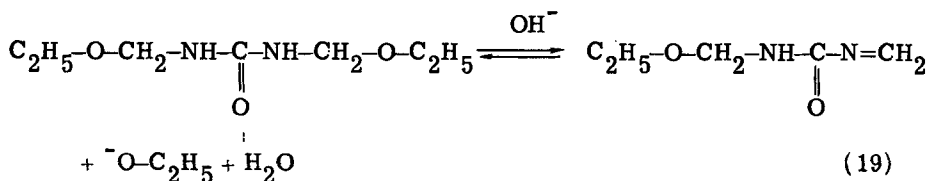
The formation of methylene bridges is supposed to proceed only in the acid region according to Eqs. (16) and (17) [21, 22]. By using the highly sensitive method of determining methylene bridges, the formation of methylene bridges in alkaline media was also detected. Here, the rate constants depend considerably on the formaldehyde/melamine molar ratio (Fig. 4).



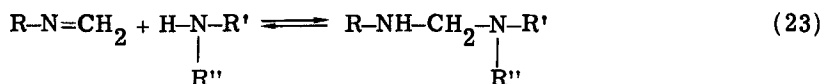
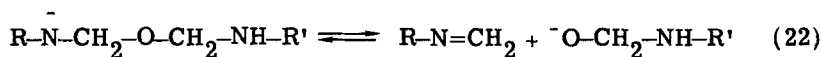
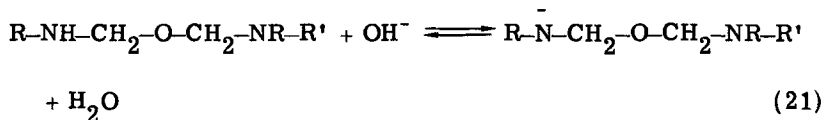
The formation of methylene bridges immediately from free Schiff's bases (18) and amino groups has been discussed by various authors [23, 24]:



However, this reaction has not been shown experimentally. Berge and co-workers [20, 21] succeeded in detecting Schiff's bases as intermediate products in the base-catalyzed cleavage of bis(ethyl-carbamidomethyl ester) by reacting it with piperidine:



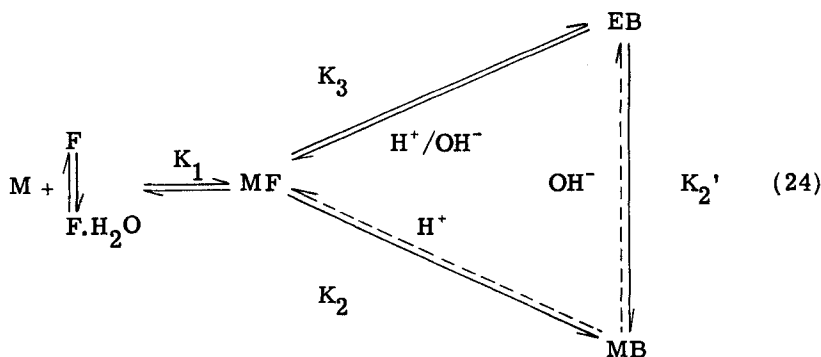
In our investigations the high rate constants of dimethylene ether formation and cleavage (k_3 and k_{-3} , Fig. 5) suggest that free Schiff's bases are formed by base-catalyzed cleavage of ether bridges. These reaction products may react reversibly with hydroxymethylene groups to form ether bridges and with amino or imino groups to form methylene bridges:



where R and R' = amino resin residues; R'' = H, hydroxymethyl groups.

If this suggestion holds true, the rate constant of methylene bridge formation should pass a minimum and increase as the pH value increases. Figure 4 shows this suggestion to be right. Depending on the pH value, the two possible Reactions (16) and (17) or Eqs. (21)-(23) contribute to a smaller or larger degree to the formation of methylene bridges.

In summary, the overall reaction of the hydroxymethylation of melamine and the oligocondensation of hydroxymethyl compounds can be described as



Hydroxymethylmelamines are formed from melamine (M) and formaldehyde (F) after dehydration of formaldehyde hydrate (F.H₂O) and are converted to methylene bridges (MB, K₂) and dimethylene ether bridges (EB, K₃) by base- and acid-catalyzed reactions. Additionally, the formation of methylene bridges by base-catalyzed scission of ether bridges appears possible (K₂').

Therefore, under the conditions of reaction of amino resin synthesis, dimethylene ether bridges and methylene bridges are formed simultaneously. The proposed model allows calculation of the concentration of

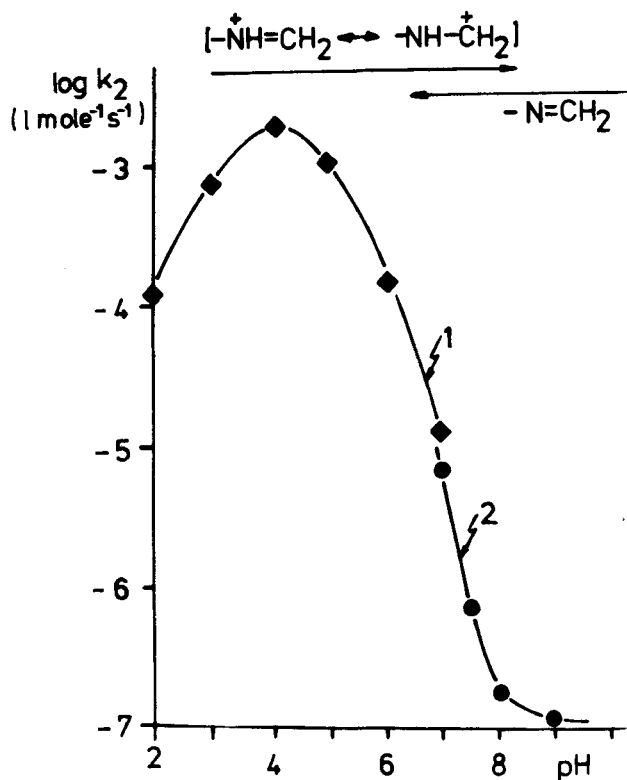


FIG. 6. Rate constants of methylene bridge formation. Curve 1: Sato and Ouchi [6]. Curve 2: Measurements by the authors. The values reported by Sato were recalculated with the values of the activation energy, $c_{F_0} = 1.0 \text{ mol/L}$, $F/M = 2.0$, 70°C .

the linking groups. The rate constants at pH 7-10 combine satisfactorily with the values calculated by Sato [6] for acid-catalyzed methylene bridge formation at pH 2-7 (Fig. 6). The constants reported by Sato were recalculated by way of the activation energies of methylene bridge formation (Table 5) with respect to the reaction conditions chosen in our experiments.

The strong dependence of the rate constants of the individual reactions on the reaction parameters, particularly on the pH value, demonstrates that the reproducibility of formaldehyde-melamine reactions is possible only under constant reaction conditions (Table 6).

TABLE 6. Numerical Values of the Rate Constants at Initial Formaldehyde Concentrations of 1.0 and 0.1 mol/L

Reaction conditions				Rate constants ($k_n \times 10^3$)				
C_{F_0} mol/L	F/M	T, °C	pH	k_1 , L·mol ⁻¹ ·s ⁻¹	k_{-1} , s ⁻¹	k_2 , L·mol ⁻¹ ·s ⁻¹	k_3 , L·mol ⁻¹ ·s ⁻¹	k_{-3} , L·mol ⁻¹ ·s ⁻¹
1.0	3.0	50	7	1.29	0.398	0.052	2.88	0.068
			8	1.58	0.398	0.012	2.51	0.186
		9	1.82	0.369	0.002	5.37	0.209	
	70	7	3.71	1.28	0.125	5.49	0.1	
		8	4.16	1.2	0.065	4.27	0.275	
		9	5.01	0.948	0.032	8.91	0.661	
0.1	3.0	50	7	0.99	0.410	0.063	2.99	0.053
			8	1.10	0.430	0.01	2.6	0.121
		9	1.31	0.419	0.002	5.88	0.158	
	70	7	3.61	0.936	0.105	5.66	0.12	
		8	4.01	0.801	0.056	5.11	0.187	
		9	5.11	0.790	0.031	6.79	0.506	

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