

Kinetics of the Addition Stage in the Melamine-Formaldehyde Reaction

M. GORDON, *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland*, and A. HALLIWELL and T. WILSON, *Research Division, Formica Limited, Maidenhead, Berks, England*

Synopsis

The addition reaction between melamine and formaldehyde has been kinetically separated from the subsequent condensation stage by suitable choice of concentration and temperature conditions. The reaction, which is reversible, has been monitored by estimation of the free formaldehyde content of the system. It has been investigated over the range of mean degree of methylation $1 < R' < 3.7$ of the melamine nuclei, the temperature range 25-55°C., and the pH range 5.7-10.2. The rate data thus obtained have been treated according to the random reversible addition scheme for which reasonable, first approximation, agreement was obtained. Average kinetic and thermodynamic constants have been calculated and are discussed in terms of the present model. The factors which are likely to cause deviations from randomness are described. The addition of formaldehyde to melamine proceeds by superposition of an OH⁻-catalyzed step with a minor solvent-catalyzed or uncatalyzed one.

INTRODUCTION

The kinetics of the addition reaction between melamine and formaldehyde have not been widely studied. Okano and Ogata¹ reported on this reaction on the basis that the degree of methylation of the melamine nuclei did not exceed 3. Evidence from our earlier work² on the equilibrium of this reaction showed that degrees of methylation greater than 3 do occur, even when the initial mole ratio (F) of formaldehyde to melamine in a reaction mixture is less than 3:1. We were able to show, from measurements of the methylol distributions in equilibrium mixtures of different F values, that the system could be described to a first approximation at least, by assuming random reaction between the formaldehyde molecules and the six reactive hydrogen atoms of melamine. The parameters which accounted for deviations from randomness were calculated. These were to allow for a deactivation effect of reduced reactivity of secondary amino groups compared to primary ones and for a rather weak activation effect due to successive methylation of the melamine nucleus as a whole.

In the present paper the kinetics of the reaction are described in terms of the random reaction scheme, and a number of average kinetic and thermodynamic constants have been calculated. The magnitude and direction of effects which cause the system to deviate from randomness

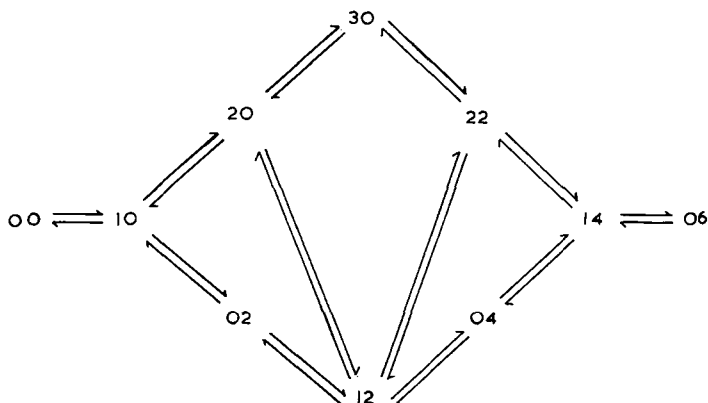
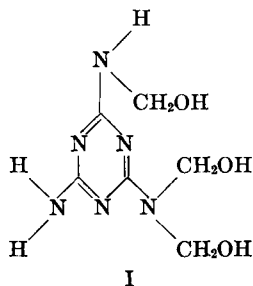


Fig. 1. Reaction scheme for formation of methylol melamines.

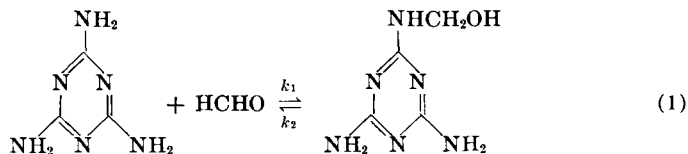
are also deduced, and these agree semiquantitatively with the conclusions drawn from the equilibrium studies. A more elaborate (computer) treatment would be required for quantitative analysis of the kinetic results in terms of substitution parameters.

The reaction scheme for the general case is shown in Figure 1.

The methylol melamines are designated by the symbols i, j , where i indicates the number of CH_2OH groups borne on NHCH_2OH groups, and j the number of CH_2OH on $\text{N}(\text{CH}_2\text{OH})_2$ groups in a given compound. For example, 12 ($i = 1, j = 2$) describes the compound I.



The random reaction scheme is shown in eq. (1).



It is assumed that both methylation and demethylation reactions occur in a random manner with rate constants k_1 and k_2 . The distributions of the methylol compounds will follow at all times a random distribution, and the mean degree of reaction of the distribution at any stage is cal-

culable from the fraction of amino hydrogen atoms ($-H$) which are methylolated.

The rate of change of formaldehyde concentration is given by eq. (2).

$$d[\text{HCHO}]/dt = -k_1[\text{HCHO}][-\text{H}] + k_2[-\text{CH}_2\text{OH}] \quad (2)$$

At equilibrium,

$$\{ [(6/F) - 1] + a_e/a_0 \} - K[(1/a_e) - (1/a_0)] = 0 \quad (3)$$

where F is the molar ratio of the reactants (formaldehyde/melamine), a_e is the equilibrium concentration of free formaldehyde, a_0 is the initial concentration of free formaldehyde, k_1 is the second-order rate constant for methylation, k_2 is the first-order rate constant for demethylation, and K is the equilibrium constant for the demethylation reaction.

$$K = k_2/k_1 \quad (4)$$

The solution of eq. (2) is given by:

$$k_1 t = -\frac{1}{Y} \ln \left[\frac{(2a + g + K - Y)(2a_0 + g + K + Y)}{(2a + g + K + Y)(2a_0 + g + K - Y)} \right] \quad (5)$$

where

$$g = a_0[(6/F) - 1] \quad (6)$$

and

$$Y = \sqrt{(g + K)^2 + 4Ka_0} \quad (7)$$

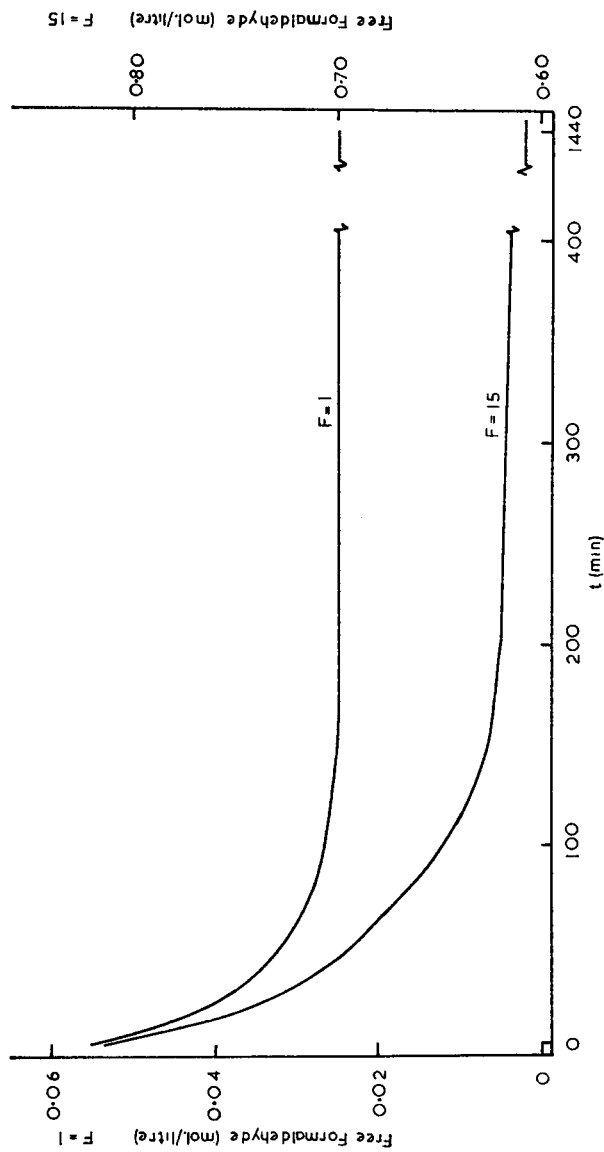
EXPERIMENTAL

Reaction mixtures containing melamine (0.1 mole), formaldehyde (0.05–1.5 mole) and total water (100.0 mole) have been reacted at thermostatically controlled temperatures of 25, 30, 35, 45, and 55°C., and at pH levels of 5.7, 6.6, 7.5, 8.6, 9.5, and 10.2; pH adjustment of the formaldehyde and melamine solutions, by using 2*N* sodium hydroxide solution, or formic acid, was made at the reaction temperature prior to mixing the reactants.

At measured intervals of time, the reaction mixture was sampled, and the free formaldehyde content of the system was determined by using a modification of the iodine-sulfite method as used by de Jong and de Jonge.³ This procedure was repeated until the rate of decrease of the free formaldehyde content of the system reached zero or became negligible (Fig. 2). The experimental data thus obtained were plotted as free formaldehyde against time, and from smoothed graphs of these values the approximate data for the equilibrium and kinetic cases were derived.

Determination of Free Formaldehyde

A volume of reaction mixture containing approximately 1.5×10^{-3} mole of formaldehyde was cooled to 2–3°C. and neutralized with 0.3*N*

Fig. 2. Typical rate curves for both low and high values of F .

hydrochloric acid, phenolphthalein being used as an indicator. Then 2*N* sodium sulfite solution (2 ml.) was added and the liberated alkali continuously neutralized with 0.3*N* hydrochloric acid, the solution being kept a pale pink color to phenolphthalein. During the titration the temperature of the solution was maintained at 2–3°C. When no further acid was required over a 10-min. interval the reaction was considered to be complete; the total titration time was about 1 hr. The pH was then adjusted to about 4 by the addition of 1*N* acetic acid (5 ml.), and the excess sulfite destroyed with 0.1*N* iodine solution, starch solution being used as an indicator. The bisulfite compound was then decomposed with 2*N* sodium carbonate solution (25 ml.) and the liberated sulfite titrated with 0.1*N* iodine solution. The formaldehyde, in moles/liter, was calculated as

$$\text{Formaldehyde in sample} = 0.5Tf/V$$

where *T* is iodine titer in milliliters, *f* is normality of the iodine solution, and *V* is volume.

RESULTS

The experimental results are set out in Tables I–III with free formaldehyde concentration as a function of time.

DISCUSSION

Equilibrium Case

The information required for the determination of the equilibrium constant was obtained from plots of the free formaldehyde content of the system against time. It was found, in general, that the free formaldehyde content decreased steadily over a number of days, presumably owing to disturbance of the formaldehyde–methylol equilibrium through the removal of some of the methylol groups by the slow condensation reaction which is always present. Nevertheless, equilibrium values of the free formaldehyde content were readily estimated as that value in the region where the rate of disappearance of formaldehyde reached zero or a negligible value.

Equilibrium Constant for Demethylation as a Function of *F*. The equilibrium condition is described by eq. (3). By plotting $[(6/F) - 1] + a_e/a_0$ against $[(1/a_e) - (1/a_0)]$ a good straight line is obtained (see Fig. 3) with a slope of 0.237. This procedure gives greater weight to the results at low *F* value where deviations from randomness are less important. However, when individual *K* values are calculated (see Table IV), a steady increase of *K* over a 1.65-fold range is observed as *F* increases 30-fold. This reflects deviations from randomness through substitution effects.

Equilibrium Constant for Demethylation as a Function of Temperature. By using eq. (3), the *K* values were calculated and are shown in Table V.

TABLE I
Concentration a of Formaldehyde as a Function of Time^a

F	Initial (a_0)	Formaldehyde concn. a , mole/l.										Equilibrium (a_e)
		10 min.	25 min.	50 min.	75 min.	100 min.	125 min.	150 min.				
0.5	0.0277	0.0245	0.0206	0.0174	0.0154	0.0140	0.0132	0.0125	0.0118	0.0118	0.0118	
1.0	0.0553	0.0470	0.0382	0.0317	0.0285	0.0267	0.0257	0.0250	0.0247	0.0247	0.0247	
2.916	0.1609	0.1440	0.1280	0.1110	0.1000	0.0935	0.0895	0.0868	0.0812	0.0812	0.0812	
5.0	0.2747	0.2475	0.2200	0.1985	0.1860	0.1775	0.1720	0.1670	0.1565	0.1565	0.1565	
7.0	0.3843	0.3530	0.3160	0.2900	0.2750	0.2630	0.2550	0.2490	0.2440	0.2440	0.2440	
10.0	0.5469	0.5020	0.4730	0.4450	0.4250	0.4080	0.3980	0.3900	0.3790	0.3790	0.3790	
15.0	0.8137	0.7750	0.7340	0.6920	0.6660	0.6500	0.6330	0.6280	0.6151	0.6151	0.6151	

^a $F = 0.5-15.0$; pH 9.5; temperature 45°C.

The temperature dependence of K is shown in the van't Hoff plot (Fig. 4), giving similar heats of reaction of 2.94 and 2.80 ± 0.3 kcal./mole for $F = 3.0$ and 7.0, respectively. In subsequent calculations the average value $\Delta H^\circ = 2.87$ has been used.

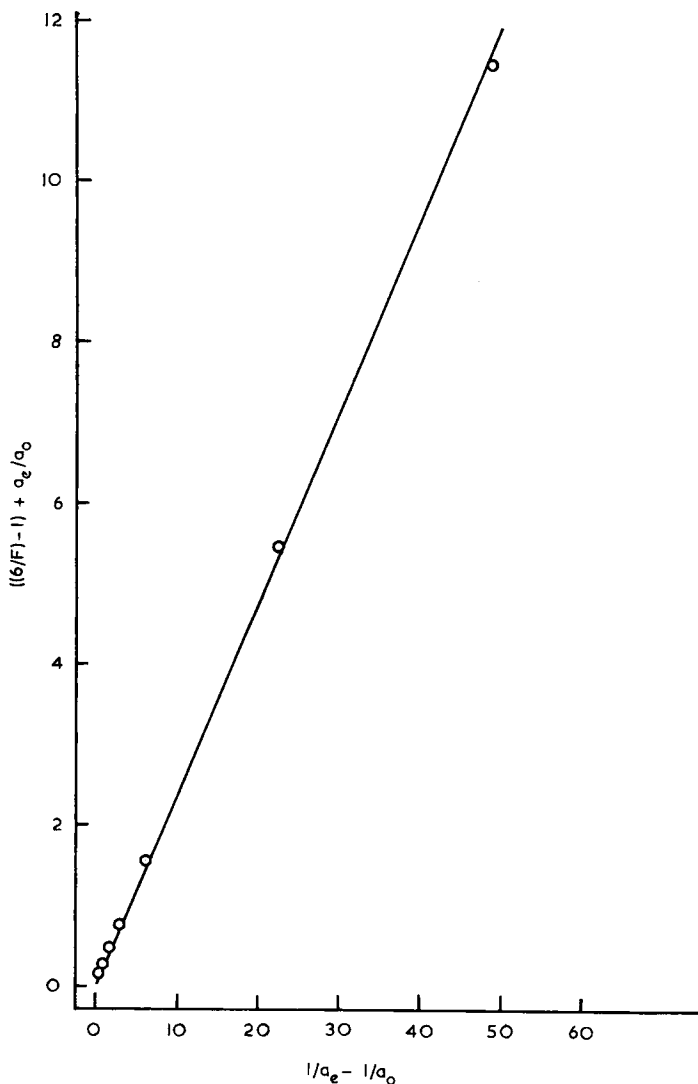


Fig. 3. Plot of equilibrium data: $[(6/F) - 1] + a_e/a_0$ vs. $[(1/a_e) - (1/a_0)]$.

Using the data in Table V, we have calculated (Table VI) the standard heat of the demethylation reaction $\Delta H^\circ = -R[\partial \ln K/\partial(1/T)]$, its standard free energy change ($\Delta G^\circ = -RT \ln K$), and its standard entropy change ($\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$). In as much as the reaction deviates

TABLE II. Concentration a of Formaldehyde as a Function of Time*

F	Temperature, °C.	Time	Formaldehyde concn. a , mole/l.
3.0	25	Initial (a_0)	0.1667
		2 hr.	0.1570
		5 hr.	0.1460
		10 hr.	0.1300
		15 hr.	0.1180
		20 hr.	0.1080
		25 hr.	0.1000
		30 hr.	0.0950
		Equilibrium (a_e)	0.0740
		3.0	30
30 min.	0.1600		
1 hr.	0.1540		
2 hr.	0.1440		
3 hr.	0.1360		
4 hr.	0.1280		
5 hr.	0.1220		
6 hr.	0.1170		
Equilibrium (a_e)	0.0790		
3.0	35		
		25 min.	0.1520
		50 min.	0.1400
		100 min.	0.1230
		150 min.	0.1080
		200 min.	0.0970
		250 min.	0.0920
		300 min.	0.0890
		Equilibrium (a_e)	0.0880
		3.0	45
10 min.	0.1440		
25 min.	0.1280		
50 min.	0.1110		
75 min.	0.1000		
100 min.	0.0935		
125 min.	0.0895		
150 min.	0.0868		
Equilibrium (a_e)	0.0812		
3.0	55		
		10 min.	0.1420
		20 min.	0.1280
		40 min.	0.1100
		60 min.	0.1030
		80 min.	0.0990
		100 min.	0.0960
		120 min.	0.0950
		Equilibrium (a_e)	0.0810

(continued)

TABLE II (continued)

<i>F</i>	Temperature, °C.	Time	Formaldehyde concn. <i>a</i> , mole/l.
7.0	25	Initial (a_0)	0.3871
		5 hr.	0.3300
		10 hr.	0.3000
		20 hr.	0.2660
		30 hr.	0.2500
		40 hr.	0.2410
		50 hr.	0.2330
		60 hr.	0.2250
		Equilibrium (a_e)	0.2180
7.0	30	Initial (a_0)	0.3860
		2 hr.	0.3500
		4 hr.	0.3270
		8 hr.	0.2290
		12 hr.	0.2750
		16 hr.	0.2600
		20 hr.	0.2500
		24 hr.	0.2420
		Equilibrium (a_e)	0.2220
7.0	35	Initial (a_0)	0.3853
		10 min.	0.3650
		25 min.	0.3420
		50 min.	0.3150
		75 min.	0.2970
		100 min.	0.2840
		125 min.	0.2740
		150 min.	0.2660
		Equilibrium (a_e)	0.2300
7.0	45	Initial (a_0)	0.3843
		10 min.	0.3530
		25 min.	0.3160
		50 min.	0.2900
		75 min.	0.2750
		100 min.	0.2630
		125 min.	0.2550
		150 min.	0.2490
		Equilibrium (a_e)	0.2440
7.0	55	Initial (a_0)	0.3832
		10 min.	0.3250
		20 min.	0.2960
		40 min.	0.2720
		60 min.	0.2610
		80 min.	0.2540
		100 min.	0.2500
		120 min.	0.2470
		Equilibrium (a_e)	0.2400

* pH 9.5; temperature 25–55°C.

TABLE III
Concentration a of Formaldehyde as a Function of Time^a

pH	Time, min.	Formaldehyde concn. a , mole/l.
5.7	Initial (a_0)	0.1654
	25	0.1520
	50	0.1430
	100	0.1280
	150	0.1180
	200	0.1100
	250	0.1035
	300	0.0990
	Equilibrium (a_e)	0.0740
	6.6	Initial (a_0)
25		0.1540
50		0.1450
100		0.1310
150		0.1200
200		0.1130
250		0.1070
300		0.1020
Equilibrium (a_e)		0.0780
7.5		Initial (a_0)
	25	0.1560
	50	0.1480
	100	0.1340
	150	0.1230
	200	0.1150
	250	0.1090
	300	0.1050
	Equilibrium (a_e)	0.0840

(continued)

from the random scheme, these thermodynamic functions refer to average values over the various positions on variously substituted melamines.

Equilibrium Constant for Demethylation as a Function of pH. By using eq. (3), the K values in Table VII were calculated for various pH values. It can be seen in Table VII that the equilibrium constant is reasonably independent of the pH.

Fit of the Kinetic Results

In view of the results obtained for the equilibrium data it was considered worthwhile pursuing the kinetic treatment. The methylation rate constants (k_1) were calculated (Table VIII) by using eq. (5) for $K = 0.237$ mole/l. (Fig. 3).

Over the 30-fold range of F values, the rate constant k_1 is seen to vary over a fourfold range. The assumption of randomness of the reaction will, therefore, give at best a semiquantitative picture of the system. A typical plot given by the results according to eq. (5) is shown in Figure 5.

TABLE III (continued)

pH	Time, min.	Formaldehyde concn. a , mole/l.
8.6	Initial (a_0)	0.1654
	25	0.1540
	50	0.1420
	100	0.1270
	150	0.1170
	200	0.1100
	250	0.1050
	300	0.1000
	Equilibrium (a_e)	0.0860
9.5 ^b	Initial (a_0)	0.1609
	10	0.1440
	25	0.1280
	50	0.1110
	75	0.1000
	100	0.0935
	125	0.0895
	150	0.0868
	Equilibrium (a_e)	0.0812
10.2	Initial (a_0)	0.1654
	2	0.1510
	5	0.1340
	10	0.1160
	15	0.1060
	20	0.0990
	25	0.0950
	30	0.0920
	Equilibrium (a_e)	0.0870

^a $F = 3.0$; pH = 5.7–10.2; temperature 45°C.

^b $F = 2.916$.

Methylation Rate Constant as a Function of Temperature. The data in Table IX were plotted on an Arrhenius plot, from which the activation energy of the reaction was calculated (Fig. 6). The agreement between the 3:1 and 7:1 systems was such that the calculation of an average activation energy was reasonable.

The demethylation rate constant (k_2) was calculated from the methylation rate constant and the equilibrium constant by using eq. (4). The Arrhenius plot of these data is also shown in Figure 6. The activation energies calculated from this plot are: $\Delta E_1^* = 23.6$ kcal./mole; $\Delta E_2^* = 26.7$ kcal./mole.

The mean thermodynamic data calculated by using these constants are shown in Table X. The frequency factors were obtained from the intercept of the Arrhenius plot.

In Table X we have included the value for ΔS^* and ΔG^* for the first-order demethylation reaction obtained by using the equation:

$$\Delta G^* = -RT \ln k + RT \ln(\bar{k}T/h) \quad (8)$$

TABLE IV
Equilibrium Constant for Demethylation as a Function of F^a

F	K , mole/l.
0.5	0.235
1.0	0.243
2.916	0.257
5.0	0.280
7.0	0.329
10.0	0.362
15.0	0.393

^a pH = 9.5; temperature 45°C.

TABLE V
Equilibrium Constant for Demethylation as a Function of Temperature^a

F	Temperature, °C.	K , mole/l.
3.0	25	0.192
3.0	30	0.222
3.0	35	0.248
2.916	45	0.257
3.0	55	0.324
7.0	25	0.210
7.0	30	0.226
7.0	35	0.259
7.0	45	0.329
7.0	55	0.327

^a pH = 9.5.

TABLE VI
Mean Thermodynamic Data for the Demethylation Reaction over Temperature
Range 298–328°K.

Mean ΔH° , cal./mole	Mean ΔG° , cal./mole	Mean ΔS° , cal./mole/deg.
2900	850	6.5

TABLE VII
Equilibrium Constant for Demethylation as a Function of pH^a

pH	K , mole/l.
5.7	0.193
6.6	0.217
7.5	0.257
8.6	0.273
9.5	0.257 ^b
10.2	0.281

^a $F = 3.0$; temperature 45°C.

^b $F = 2.916$.

TABLE VIII
Methylation Rate Constant as a Function of F

F	$k_1 \times 10^4$, l./mole-sec.
0.5	6.40
1.0	7.67
2.916	4.58
5.0	3.75
7.0	3.33
10.0	2.45
15.0	1.95

TABLE IX
Methylation Rate Constant as a Function of Temperature^a

F	Temperature, °C.	$k_1 \times 10^4$, l./mole-sec.
3.0	25	0.25
3.0	30	0.64
3.0	35	2.30
2.916	45	6.25
3.0	55	7.10
7.0	25	0.22
7.0	30	0.37
7.0	35	2.30
7.0	45	4.30
7.0	55	6.80

^a pH = 9.5.

TABLE X
Mean Thermodynamic Data over the Temperature Range 298–328°K.

	Mean ΔE^* , cal./mole	Mean ΔG^* , cal./mole	Mean ΔS^* , cal./mole/deg.	X
Methylation	23,600			6×10^{12} l./mole-sec.
Demethylation	26,700	24,500	3.6	2×10^{14} /sec.

TABLE XI
Methylation Rate Constant as a Function of pH^a

pH	$k_1 \times 10^4$, l./mole-sec.	
	Exptl.	Calcd.
5.7	1.59	1.45
6.6	1.44	1.46
7.5	1.44	1.50
8.6	1.78	2.11
9.5	6.25 ^b	6.71
10.2	28.00	27.92

^a $F = 3.0$; temperature 45°C.

^b $F = 2.916$.

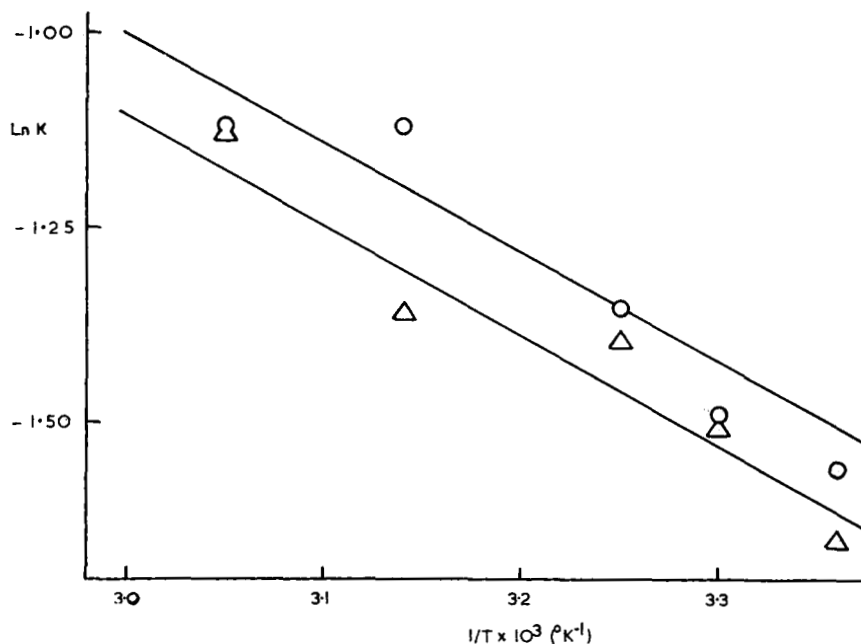


Fig. 4. van't Hoff plot of equilibrium data: (Δ) $F = 3$; (\circ) $F = 7$.

where $\bar{k} =$ Boltzmann constant and $h =$ Planck const. from the theory of absolute reaction rates.⁴

Methylation rate constant as a function of pH ($F = 3.0$; Temperature 45°C). Table XI shows the dependence of k_1 on pH found experimentally, and the successful splitting of this rate constant into two terms depending on a solvent-catalyzed (or uncatalyzed) reaction with constant k_0 and an OH^- -catalyzed reaction with constant k_{OH^-} :⁵

$$k_1 = k_0 + k_{\text{OH}^-}[\text{OH}^-] \quad (9)$$

The hydroxyl ion concentration was calculated from the pH by using the equation

$$\log[\text{OH}^-] = -14 + \text{pH} \quad (10)$$

The best fit was obtained by choosing the values $k_0 = 1.45 \times 10^{-4}$ l./mole-sec. and $k_{\text{OH}^-} = 16.65$ l.²/mole²-sec.

General Discussion of the M/F Reaction

The equilibrium-temperature data reveal a mild exothermicity for methylation ($\Delta H^\circ = -2.9$ kcal./mole), in conjunction with the theoretically expected unfavorable entropy change ($\Delta S^\circ = -6.5$ kcal./mole/deg.); this leaves only a small driving force ($\Delta G^\circ = -0.8$ kcal./mole).

The theoretical prediction of the random model was that the resultant plot from eq. (3) would be one straight line passing through the origin which would satisfy all values of F . It was found that there were devia-

tions from this ideal case, viz.: (1) the individual F values gave plots of different slope; (2) the best line through the experimental points only would have yielded a small positive intercept on the time axis. Both of these observations indicate a degree of nonrandomness in the system which is not accounted for in the theoretical model.

The increase in the value of K as F increases indicates that methylation becomes more difficult with successive additions. This would be

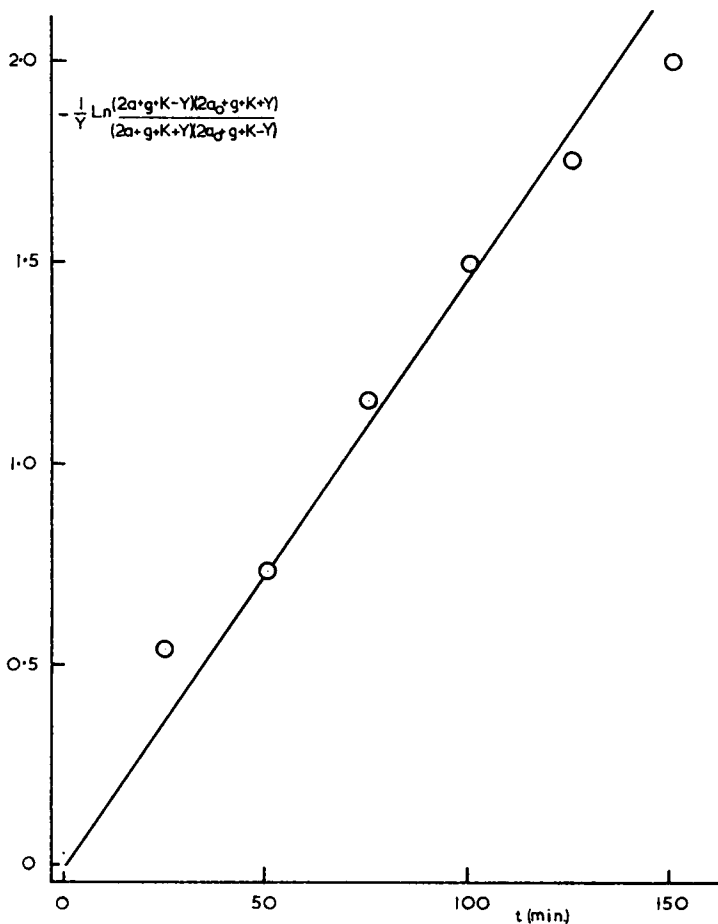


Fig. 5. Plot of rate data; temp. 45°C., pH 9.5, $F = 10$.

consistent with the predominant substitution effect reported earlier, in which the addition of a second methylol group to a given nitrogen atom becomes more difficult than the first. This is also borne out by the rate constants for methylation (Table VIII), which decrease with increasing F value.

The magnitude of the deviation from randomness is estimated in the following manner.

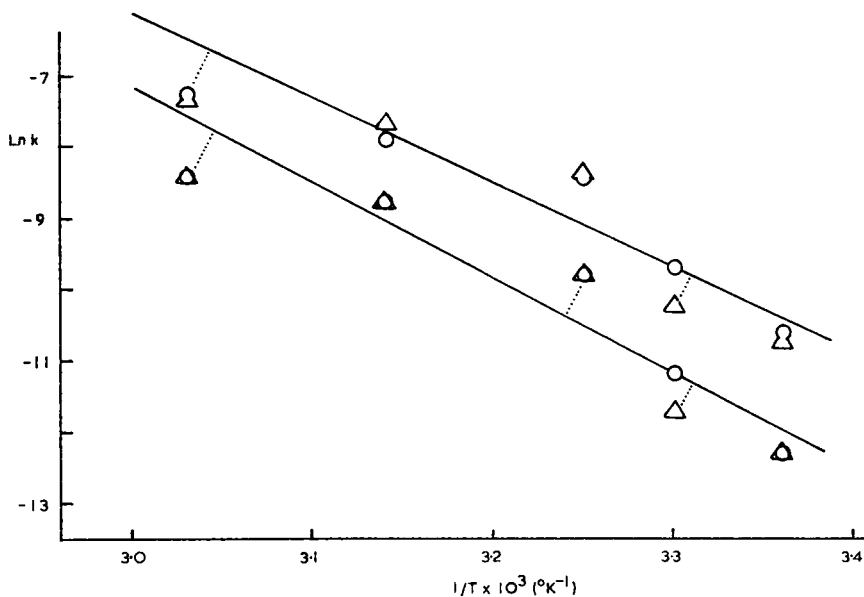


Fig. 6. Arrhenius plot of rate constants: (Δ) $F = 3$; (O) $F = 7$. (Upper plot, k_1 ; lower plot, k_2 .)

The equilibrium experimental data in Table I were fitted to the modified form of eq. (3),

$$[(\theta/F) - 1] + (a_e/a_0) - K[1/a_e - (1/a_0)] = 0 \quad (11)$$

and an optimum value of θ was calculated which yielded the best constant value of K over the whole range of F values from 0.5 to 15.0. This gave a value (Table XII) of $\theta = 4.7$. The significance of this result is to suggest that under equilibrium conditions melamine behaves with a mean reactivity equivalent to 4.7 equally reactive positions. This would be equivalent to three hydrogen atoms with a reactivity of unity and three with a reactivity of 0.57, i.e., a deactivation effect of 0.43. This result is

TABLE XII
Equilibrium Constant for Demethylation from Equation (11)*

F	K , mole/l.
0.5	0.181
1.0	0.185
2.916	0.183
5.0	0.185
7.0	0.204
10.0	0.201
15.0	0.178

* $\theta = 4.7$.

in very reasonable agreement with our earlier work in which a deactivation effect of 0.5 was reported.

The calculation of mean thermodynamic functions, by ignoring substitution effects, is justified by the calculation of the equilibrium-state free-energy contributions of the two substitution effects,² ΔG_x^\ddagger due to the addition of a methylol group to a melamine molecule and ΔG_y^\ddagger due to the localized effect in the formation of a $N(\text{CH}_2\text{OH})_2$ group. For demethylation $\Delta G_x^\ddagger = +150$ cal./mole, $\Delta G_y^\ddagger = -300$ to -600 cal./mole. The contribution to the free energy of activation would be $1/2 (\Delta G_x^\ddagger + \Delta G_y^\ddagger) = -75$ to -225 cal./mole, in comparison to the mean value calculated for the random kinetic scheme of 24,500 cal./mole.

The first-order demethylation reaction is seen to have a normal frequency factor and a positive entropy of activation due to the splitting of a bond.

The results of the variation of the methylation rate constant with pH (Table XI) are very satisfactory. In addition to the uncatalyzed and OH^- -catalyzed reactions, it is conceivable that there would be a H^+ -catalyzed reaction also. However, this would only become apparent at very low pH values, and for the present reaction systems it is considered to be negligible. At low pH values measurements would be difficult owing to the incursion of crosslinking reactions.

The authors wish to thank the directors of Formica Limited for permission to publish this work.

References

1. M. Okano and Y. Ogata, *J. Am. Chem. Soc.*, **74**, 5728 (1952).
2. M. Gordon, A. Halliwell, and T. Wilson, *Chemistry of Polymerisation Processes*, Monograph No. 20, 1966, Society of Chemical Industry, London.
3. J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **71**, 890 (1952).
4. S. Glasstone, *Textbook of Physical Chemistry*, McMillan, London, 1953.
5. R. P. Bell, *Acid-Base Catalysis*, Clarendon Press, Oxford, 1941.

Résumé

La réaction d'addition du formaldéhyde à la mélamine a été étudiée cinétiquement séparée de la condensation ultérieure par un choix approprié des conditions de concentration et de température. La réaction est irréversible, et a été suivie par dosage de la teneur en formaldéhyde libre du système. On l'a étudiée dans un domaine de degré moyen de méthylation $1 < R' < 3.7$ des cycles de mélamine sur un domaine de température de 25 à 55°C, et un domaine de pH de 5.7 à 10.2. Les données de vitesse ainsi obtenues ont été traitées suivant le schéma d'addition réversible pour lesquels en première approximation on obtient un bon accord. Les constantes cinétiques moyennes et thermodynamiques ont été calculées et sont discutées sur la base du présent modèle. Les facteurs qui probablement causent des déviations de la statistique sont décrits. L'addition de formaldéhyde à la mélamine résulte de la superposition d'une étape catalysée par l'ion OH^- avec une étape de moindre importance catalysée par un solvant ou non-catalysée qui se superpose.

Zusammenfassung

Die Additionsreaktion zwischen Melamin und Formaldehyd wurde kinetisch durch geeignete Wahl von Konzentrations- und Temperaturbedingungen von der darauffolgenden Kondensationsreaktion getrennt. Die reversible Reaktion wurde durch Bestimmung des freien Formaldehyds im System verfolgt. Sie wurde im mittleren Methylolierungsgradbereich $1 < R' < 3,7$ der Melaminkerne, im Temperaturbereich 25–55°C und im pH-Bereich 5,7–10,2 untersucht. Die so erhaltenen Geschwindigkeitsdaten wurden nach dem Schema für statistische reversible Addition ausgewertet und dabei eine brauchbare Übereinstimmung in erster Näherung erhalten. Mittlere kinetische und thermodynamische Konstanten wurden berechnet und an Hand des aufgestellten Modells diskutiert. Die Faktoren, welche wahrscheinlich Abweichungen vom statistischen Verhalten bedingen, werden beschrieben. Die Addition von Formaldehyd an Melamin erfolgt durch Überlagerung einer OH⁻-katalysierten Reaktion mit einer weniger bedeutenden, lösungsmittelkatalysierten oder unkatalysierten.

Received March 28, 1966

Prod. No. 1374