SYNTHESIS OF MELAMINE FROM UREA, III

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Introduction

It was reported in the previous papers[1,2] that in the reaction of yielding melamine from urea, the first step is the escape of ammonia from urea and the second step is the reaction between ammonia and cyanuric acid which are formed in the first step. Namely, the hydroxyl radicals of cyanuric acid are replaced by amino radicals, and at the same time the water is produced. Consequently, melamine is formed according to the next process, urea→cyanuric acid→ammelide→ammeline→melamine. The yield of melamine was 95~99% on the assumption that the dehydrated water formed in the above second step decomposes urea, ammelide, ammeline and melamine and the water does not remain. The author studied kinetically the successive reaction of ammelide→ammeline→melamine in the reaction of yielding melamine from urea.

Experimentals

Microautoclaves, the capacity of which is about 1 cc, are used in measuring the velocity of the formation of melamine. The autoclaves are protected from corrosion by the silver lining. At the reaction temperature (the time necessary to the reaction temperature is about 15 minutes), the autoclaves are kept for each reaction time and cooled rapidly by ice water.

Experimental Results

The conditions of this experiment are as follows, packing ratios are 0.5 and 0.3 g/cc**, temperatures 265, 275, 290, 300 and 310°C and time range, up to 8 hours. The weight percentage of solid formed for the urea used and that of each component in solid are shown in Fig. 1. The analysis is all the same as the previous paper[1] but the quantities of ammelide and ammeline are calculated from the nitrogen content measured by Kjeldahl.
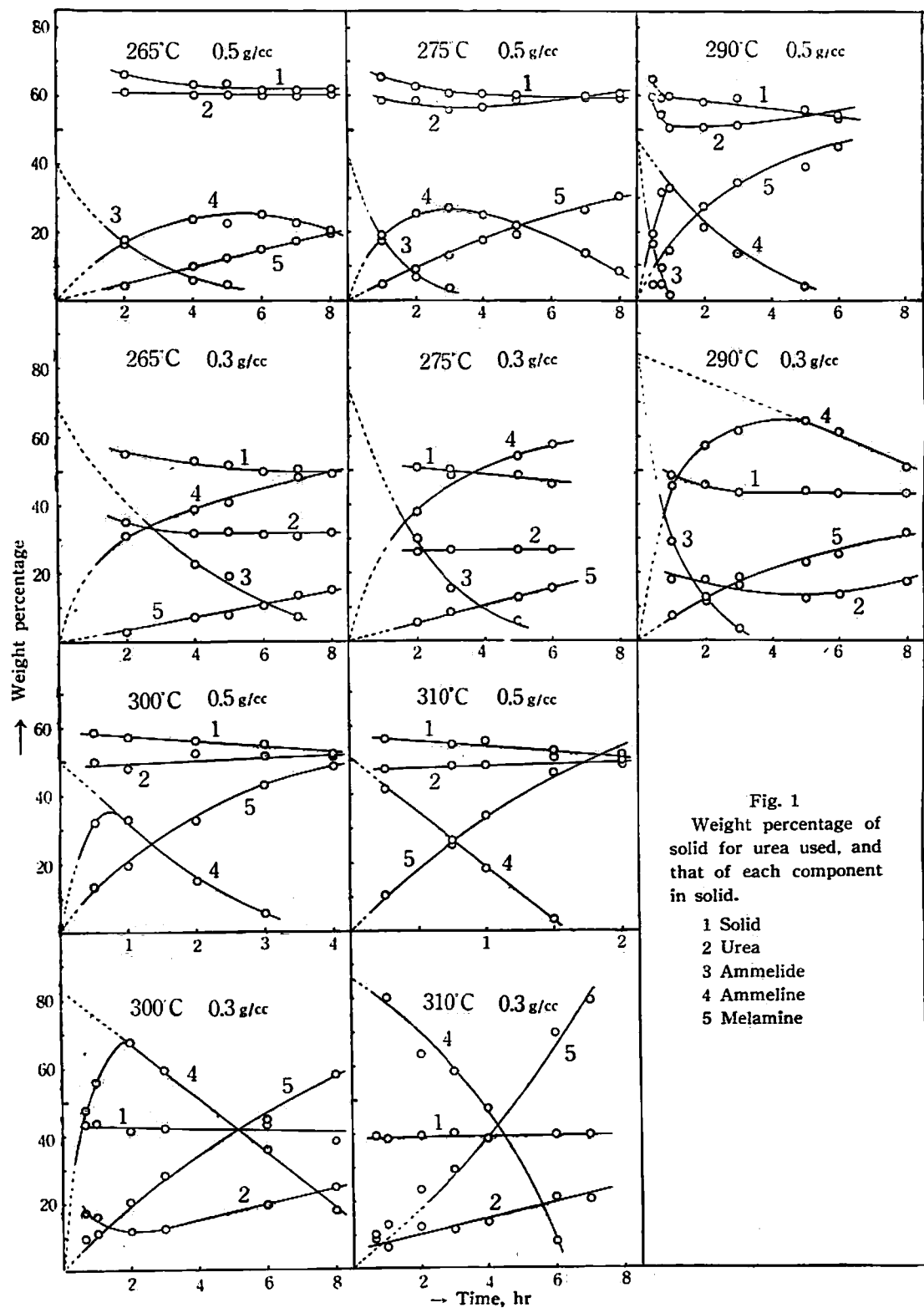
After the formation of cyanuric acid in the reaction of yielding melamine from urea, as the reaction type is dehydration, the water formed may decompose urea, ammelide, ammeline and melamine. In Fig. 1, the quantities of solid products after
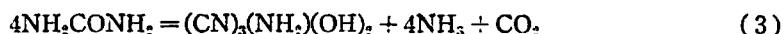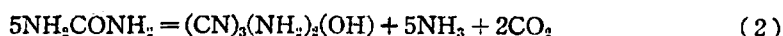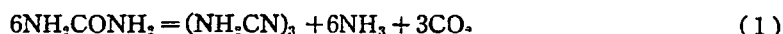
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** The packing ratios of 0.5 and 0.3g/cc are chosen because of difficulty of packing above 0.5 g/cc and analysing below 0.3 g/cc.

1) H. Kinoshita, *This Journal*, **23**, 1 (1953)
2) H. Kinoshita, *ibid.*, **24**, 19 (1954)

Fig. 1
Weight percentage of
solid for urea used, and
that of each component
in solid.

1 Solid
2 Urea
3 Ammelide
4 Ammeline
5 Melamine

drying are considered as constant irrespective of the slight decrease with the lapse of time. Moreover, the quantities of urea in solid are also considered as constant regardless of the slight increase at high temperature. It is anticipated that the decomposition of each component by dehydrated water is smaller except in the initial period of reaction as there is small pressure increase or pressure constant at 275°C or above 300°C[1]. So the composition of gas phase and the concentrations of ammonia in liquid phase may be almost constant. The concentrations of ammonia in liquid phase at each time in Tables are nearly constant. The concentration of ammonia is calculated as follows: first of all, the total ammonia in autoclave is calculated from the quantity of each solid component by using the following equations. In each of the below equations, the same equations are introduced in the cases of urea, ammelide, ammeline and melamine which are decomposed by dehydrated water.

$$6NH_2CONH_2 = (NH_2CN)_3 + 6NH_3 + 3CO_2 \qquad (1)$$

$$5NH_2CONH_2 = (CN)_3(NH_2)_2(OH) + 5NH_3 + 2CO_2 \qquad (2)$$

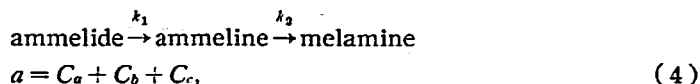$$4NH_2CONH_2 = (CN)_3(NH_2)(OH)_2 + 4NH_3 + CO_2 \qquad (3)$$

Next, the quantity of ammonia in gas phase and the concentration of it in liquid phase are calculated on the assumption that the composition of gas phase is NH_3: $CO_2 = 2:1$. The pressures at 265, 290 and 310°C are interpolated in the curves of pressures and temperatures at 250, 275, 300 and 325°C, and the specific gravity of liquid phase is assumed as constant (1g/cc)[*], regardless of the variation of each component.

Kinetical Considerations

At the temperature and time ranges of this experiment, the reaction product consists of ammelide, ammeline and melamine, and at higher temperature ammelide does not exist except in the initial period of reaction. In the calculation of reaction velocity, it is assumed that the solid product, urea and the concentration of ammonia in liquid phase are all constant at each temperature and packing ratio. Moreover, it is assumed that ammelide and ammeline are dissolved in melted urea because that ammelide or ammeline does not melt at experimental temperature, and that the ammeline is formed in urea by the reaction between ammelide and ammonia and successively melamine is formed by the reaction between ammeline and ammonia. And the reaction velocity of the above two steps of successive reaction are calculated as homogeneous and bimolecular reaction in urea. The initial concentration of ammelide (at lower temperature) or ammeline (at higher temperature) is obtained by extrapolating the quantity of solid from which is excepted the quantity of urea to the starting time of reaction. k_1 and k_2 are calculated at the temperatures of 265, 275 and 290°C, and

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[*] The specific gravity of liquid phase in experimental condition is considered as about 1g/cc, from the situation of the surface of liquid phase in autoclave.

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k_2 only at 300 and 310°C.

$$\text{ammelide} \xrightarrow{k_1} \text{ammeline} \xrightarrow{k_2} \text{melamine}$$

$$a = C_a + C_b + C_c, \tag{4}$$

$\quad a =$ initial concentration of ammelide or ammeline

$\quad C_a, C_b$ and $C_c =$ concentrations of ammelide, ammeline and melamine.

Rate constant of the reaction of ammelide → ammeline When the concentrations of ammelide and ammonia in liquid phase are $[C_a]$ and $[NH_3]$, the decreasing velocity of ammelide is as follows:

$$-\frac{dC_a}{dt} = k_1[NH_3][C_a]. \tag{5}$$

The equation (5) is solved as follows on the assumption that $[NH_3]$ is constant.

$$k_1 = \frac{2.303}{[NH_3]t}\log\frac{a}{C_a}. \tag{6}$$

The rate constants of the first step, k_1, at the temperatures of 265, 275 and 290°C obtained by using the above equation are shown in Table 1.

Table 1

Temp. °C	Packing ratio g/cc	a %	Urea %	NH_3 mole/l	Time hr	C_a %	k_1 1/mole, hr	k_1^* 1/mole, hr
265	0.5	40	60.4	8.9	2	16.5	0.050	
					4	5.9	54	
					5	4.6	49	
							0.051 mean	
〃	0.3	68	32.1	10.4	4	22.7	0.027	0.077
					5	19.2	24	
					7	7.2	31	
							0.027 mean	
275	0.5	42	58.4	8.7	1	17.8	0.099	
					2	6.8	104	
					3	3.7	93	
							0.099 mean	
〃	0.3	73	26.7	9.3	2	30.0	0.048	0.140
					3	15.5	55	
					5	6.3	53	
							0.052 mean	
290	0.5	47	52.5	9.3	2/4	16.4	0.226	
					3/4	4.7	331	
					1	1.7	356	
							0.304 mean	
〃	0.3	84	15.9	10.4	1	29.1	0.102	0.474
					2	11.8	95	
					3	3.9	99	
							0.099 mean	

In Table 1, the value of k_1 at the packing ratio of 0.5g/cc is 2~3 times of that of 0.3g/cc. The effect of pressure may be considered as the pressure becomes higher when the packing ratio becomes larger. On the other hand, the ratio of the quantities of urea as a solvent in the cases of two packing ratios is 2~3.5: 1. Namely, the rate constant is proportional to the concentration of urea, and so the larger the packing ratio—the higher the concentration of urea, the larger the rate constant.

Moreover, in the previous paper[2], the reaction between water insoluble (N=49.4%) and ammonia proceeds slightly at 300°C, and the reaction between ammeline and ammonia does not proceed at 300°C, it is capable to consider that the reaction between ammelide or ammeline and ammonia does not proceed when the urea does not exist. Consequently, it is assumed that the rate constant k_1 when the mole-fraction of solvent is N_s, is equal to the product of $k_1{}^*$ which is the rate constant at infinite dilution, and N_s^n.

$$k_1 = k_1{}^* \ N_s^n. \tag{7}$$

The value of $k_1{}^*$ and n (constant peculiar to the reaction) are obtained by solving the two equations for k_1 and N_s. The value of n to the reaction of ammelide→ammeline are 1.2~1.5. By using $k_1{}^*$ in Table 1, the relation between $\log k_1{}^*$ and $1/T$ is obtained as in Fig. 2. As ammelide exists in shorter time at initial period of reaction above 290°C, the value of $k^*{}_1$ above 290°C may be inaccurate. And so the straight line of $\log k_1{}^*$ and $1/T$ is drawn for two points of 265 and 275°C, and from the inclination of this straight line, the activation energy of the reaction of ammelide→ammeline is evaluated as 32.2 Kcal.
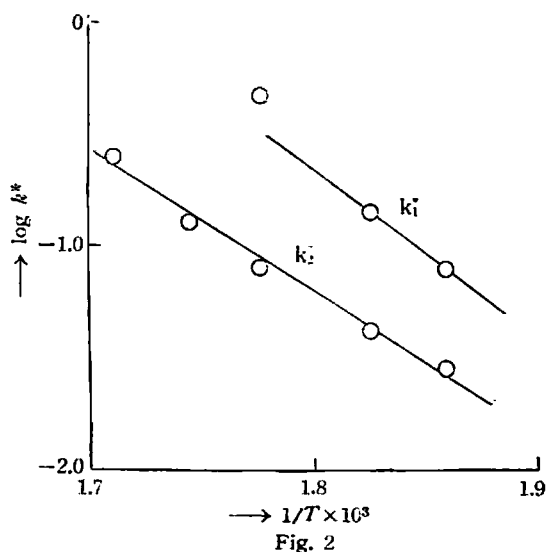

Fig. 2

Rate constant of the reaction of ammeline → melamine

a) Below 275°C. In the successive reaction as ammelide → ammeline → melamine, the velocity of the formation of ammeline is shown when the rate constant of the decrease of ammelide is k_1, and that of the formation of melamine is k_2, thus:

$$\frac{dC_b}{dt} = k_1[NH_3][C_a] - k_2[NH_3][C_b]. \tag{8}$$

The equation (8) is solved as follows[3] on the assumption that $[NH_3]$ is constant as in the equation (5).

$$C_b = a\frac{k_1}{k_2 - k_1}(e^{-k_1[NH_3]t} - e^{-k_2[NH_3]t}).$$

$$C_c = a - C_a - C_b$$
$$= a\left(1 - \frac{k_2 e^{-k_1[NH_3]t} - k_1 e^{-k_2[NH_3]t}}{k_2 - k_1}\right). \tag{9}$$

The value of k_2 is obtained graphically by using the value of k_1, which is shown in Table 1. The value of k_2 at the temperatures of 265 and 275°C are shown in Table 2. There exists the same tendency in the value of k_2 at each packing ratio

3) S. Glasstone, *Elements of Physical Chemistry*, p 603 (1950)

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Table 2

Temp. °C	Packing ratio g/cc	a %	Urea %	NH_3 mole/l	k_1 1/mole, hr	Time hr	C_c %	k_2 1/mole, hr	k_2^* 1/mole, hr
265	0.5	40	60.4	8.9	0.051	2	4.2	0.019	
						4	10.0	16	
						5	12.2	14	
						6	14.9	14	
						7	17.3	14	
						8	19.5	14	
								0.015 mean	
"	0.3	68	32.1	10.4	0.027	4	7.2	0.0069	0.028
						5	7.9	53	
						6	10.6	54	
						7	13.8	58	
						8	15.1	52	
								0.0057 mean	
275	0.5	42	58.4	8.7	0.099	2	9.0	0.028	
						3	13.1	24	
						4	17.8	23	
						5	22.0	24	
						7	26.7	20	
						8	30.6	22	
								0.024 mean	
"	0.3	73	26.7	9.3	0.052	2	5.8	0.013	0.041
						3	8.7	10	
						5	12.9	069	
						6	15.5	65	
								0.0091 mean	

in Table 2 as in the value of k_1. The value of k_2^*, which is the rate constant of infinite dilute solution, is obtained approximately by using the same equation as that of (7).

b) Above 290°C. As ammelide exists in shorter time at the initial period of reaction, the first step of the successive reaction is neglected and the rate constant of the second step k_2 is calculated. The values of k_2 in Table 3 are obtained by using the following equation which is led as in the case of the reaction of ammelide→ ammeline.

$$k_2 = \frac{2.303}{[NH_3]t} \log \frac{a}{C_b}$$
$$= \frac{2.303}{[NH_3]t} \log \frac{a}{a - C_c}. \qquad (10)$$

In this case also, k_2^* is obtained by using the same equation as (7) because the value of k_2 is different with packing ratio.   The values of n in this case are 1.6~2.3. By using k_2^* in Tables 2 and 3, the relation between log k_2^* and $1/T$ is obtained in Fig. 2. From the inclination of the straight line, the activation energy of the reaction of ammeline → melamine is evaluated as 29.5 Kcal.

Conclusions

1) In the reaction of yielding melamine from urea, the rate constants of the successive reaction as ammelide → ammeline → melamine, are calculated under the assumptions that the reaction is homogeneous and bimolecular in liquid phase, urea exists as a solvent, and the concentration of ammonia is unchangeable at each

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Table 3

Temp. C°	Packing ratio g/cc	a %	Urea %	NH_3 mole/1	Time hr	C_r %	k_2 1/mole, hr	k_2* 1/mole, hr
290	0.5	47	52.5	9.3	3/4	9.4	0.032	
					1	14.8	41	
					2	21.4	33	
					3	34.9	49	
					5	39.4	39	
							0.039 mean	
″	0.3	84	15.9	10.4	2	13.0	0.0081	0.078
					3	18.6	81	
					5	23.1	62	
					6	25.1	57	
					8	31.8	57	
							0.0068 mean	
300	0.5	50	50.4	8.4	2/4	13.3	0.074	
					1	19.6	59	
					2	32.6	63	
					3	43.0	78	
							0.069 mean	
″	0.3	83	16.9	7.9	2/3	9.4	0.023	0.126
					1	11.1	18	
					2	20.3	18	
					3	28.1	17	
					6	44.8	16	
					8	58.0	19	
							0.019 mean	
310	0.5	51	48.7	7.5	1/4	10.9	0.13	
					3/4	25.1	12	
					1	33.6	14	
							0.13 mean	
″	0.3	86	12.4	7.0	2/3	10.2	0.027	0.251
					1	13.2	24	
					2	23.6	23	
					3	29.6	20	
					4	38.7	21	
							0.023 mean	

temperature and packing ratio except in the initial period of reaction.

2) It is considered that the difference of rate constant by packing ratio is due to the mole-fraction of the solvent (urea), and the rate constant at infinite dilution is decided as that of the temperature.

3) Activation energies of the successive reaction as ammelide→ammeline→melamine are obtained as 32.2 and 29.5 Kcal. respectively.

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