SYNTHESIS OF MELAMINE FROM UREA, II

By Hideo Kinoshita*

Introduction

It was reported[1] that the reaction of yielding melamine from urea begins from 275°C, reaches equilibrium within 6 hours at 325°C and there is no considerable change in the quantity and the yield of melamine above 325°C. And it was recognized that the reaction velocity is faster, as the packing ratio is greater and so the pressure of gas phase is higher. The yield of melamine was calculated from the following equation and the maximum yield was 99.4%.

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

Moreover, as the intermediate products of this reaction, biuret, cyanuric acid and the water insoluble were obtained. The nitrogen content of this water insoluble was distributed between 45.4 and 55.7%. For the purpose of studying the process of this reaction, the author experimented the following cases, the reaction of urea under the condition of existing excess ammonia, the reaction between cyanuric acid and ammonia, the reaction between the water insoluble and ammonia, and the reaction between melamine and water. These results are compared with those of the previous paper, and moreover the author makes clear that the water insoluble consists of ammelide and ammeline.

Samples and Experimental

Samples

Urea and melamine Commercial urea and melamine are recrystallized from water.

Cyanuric acid Urea is heated for several hours at 200°C under atmospheric pressure. After the product is washed with a small amount of water, dissolved in $3N\text{-}H_2SO_4$ and boiled for 8 hours. The needle crystal which is deposited after cooling, is dried at 100°C. The nitrogen content is 32.4~32.6%.

Water insoluble (N=49.4%) After heating urea under the following conditions—250°C, 6 hours and the packing ratio, 0.3 g/cc, the reaction product is washed with hot water and dried.

Water insoluble (N=55.1%) After heating urea under the following conditions—300°C, an hour and the packing ratio, 0.5 g/cc, the reaction product is washed with hot water and dried.

Experimental method

The experimental method is the same as that of the previous paper and the

* Saikyo University

1) H. Kinoshita, *This Journal*, 23, 1 (1953)

The Review of Physical Chemistry of Japan Vol. 24 No. 1 (1954)

quantity of the liquid ammonia added is weighed by the apparatus as shown in Fig. 1—A; liquid ammonia reservoir, D; gauge glass, H; reaction vessel, E, F and G; high pressure valves (G; valve of the reaction vessel), B and C; joints of the gauge glass and the steel pipe. The air in both the gauge glass and the reaction vessel are pumped out through G and F. After closing F and G, by opening the valve E, liquid ammonia is made to flow down in the gauge glass, and liquid ammonia is introduced into the reaction vessel through the valve G. The quantity of liquid ammonia which is to flow down in the reaction vessel corresponds to $(D-d)V$, when the volume of liquid ammonia is V, and the density of liquid ammonia and saturated vapor are D and d respectively.

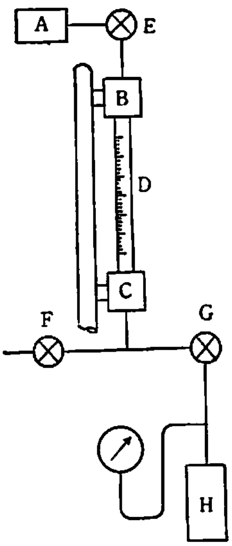

Fig. 1

Experimental Results and Considerations

Effect of excess ammonia on the reaction of yielding melamine from urea It is assumed in the previous paper that in the reaction of yielding melamine from urea, the first step is the formation of biuret and cyanuric acid from the escape of ammonia from urea and the second step is the formation of the water insoluble by the reaction between cyanuric acid and ammonia evolved. If this assumption is true, the excess ammonia added on urea will suppress the reaction of first step and consequently the residual urea will increase and moreover the reaction of second step will be accelerated. It was reported in the patent[2] of du Pont that the excess ammonia is not necessary to the formation of melamine from urea. For the purpose of confirmation of these points, the author experimented under the following conditions—mole ratios of urea and ammonia are 1:1 and 1:2, temperature, 300 and 350°C. The analysis of the reaction product is compared with that of the previous paper (Exp. Nos. 21 and 23) in Table 1.

From these experiments, it is capable to summarize as follows,

(a) Residual urea increases in the presence of excess ammonia. So the escape of ammonia from urea may be suppressed, but the effect of excess ammonia does not increase in the case of excess ammonia added over a mole to a mole of urea.

(b) The reaction between the water insoluble and ammonia is accelerated by excess ammonia. Namely, in the reaction of urea only, the quantity of the water insoluble formed in 6 hours at 300°C is 19.9%, but in the case of excess ammonia over a mole, the water insoluble does not exist under the same conditions. Consequently, the effect of excess ammonia on the yield of melamine is noticed at a temperature of 300°C, but not at a temperature of 350°C.

2) Brit. Pat. No. 628,250 Aug. 25 (1949)

(c) It was assumed in the previous paper that in the reaction of yielding melamine

Table 1. Weight percentage of each component for urea used, yield of melamine, nitrogen content of water insoluble and the final pressure

Exp. No.	Temp. (°C)	Time (hrs)	Urea/NH_3 (mole ratio)	Solid total	Water insoluble		Water soluble			Yield of melamine	Press. (kg/cm^2)
					total	N%	total	urea	melamine		
21	300	6	1/0	44.2	19.9	53.6	24.3	10.4	13.9		274
43	〃	〃	1/1	48.0			48.0	20.6	27.4	98.9	306
44	〃	〃	1/2	50.2			50.2	24.4	25.8	97.4	458
23	350	〃	1/0	36.7			36.7	4.2	32.5	97.3	330
45	〃	1	1/1	41.8			41.8	11.5	30.3	97.7	344
46	〃	〃	1/2	42.5			42.5	12.1	30.4	98.7	421

total packing ratio 0.3 g/cc

from urea, the process, urea→cyanuric acid→water insoluble→melamine, exists. And there is no considerable change in pressure after reaching the reaction temperature in this experiment as in the previous one. Consequently, it is capable to conclude that melamine is formed by the escape of ammonia from urea and by the reaction between the water insoluble and ammonia.

Reaction between cyanuric acid and ammonia It was supposed in the process of yielding melamine from urea that the first step is the formation of cyanuric acid by the escape of ammonia from urea, and the second step is the reaction between cyanuric acid and ammonia. For the purpose of studying the yield of melamine in the reaction between cyanuric acid and ammonia at the mole ratio of 1:3, the experiments in the temperature range, 225~375°C, are performed up to 6 hours.

The analysis of the reaction product is compared with that of the previous paper (Exp. Nos. 20~24) in Table 2. The relations between pressure and time at the above temperatures are shown in Fig. 2.

From these experiments, it is capable to summarize as follows:

(a) As there is no change in the pressure and in the amount of cyanuric acid at 225°C, the reaction between cyanuric acid and ammonia does not occur below 225°C.

(b) At a temperature of 250°C, the pressure decreases in about an hour, and increases slowly through minimum. The solid products formed at the time of $1\frac{1}{3}$ hours are urea and cyanuric acid, whose

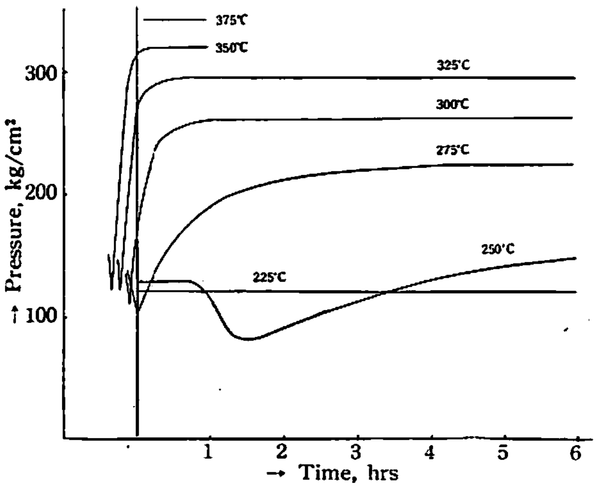

Fig. 2

The Review of Physical Chemistry of Japan Vol. 24 No. 1 (1954)

quantities are 61.3 and 21.7% respectively. The total amount of cyanuric acid and urea is 83.0%, and this is more than the quantity of initial cyanuric acid, 71.7%. On the other hand, the solid products formed in 3 and 6 hours are urea, cyanuric acid and water insoluble, whose quantities are 38.6, 5.6, 30.8% and 16.1, 1.5, 47.8% respectively. Accordingly, in the reaction between cyanuric acid and ammonia, the first step is the formation of urea and the urea formed decreases afterward, and simultaneously cyanuric acid decreases and the water insoluble is formed. From these results, it is admitted that the pressure drop depends on the formation of urea, and the pressure rise depends on the ammonia and carbon dioxide which are formed by the reaction between urea and water.

Table 2 Weight percentage of each component for cyanuric acid and ammonia used, yield of melamine and nitrogen content of water insoluble

Exp. No.	Temp. (°C)	Time (hrs)	Solid total	Water insoluble		Water soluble				Yield of melamine
				total	N%	total	urea	cyanuric acid	melamine	
47	225	6	71.7			71.7		71.7		
48	250	$1\frac{1}{3}$	83.0			83.0	61.3	21.7		
49	〃	3	75.0	30.8	48.9	44.2	38.6	5.6		
50	〃	6	65.4	47.8	49.1	17.6	16.1	1.5		
51	275	〃	51.5	35.5	50.3	16.0	14.3		1.7	
20	〃	〃	51.9	33.6	50.3	18.3	14.3		4.0	
52	300	〃	44.6	24.3	54.4	20.3	7.7		12.6	
21	〃	〃	44.2	19.9	53.6	24.3	10.4		13.9	
53	325	〃	39.0			39.0	8.0		31.0	96.3
22	〃	〃	38.7			38.7	7.1		31.6	97.0
54	350	1	37.7			37.7	5.7		32.0	96.8
23	〃	6	36.7			36.7	4.2		32.5	97.3
55	375	1	37.6			37.6	4.7		32.9	98.7
24	〃	3	36.8			36.8	3.9		32.9	97.7

total packing ratio 0.3 g/cc

(c) Above 275°C, a rapid pressure drop appeared before reaching the reaction temperature, and this depends on the formation of urea as in the reaction at 250°C. The lower the temperature is, the more time the pressure drop takes. The final pressure and the quantity of each reaction product are all the same as in the reaction of urea only.

(d) There exists no cyanuric acid above 275°C and exists no water insoluble in 6 hours above 325°C. The quantities of melamine at 275~375°C are all the same as in the reaction of urea only. Consequently, above 275°C, the same state is observed in the reaction between cyanuric acid and ammonia at the mole ratio of 1 : 3 as in the reaction of urea only.

(e) It is demonstrated that the process of the reaction of urea at 250°C, is urea → cyanuric acid → water insoluble, from the facts that the urea is formed by the reaction between cyanuric acid and ammonia, and that the water insoluble is formed afterward. Moreover, the nitrogen content of the water insoluble is higher as the temperature is higher. As reported later, the water insoluble consists of ammelide and ammeline, so it may be considered that the process of yielding melamine from the water insoluble at higher temperature is as follows: cyanuric acid→ammelide→ammeline→melamine.

The reaction between ammonia and water insoluble which is formed in the reaction of yielding melamine from urea It is considered that the water insoluble which is formed in the reaction of yielding melamine from urea may be the intermediate substance in this reaction. So the yield of melamine in the reaction between this water insoluble and ammonia is studied. The water insolubles of N=49.4 and 55.1% are used, and the reaction temperatures are 300~375°C, and 300~425°C respectively. The analysis of the reaction products and the final pressures are tabulated in Tables 3 and 4. The pressure after reaching the reaction temperature almost remains unchanged.

Table 3 Weight percentage of each component for water insoluble (N=49.4%) used, yield of melamine, nitrogen content of water insoluble and the final pressure

Exp. No.	Temp. (°C)	Time (hrs)	Solid total	Water insoluble		Water soluble			Yield of melamine	Press. (kg/cm²)
				total	N%	total	urea	melamine		
56	300	6	90.4	64.5	54.9	25.9	5.3	20.6		238
57	325	〃	79.5			79.5	11.9	68.6	98.1	261
58	350	〃	74.8			74.8	5.9	68.9	95.7	292
59	375	1	74.4			74.4	4.4	70.0	96.4	313

total packing ratio 0.326 g/cc

Table 4 Weight percentage of each component for water insoluble (N=55.1%) used, yield of melamine, nitrogen content of water insoluble and the final pressure

Exp. No.	Temp. (°C)	Time (hrs)	Solid total	Water insoluble		Water soluble= melamine	Yield of melamine	Press. (kg/cm²)
				total	N%			
60	300	6	98.9	98.9	55.2			105
61	350	1	97.8	90.6	55.1	7.2		112
62	375	〃	87.7	31.3	55.0	56.5		142
63	400	〃	78.5			78.5	95.0	168
64	425	〃	79.5			79.5	96.3	181

total packing ratio 0.3 g/cc

2 g of ammonia is used for 5 g of the water insoluble (N=49.4%). Assuming that the water insoluble consists of ammelide and ammeline, that of N=49.4% corresponds to the mixture of equal mole ratio. And so the quantity of ammonia required from equation (2) is 1 to 5 g of the water insoluble. At 300°C the water insoluble of N=55.1% (ammeline) is formed by the reaction between the water insoluble of N=49.4% and ammonia, and above 325°C the water insoluble does not exist and melamine and urea

are formed. In Table 3, the yield of melamine is calculated from the following assumptions—melamine is formed according to the reaction of equation (2), and by the water which is formed in equation (2) melamine is decomposed to urea, ammonia and carbon dioxide and the water does not remain. Namely, the urea is formed according to the reaction of equation (3) and by the remaining water melamine is decomposed to ammonia and carbon dioxide according to equation (4).

$$(CN)_3(NH_2)_2OH + (CN)_3(OH)_2NH_2 + 3NH_3 = 2(NH_2CN)_3 + 3H_2O \qquad (2)$$

$$(NH_2CN)_3 + 3H_2O = 3(NH_2)_2CO \qquad (3)$$

$$(NH_2CN)_3 + 6H_2O = 3(NH_2)_2CO + 3H_2O = 6NH_3 + 3CO_2 \qquad (4)$$

In the reaction between the water insoluble (N=55.1%) and ammonia, assuming that the water insoluble is ammeline, the quantity of ammonia required, is calculated from equation (5). From the same assumption that by the water which is formed in the reaction of equation (5), melamine is decomposed to ammonia and carbon dioxide, the yield of melamine is calculated by using equation (6) which is derived by adding up (5) and $\frac{1}{6}\times(4)$.

$$(CN)_3(NH_2)_2OH + NH_3 = (NH_2CN)_3 + H_2O \qquad (5)$$

$$(CN)_3(NH_2)_2OH + NH_3 = \frac{5}{6}(NH_2CN)_3 + NH_3 + \frac{1}{2}CO_2 \qquad (6)$$

In this case, urea does not exist. The water formed in equation (5) and the melamine decomposed according to equation (3) or (4), is less than in the reaction between the water insoluble (N=49.4%) and ammonia. As the pressure of gas phase is fairly lower than in the case of N=49.4%, the urea which is formed in the process of the reaction between water and melamine, may be decomposed to ammonia and carbon dioxide.

The water insoluble (N=49.4%) reacts fairly with ammonia to higher nitrogen content at 300°C and the reaction is completed in 6 hours at 325°C. On the contrary, the water insoluble (N=55.1%) reacts slightly with ammonia at 350°C.

From the above results, it is made clear that melamine is formed from the water insoluble through the process, ammelide→ammeline→melamine.

The reaction between melamine and water Assuming that the reaction of yielding melamine from urea proceeds according to equation (1), it may be considered that 3 molecules of water which is formed by dehydration, decompose 3 molecules of urea, or that 6 molecules of water decompose 1 molecule of melamine.

$$6(NH_2)_2CO = (NH_2CN)_3 + 3(NH_2)_2CO + 3H_2O = (NH_2CN)_3 + 6NH_3 + 3CO_2 \qquad (7)$$

$$6(NH_2)_2CO = 2(NH_2CN)_3 + 6H_2O = (NH_2CN)_3 + 6NH_3 + 3CO_2 \qquad (8$$

For the purpose of studying these facts, the reaction between melamine and water at the mole ratio of 1:3 is performed. The way of adding water is the same as that[3] of the

3) R. Kiyama and H. Kinoshita, *This Journal*, 21, 9 (1951)

previous paper. The melamine and water at the mole ratio of 1:3 corresponds to urea by assuming the reverse reaction of equation (8). Consequently, 6 molecules of water decompose 1 molecule of melamine and so 1 molecule of melamine, namely 50% of it used, will remain. The analysis of the reaction product and the final pressure are shown in Table 5.

The relation between pressure and time at each temperature is almost the same as in the reaction of urea only.

Table 5 Weight percentage of each component for melamine used, nitrogen content of water insoluble and the final pressure

Exp. No.	Temp. (°C)	Time (hrs)	Solid total	Water insolube		Water soluble			Press. (kg/cm²)
				total	N%	total	urea	melamine	
65	225	6	92.6	18.8	50.3	73.8		73.8	65
66	250	"	75.5	31.2	49.2	44.3		44.3	164
67	275	"	70.0	18.2	50.5	51.7		51.7	221
68	300	"	62.2	9.8	48.5	52.4		52.4	269
69	325	"	57.4			57.4	8.0	49.4	289
70	350	"	57.4			57.4	5.7	51.7	309
71	375	"	56.0			56.0	4.3	51.7	329
72	400	3	53.4			53.4	1.7	51.7	352

total packing ratio 0.3 g/cc

The water insoluble exists so far as 6 hours at 300°C, disappears in the experimental time range above 325°C, and urea does not exist below 300°C, decreases above 325°C. The amounts of water insoluble and urea are maximum at 250°C and 325°C respectively. The maximum amount of melamine remains at 250°C, and above 275°C the mean value of remaining melamine is about 51.6%. Nitrogen content of water insoluble is about 50%. As described later, this water insoluble can be separated into two parts by picric acid and so this is considered as the same substance as that formed in the reaction of urea only. Below 300°C, as the pressure is fairly lower, urea may be decomposed if it is formed. Urea and melamine remain above 325°C. The amounts of the residual melamine above 275°C are about 50% even though the water insoluble exists. Consequently, the assumption that 1 molecule of melamine is formed from 6 molecules of urea, includes the error of several percentage. From these results, it becomes clear that melamine is decomposed by water through the following process, melamine→ammeline →ammelide→.

The water insoluble substance

The nitrogen content of the water insoluble which is formed in the reaction of urea only, and in the reactions between cyanuric acid and ammonia, and between melamine and water, is distributed between that of ammelide and ammeline. The maximum value (N=55.7%) is much the same as ammeline (N=55.1%), and the minimum value (N=45.4%) is slightly higher than ammelide (N=43.8%). Consequently, the water

The Review of Physical Chemistry of Japan Vol. 24 No. 1 (1954)

insoluble (N=about 55%) is assumed as ammeline, and that (N<55%), is assumed as the mixture of ammeline and ammelide. These water insoluble are treated with picric acid and confirmed by HCl salt.

From H_2SO_4 solution of the water insoluble (N=55.1%), yellow and needle crystalline picrate is formed by picric acid. The quantity of this picrate corresponds to 95% of the water insoluble used, and the nitrogen content is 30.8%. Moreover, white precipitate is formed by neutralizing the hot water solution of this picrate with ammonia. The nitrogen content of this white precipitate is 55.1%. Consequently, this picrate may be the picrate of ammeline-$(CN)_3(NH_2)_2OH \cdot C_6H_2(OH)(NO_2)_3$, N=31.4%. On the other hand, from H_2SO_4 solution of the water insoluble (N=49.4%), yellow picrate is formed by picric acid. The nitrogen content is the same as the former and that of the white precipitate which is formed by neutralizing the hot water solution of this picrate with ammonia, is 55.2%. So the picrate in this case is also that of ammeline. The nitrogen content of white precipitate, which is formed by neutralizing H_2SO_4 solution with ammonia after the picrate is removed, is 43.8%, so this precipitate may be ammelide (N=43.8%). The amount of ammeline is about 45~50%, and of ammelide is about 40~45%, so the water insoluble (N=49.4%) may be the mixture of almost equal mole of ammeline and ammelide. Consequently, in the water insoluble (N>49.4%), the amount of ammeline is more than that of ammelide, and in the water insoluble (N<49.4%), ammelide is more than ammeline. The picrate of ammelide is not formed from H_2SO_4 solution. The solubility of picrate and of HCl salt of ammelide, are fairly greater than those of ammeline, so ammeline and ammelide may be separated.

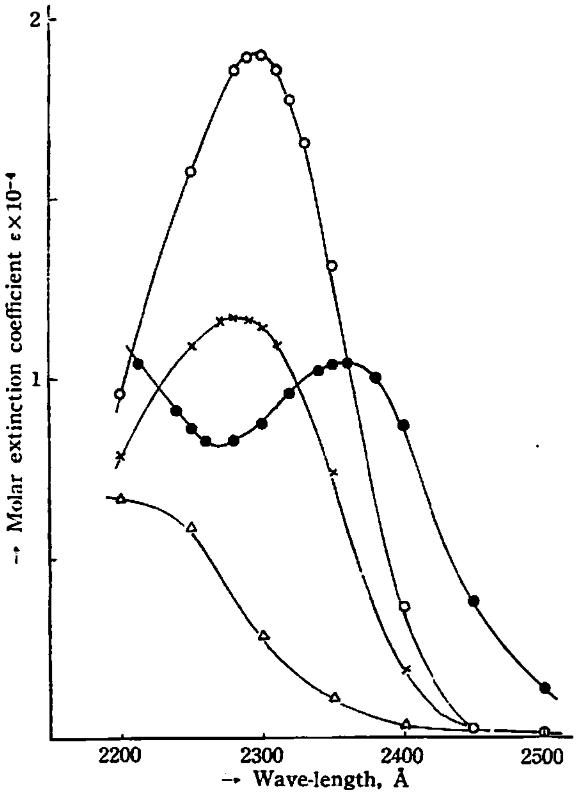

Fig. 3

● melamine, ○ ammeline,
△ ammelide, × water insoluble (N=49.4%)

The crystals are prepared by cooling the hot 3N-HCl solutions of ammelide, ammeline and melamine. The nitrogen contents of these HCl salts, and those calculated are shown in Table 6.

From these results, it is concluded that the water insoluble (N=55.1%) is ammeline

Table 6

	Calc.	Exp.
Melamine-HCl	51.6	51.6
Ammeline-HCl	42.8	43.0
Ammelide-HCl	34.0	34.6

and that (N<55.1%) is the mixture of ammelide and ammeline at least in H_2SO_4 solution. Ammelide, ammeline and HCl salts of both, are decomposed above 400°C. The absorption spectra of ultraviolet ray of ammelide, ammeline and water insoluble* (N=49.4%) in 0.019N-H_2SO_4 solution are compared with that of melamine in Fig. 3. The absorption of ammeline in an acid solution is stronger than that of melamine, and the absorption of ammeline and melamine reaches maximum at 2300 and 2360 Å respectively. The absorption of the water insoluble (N=49.4%) exists in the middle of the absorption of ammeline and ammelide. Absorption spectrum is measured by a Beckman Model DU Spectrophotometer and the error of ε exists within ±100, $\varepsilon = \frac{1}{cd} \log I_0/I$: c, concentration, mole/l: d, length of absorption cell, cm.

The author wishes to express his hearty thanks to Prof. R. Kiyama for his encouragement and revision.

The Laboratory of Physical Chemistry,
Kyoto University

* Molecular weight is assumed as 127.5.