SYNTHESIS OF MELAMINE FROM UREA, IV

By Hideo Kinoshita*

Introduction

In the previous papers[1,2,3] it becomes clear that when the urea is heated in autoclave, melamine is formed by passing through biuret, cyanuric acid, ammelide and ammeline. Moreover, the successive reaction of ammelide→ammeline→melamine was studied kinetically and the activation energies of the above two steps are calculated. For the purpose of further studying the reaction of the formation of biuret and cyanuric acid, the reactions at lower temperature in closed and open vessels are performed.

Experimentals

Reaction in closed vessel The experimental conditions are as follows: temperatures are 133 (melting point of urea), 150 and 175°C, packing ratios 0.3 and 0.5g/cc, and time range, up to 6 hours. The experimental procedure is the same as in the previous papers[1,2], namely the autoclave is heated after packing the urea and evacuating the air.

Reaction in open vessel After packing 5g of urea, the glass test tube (20cm long and 1.7cm wide) is heated in an oil bath. The experimental time range and temperatures are the same as in the case of the reaction in closed vessel.

The analysis of the reaction products is performed by the same method as in the previous paper[1].

Results

The relations between pressure and time during the reaction in closed vessel are shown in Fig. 1. In the case of packing ratio of 0.5g/cc, the pressure is higher than in the case of 0.3g/cc. The increase of pressure is linear against time and gradually at 133°C and fast in the initial period and becomes gradually after one hour at 150 and 175°C. The weight percentages of each component to the urea used are shown in

* Saikyo University

1) H. Kinoshita, *This Journal*, 23, 1 (1953)
2) H. Kinoshita, *ibid.*, 24, 19 (1954)
3) H. Kinoshita, *ibid.*, 24, 67 (1954)

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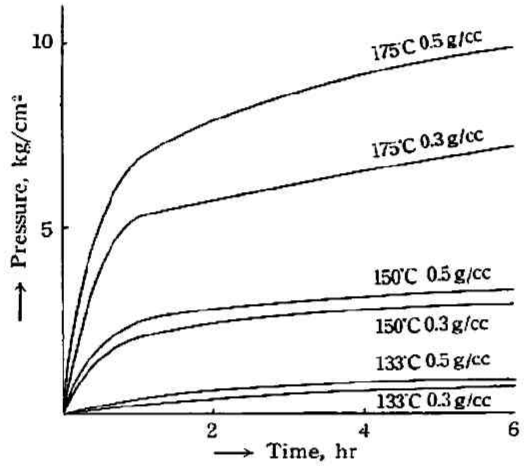

Fig. 1

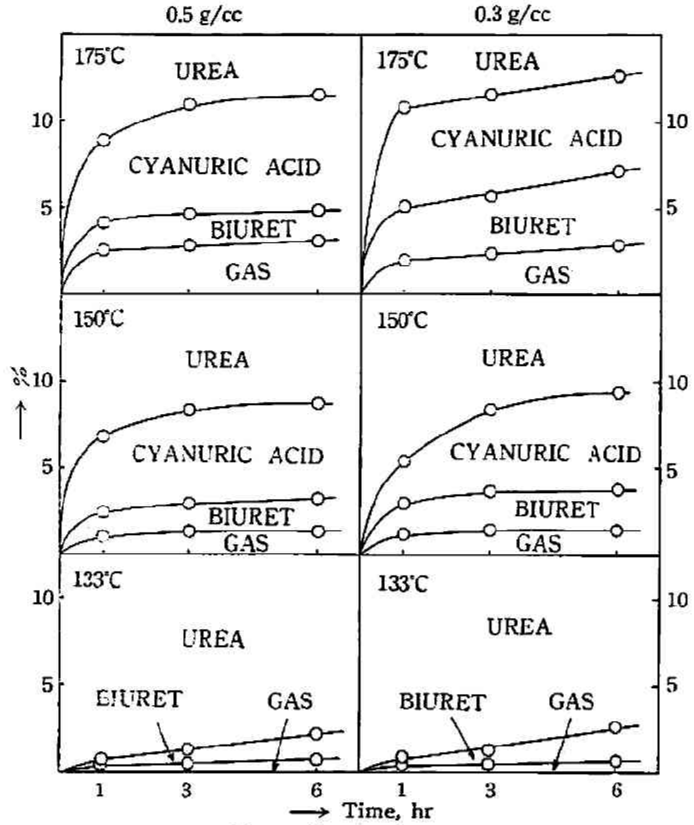

Fig. 2 In closed vessel

Figs. 2 and 3, and each domain means the quantities of the gas which is subtracted the quantity of dried solid from that of urea used, biuret, cyanuric acid and urea. The quantities of gas calculated from pressure in Fig. 1 and from the quantities of the reaction products are almost coincident with those of gas in Fig. 2. At a reaction of 175°C in open vessel, the latter half of this reaction is excluded because the vaporization becomes larger as time goes on.

These results are summarized as follows.

a) **Effect of temperature** The reaction products at the temperatures of 150 and 175°C in closed and open vessels consist of biuret and cyanuric acid and at a temperature of 133°C only of biuret. The quantities of the reaction products are larger as the temperature is higher.

b) **Effect of packing ratio** At the reaction in closed vessel, the ratio of biuret to urea used in the case of the packing ratio of 0.3 g/cc, is slightly larger than in the case of 0.5 g/cc. The ratio of biuret to cyanuric acid becomes larger as the packing ratio becomes smaller. Moreover, the reaction products in open vessel are much larger in quantity than those in closed vessel and the ratio of biuret to cyanuric acid at the temperatures of 150 and 175°C in open vessel is larger than that in closed vessel.

c) **Effect of time** At the temperature of 133°C, the increase of the reaction

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product is almost linear against time and gradually in both vessels. On the other hand, at the temperature of 150 and 175°C, the velocity of the decomposition in the initial period is fast in closed vessel and the velocity of the decomposition in open vessel is faster than in closed vessel and the decrease of the velocity of the decomposition after the initial period is not so fast as in closed vessel.

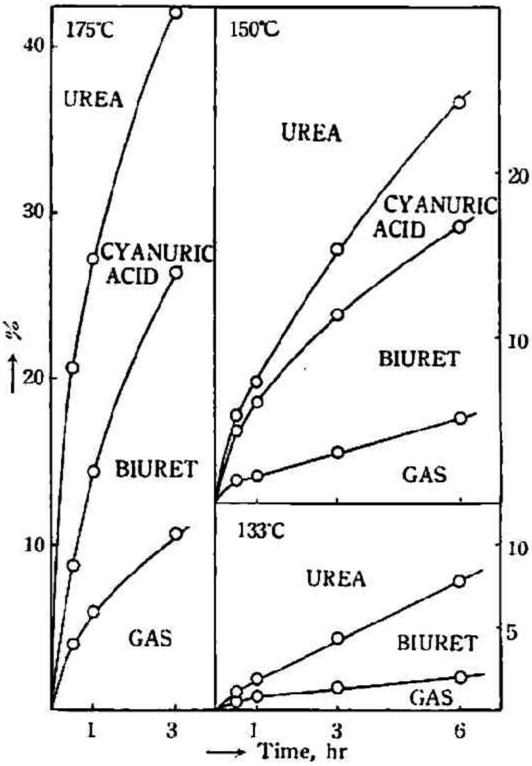

Fig. 3 In open vessel

Considerations

According to Werner[4], by the decomposition of urea, cyanic acid and ammonia are formed, and next biuret is formed by the reaction between the cyanic acid formed and the urea remaining, and cyanuric acid is formed by the polymerization of the cyanic acid formed. Moreover, it is confirmed that the quantities of the products formed on the decomposition of biuret at the temperature of 192°C and time of 10 minutes, are cyanuric acid 24.85%, urea 26.42%, ammelide 2.88%, gas and vaporization 23.45% respectively and 22.40% of biuret remains. From these facts, Werner has considered the next equilibrium between biuret, urea and cyanic acid.

$$NH_2CONH_2 + HNCO \rightleftarrows NH_2CONHCONH_2.$$

According to Werner, the process of the formation of cyanuric acid and biuret from urea may be as follows.

$$\begin{array}{c} NH_2CONH_2 \xrightarrow[-NH_3]{} HNCO \xrightarrow[\text{polymerization}]{} (HNCO)_3. \\ + \\ NH_2CONH_2 \\ \uparrow\downarrow \\ NH_2CONHCONH_2 \end{array}$$

On the other hand, from this experiment the effect of pressure of ammonia on the formation of biuret and cyanuric acid from urea may be considerable. Namely, at the reaction in open vessel, the total quantities of products at all temperatures and the ratio of biuret to cyanuric acid at 150 and 175°C are fairly larger than in closed vessel.

It is considered that the escape of ammonia from urea is suppresed when the pres-

4) E. A. Werner, *J. Chem. Soc.*, 103, 1010, 2275 (1913)

sure of ammonia is higher. The fact that the ratio of biuret to cyanuric acid is smaller as the pressure is higher, may be due to the reaction between cyanic acid and urea is restricted by ammonia or to the polymerization of cyanic acid is promoted by ammonia. In the production of biuret HCl[5], Na_2HPO_4[6] and others may be used to remove the effect of ammonia. From the fact that the ratio of biuret to cyanuric acid is smaller as the pressure is higher, it is difficult to consider that cyanuric acid is produced directly by the escape of ammonia from biuret. Werner's experiment of the decomposition of biuret is also interpreted as the cyanuric acid is not produced directly from biuret.

Consequently, the process of the formation of melamine from urea is as follows.

$$NH_2CONH_2 \xrightarrow[-NH_3]{} HNCO \xrightarrow[\text{polymerization}]{} (HNCO)_3.$$

$$HNCO + NH_2CONH_2 \rightleftarrows NH_2CONHCONH_2$$

$$\xrightarrow[-H_2O]{+NH_3} (CN)_3(OH)_2(NH_2) \xrightarrow[-H_2O]{+NH_3} (CN)_3(OH)(NH_2)_2 \xrightarrow[-H_2O]{+NH_3} (NH_2CN)_3.$$

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The Laboratory of Physical Chemistry,
Kyoto University

5) I. Kitawaki *et al.*, *Bull. Gov. Chem. Ind. Res. Inst. Tokyo*, **32**, No. 6, 10 (1937)
6) P. W. Gargo, U. S. Pat., No. 2,524,049, Oct. 3 (1950)