

SYNTHESIS OF MELAMINE FROM UREA, IV

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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 paper¹⁾.

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

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

2) H. Kinoshita, *ibid.*, 24, 19 (1954)

3) H. Kinoshita, *ibid.*, 24, 67 (1954)

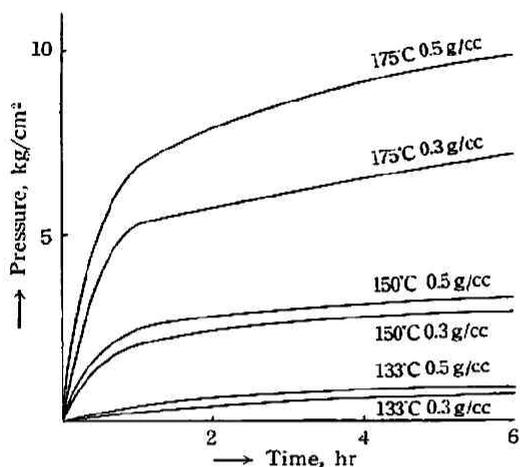


Fig. 1

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.

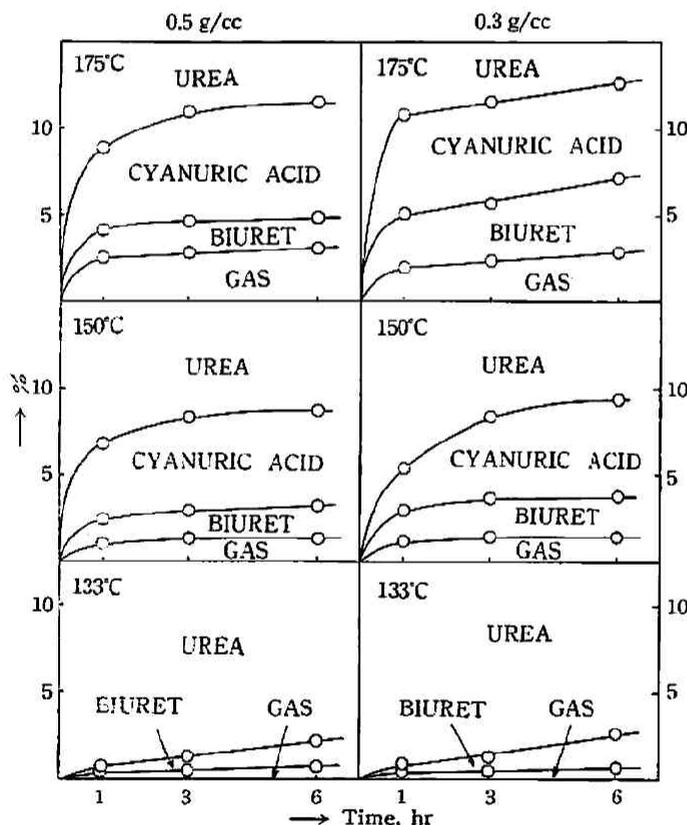


Fig. 2 In closed vessel

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.

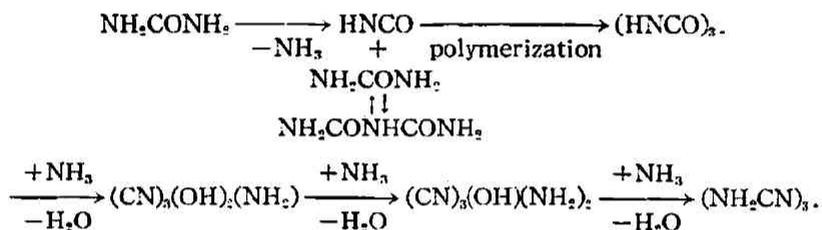
b) **Effect of packing ratio** At the reaction in closed vessel, the ratio of biuret to urea used in the case of the packing ratio of 0.3g/cc, is slightly larger than in the case of 0.5g/cc. The ratio of biuret to cyanuric acid becomes larger as the packing ratio becomes smaller. Moreover, the re-

action 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

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 HCl⁵⁾, Na₂HPO₄⁶⁾ 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.



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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)