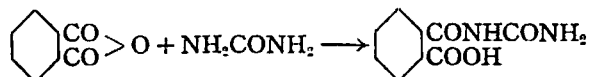


THE REACTION BETWEEN UREA AND PHTHALIC ANHYDRIDE UNDER PRESSURE

BY TAKAO YANAGIMOTO

Introduction

The pressure effects on various chemical reactions have been studied¹⁻⁴⁾ up to a pressure of about 15,000 kg/cm² by the author and his co-workers these several years. It is known that the pressure effect on a chemical reaction is caused by the difference, ΔV , of molecular volume between the reactants and the reaction products. It is expected that the condensation is accelerated by applying pressure because the reaction products have smaller volume than the reactants, that is, ΔV has negative value. In this paper the condensation of phthalic anhydride and urea is experimented as an example. Under the ordinary pressure, it is already known^{5,6)} that by heating the mixed sample containing equimolecular quantities of phthalic anhydride and urea at 120~126°C the additive reaction is carried out and the acyclic ureide of phthalic acid is produced.



The pressure effects on this reaction are studied up to a pressure of 7,000 kg/cm² and a temperature of 136°C.

Experimentals

Samples Urea: it is recrystallized from an aqueous solution of commercial urea and is used as 150 mesh fine powder.

Phthalic anhydride: it is purified by sublimating crude phthalic anhydride and is used as 150 mesh fine powder.

Both samples are dried up and allowed to remain in the desiccator with calcium chloride.

Apparatus and procedure Under the ordinary and high pressure, the experimental apparatus and the method of applying pressure were the same as the reports^{1,4)} of this Journal. The mixed sample is made by mixing the dried urea with the dried phthalic anhydride in an agate mortar at equimolecular or other definite ratio and it

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2) R. Kiyama and T. Yanagimoto, *ibid.*, 22, 34, 39 (1952)

3) T. Yanagimoto, *ibid.*, 23, 54 (1953)

4) T. Yanagimoto, *ibid.*, 24, 1 (1954)

5) A. Piutti, *Ann.*, 214, 17 (1882)

6) C. S. Smith, and C. J. Cavallito, *J. Am. Chem. Soc.*, 61, 2218 (1939)

is heated for a desired time under a desired pressure in the form of powder or of pellet made by compressing the mixed powder to a definite pressure.

Analytical method The separation of the reaction product is carried out according to the method⁵⁾ of A. Piutti as follows. The reacted sample is washed with cold water of a definite quantity, as the ureide of phthalic acid is seldom dissolved with cold water, in order to take away the unreacted one, dried up in the thermostat at 70°C. Then, the dried sample is washed with ether to remove the by-product phthalimide and the residual reaction product, the ureide, is recrystallized from the hot water. After the recrystallized ureide was dried up to a constant weight in the thermostat at 100°C, its weight is measured.

Results

At room temperature At room temperature, though the following conditions are subjected to the mixed sample of urea with phthalic anhydride, the formation of the ureide of phthalic acid does not be detected: 1) keeping the mixed sample in the desiccator for a month under ordinary pressure, 2) rubbing strongly both samples in an agate mortar, 3) applying the pressure of 7,000kg/cm² to the mixed sample for three hours.

At elevated temperature 1) The mixed samples of equimolecular quantity are heated in the sealed glass tube by use of the oil bath at a definite temperature in the range of 80~136°C. These results are shown in Fig. 1. When the mixed sample is heated at 80°C, it does not melt and the formation of the ureide of phthalic acid can

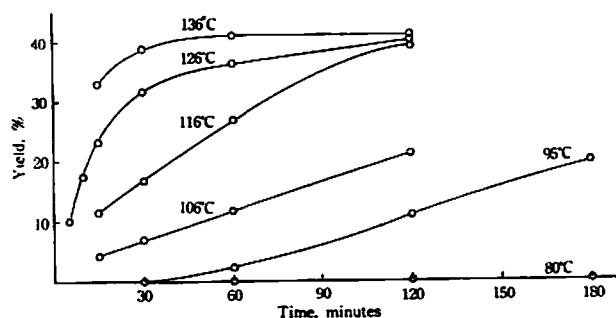


Fig. 1. The relations between yield of the ureide and time at the ordinary pressure

not be detected. At 95~116°C the temperature of the reactants rises slowly for a time higher than that of oil bath, and it is observed that the reactant melts partially and the ureide is formed. When above 126°C the temperature rises quickly, the solid sample is wholly changed to the liquid state and the formation of the ureide increases rapidly, but, as time goes on, the temperature of the reactants falls slowly to that of the oil bath, the ureide of higher melting point forms, and consequently the reactants are solidified to a hard mass. Besides, heating the reactants for a long time above

126°C, it is observed that the pressures of the reactants in the sealed glass tubes increase, and the hexagonal crystals of phthalimide produced by the decomposition of the ureide are deposited from the washed ether.

2) By compressing the mixed powder of equimolecular quantity of urea and phthalic anhydride to the various desired pressures at room temperature the pellet is made and then it is heated in a sealed glass tube for desired hours. These results are shown in Fig. 2. In the case of heating the pellet at 106°C for 30 or 60 minutes, it is melted partially and the yield of the ureide increases with elevating the pressure which makes the pellet, but over 3,000 kg/cm² the rates of increase become small. In the case of heating the pellets at 116°C, the whole samples are changed to the liquid state temporarily with increasing the temperature within about 15 minutes in spite of the magnitudes of pressure making the pellets, but in 20 minutes it is almost solidified. That is, all the pellets, in comparison with the powder sample, are entirely melted temporarily at lower temperature and have twice yields, but the difference by the magnitudes of the pressure making pellets could not be found on the yield.

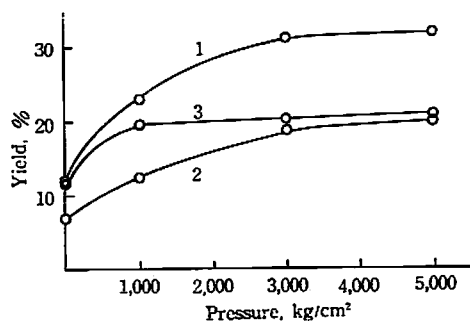


Fig. 2 The relations between yield of the ureide and pressures making the pellets

- 1: 106°C, 60 minutes heating
- 2: 106°C, 30 minutes heating
- 3: 116°C, 15 minutes heating

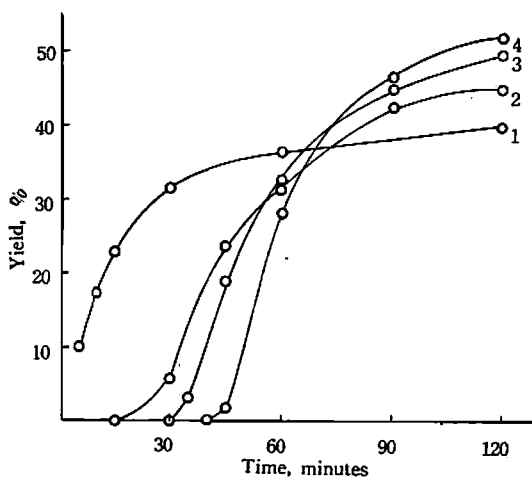


Fig. 3 The relations between yield of the ureide and time at 126°C

- 1: 1 kg/cm² 2: 1,000 kg/cm²
- 3: 2,000 kg/cm² 4: 3,000 kg/cm²

3) After the mixed powder of equimolecular quantity was heated up to about 80°C in a pressure-proof vessel, it is compressed to a desired pressure and heated to 95~136°C within about 10 minutes, but the formation of the ureide is not detected in course of this operation. When the mixed sample is heated for 2 hours at 95°C or 116°C under the ordinary pressure the yields of the ureide are 11% or 39% respectively, but under the external pressure of 1,000 kg/cm² at 95°C or 2,000 kg/cm² at 116°C for the same hours, the ureide is not detected. Under the external pressure of 1,000 kg/cm², in place of the above mentioned 2,000 kg/cm², at 116°C for 2 hours the yield of the

ureide is only a trace. The results obtained by the experiments of 126°C and 136°C under external pressures are shown in Figs. 3 and 4. In the initial stage of the reaction the rates are retarded by the external pressure and at a definite temperature the higher the pressure becomes the longer the induction period, but, with the rise of temperature the induction period on various pressures becomes shorter and almost the equal, and moreover the pressure effect decreases. After the induction period finished, it is observed that the reaction rates are accelerated and the yields of the reaction products increase with increasing pressure. Moreover, in the experiments of the above 126°C under the ordinary pressure the formation of phthalimide is observed, but under high pressure it is not observed.

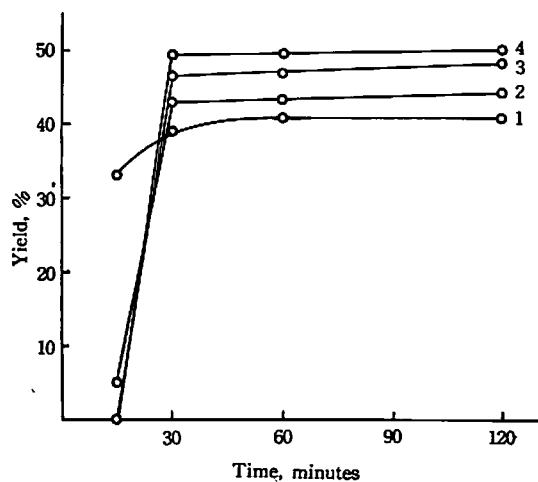


Fig. 4 The relations between yield of the ureide and time at 136°C

1: 1 kg/cm² 2: 1,000 kg/cm²
3: 2,000 kg/cm² 4: 3,000 kg/cm²

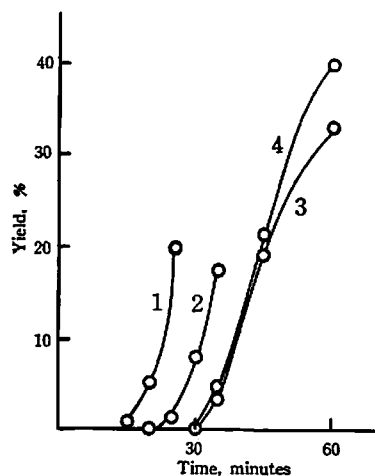


Fig. 5 The induction period in various mole ratios at 126°C, 2,000 kg/cm²

curve	mole ratio	
	urea	phthalic anhydride
1	1	4
2	1	2
3	1	1
4	1	1/2

For the purpose of observing the changes of the induction period by changing the mole ratios of urea and phthalic anhydride, this reaction in various mole ratios is carried out at 126°C under 2,000 kg/cm². These results are shown in Fig. 5. When the mole ratios of urea and phthalic anhydride are changed as 1:1, 1:2 and 1:4, it is known that the induction periods become shorter at 30, 20 and 15 minutes respectively. On the other hand, when the quantity of phthalic anhydride is decreased to 1/2 mole against 1 mole of urea, the induction period is not changed, but the yield increases to some extent.

Considerations

Numerous reactions of the solid state in inorganic substances are studied and

reported in several papers^{7,8,9}), but the reaction in organic substances is scarcely studied.

It is known⁹) that the reactions of the solid state in inorganic substances are commenced exothermically at the temperature lower than the melting point of that substance and are influenced a priori by some factors as temperature, pressure, preparation of sample, thermal history, impurity, size of powder particle, homogeneity of mixture, etc. In this experiment the influences of pressure and temperature are mainly studied, the other conditions being fixed as hard as possible.

1) From the results at room temperature, the reaction product could not be obtained by increasing the contact surface only due to the compression of the mixed sample or rubbing of both samples in the mixing.

2) It is known from the results on high temperatures under the ordinary pressure that this reaction takes place at the temperature between 80~95°C. In the solid reaction Tamman had proposed^{8,9,10}) the relations between the absolute temperature $T_D^\circ\text{K}$ (Tamman temperature) at which the reaction takes place and the absolute melting point $T_M^\circ\text{K}$, or the ratio of T_D/T_M is approximately 0.3 for metals, 0.5 for inorganic substances and 0.9 for organic compounds. As the melting points of urea and phthalic anhydride are 133°C and 131°C respectively, this experimental result that the reaction takes place at about 90°C coincides with Tamman's proposition.

It is observed by heating the powder-mixed sample under the ordinary pressure as follows; it does not melt at 80°C, but melts partially at 95~116°C and wholly above 126°C. It has been known⁹) on the solid reactions that, with the rise of temperature of the system by the heat of reaction evolved when the reaction has begun to occur, there is the case where a liquid phase is formed. For example, α -phenyl- γ -methylallyl hydrogen phthalate was observed to be transformed by heating in the solid state into γ -phenyl- α -methylallyl hydrogen phthalate which had a higher melting point, and it was known¹¹) that the melted state appeared as the intermediate stage. In the similar manner, it is considered to pass the process of melted state in this reaction. That is, in the contact surfaces of the two reactants the exothermic reaction proceeds and thereby the sample melts non-isothermally once with the rise of temperature in the system. But, it is considered that, as time goes on, the ureide is produced and here-with the temperature of the reaction system falls to that of the thermostat with the retardation of the reaction rate since the contact between both reactants is intercepted by the formed ureide and, for these reasons, the reaction system is solidified.

It has been known⁵) that the ureide of phthalic acid was decomposed by heating over about 150°C and phthalimide was formed.

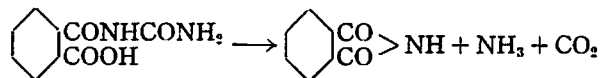
7) J. R. Partington, *An Advanced Treatise on Physical Chemistry*, 3, p. 5 (1952)

8) A. L. G. Rees, *Chemistry of the Defect Solid State*, p. 81, 90 (1954)

9) G. Cohn, *Chem. Rev.*, 42, 527 (1948)

10) G. Tamman and Q. A. Mansuri, *Z. anorg. Chem.*, 126, 119 (1923)

11) J. Kenyon and S. M. Partridge, *J. Chem. Soc.*, 207 (1937)



In this experiment, it seems reasonable to consider that, heating the mixed sample above 126°C for a long time, the gas pressure in the glass vessel increases and phthalimide is detected, is due to this decomposition.

3) It has been known in the case of heating the pellets, which are formed by compressing the mixed sample at ordinary temperature, at 106°C ~ 116°C under the ordinary pressure, that the reaction rate has the larger than that in the case of non-pellet form. In the similar manner, by using the pellets made by compression as the sample, the ion-exchange reactions¹²⁾ of PbCrO_4 — PbCl_2 and additive reactions¹³⁾ of $\text{Fe}_2\text{O}_3 + \text{MO} \longrightarrow \text{Fe}_2\text{O}_3 \cdot \text{MO}$ ($\text{M} = \text{Ni}, \text{Mg}, \text{Pb}$) has been studied under the ordinary pressure and in both cases it is known that the larger the magnitude of compression becomes, the larger the reaction rate is because of the increase of the contact surface. But, it is observed from the experiments at 106°C that the ratio of increasing of yield against that of compression at over 3,000 kg/cm² becomes small. As known from the experiments of electric resistance under high pressures on silver bromide by Kolthoff¹⁴⁾, potassium ferrocyanide by the author¹⁵⁾ and rochelle salt by Okamoto¹⁶⁾ the powder may become almost the compact one by applying the pressure of 1,500 ~ 3,000 kg/cm². Therefore, it seems reasonable to assume that the above fact is due to the decrease of the increment of the contact surfaces between the reacting particles even if the compression is over that pressure. In the case of heating the mixed sample at 116°C, though the powder sample is partially melted, the pellets are wholly melted once within about 15 minutes in order to accelerate the reaction rate by the larger contact surfaces. Therefore, the pellets have about twice yields as compared with the powder sample, but it seems that the difference of the yield by the magnitude of pressures making the pellets is not observed in order to pass the liquid state in the course of the reaction.

4) Under the pressure of 1,000 ~ 3,000 kg/cm², when the mixed samples are heated for a definite time in the pressure-proof vessel at the temperature range of 95 ~ 136°C, it is known that the initial state of the reaction has induction period, but, rising the temperature this induction period becomes short and the pressure effect on the induction period diminished. On the other hand, it is considered that under the ordinary pressure this reaction proceeds by way of the melted state. Then, it might be considered that the appearance of the induction period under pressure is caused by the lapse of the time for the melted state to occur. As this reaction is exothermic, it seems most reasonable to assume that, accumulating the more reaction heat over than

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16) F. Okamoto, *ibid.*, 24, 9 (1954)

the loss from the reaction system due to conduction, the reaction system self-heats non-isothermally and after a while the melted state appears suddenly. On the other hand, as the melting point of the mixed sample is raised¹⁷⁾ under high pressures, it is expected that with elevating the external pressure the sample is less melted. Therefore, it is considered that the higher the pressure is applied and the lower the temperature to heat is, the longer the induction period becomes. After the induction period finished, as the reaction system becomes the liquid state, the pressure effect based on the difference of molecular volume, ΔV , between the reactants and reaction products becomes effective^{4,18)}. That is, increasing the pressure the reaction rate and the yield increase. It may be assumed that, as this reaction is the condensation of one molecule formation from two molecules, the decrease of molecular volume is expected in general and besides this reaction is an exothermic one and the formation of phthalimide obtained by decomposition of the ureide is retarded by the external pressure.

The mixed sample of the excess of phthalic anhydride against urea has the shorter induction period than that of the equimolecular quantity or has good yield for the same reaction time. Because phthalic anhydride has a lower melting point than urea and is easily dispersed by heating, it seems most reasonable to assume that, increasing the excess amount of phthalic anhydride, it gets near the powder particle of urea more closely, the contact surfaces increase and consequently the initial state of the reaction is accelerated.

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*The Laboratory of Physical Chemistry,
Kyoto University*

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18) M. G. Evans and M. Polanyi, *Trans. Farad. Soc.*, **31**, 875 (1935); **32**, 133 (1936)