CHEMICAL KINETICS IN THE REACTION BETWEEN
NH_3 AND CO_2 UNDER PRESSURE.

By Ryo Kiyama and Keizo Suzuki.

The study of the field of kinetics of the reaction between NH_3 and CO_2 under pressure has scarcely been done. Therefore there are many obscure points. In the view of chemical kinetics, this investigation is carried out in order to clear the mechanism of the reaction.

Apparatus and Procedure.

The schematic layout of the equipment is shown in Fig. 1. A_1 is the reaction vessel made of mild steel, the volume of which is 43 cc ; A_2 and A_3, the bombs, each being filled with liquid NH_3 or liquid CO_2 ; A_4, the spiral tube in order to preheat CO_2 gas ; G_1 and G_2, the burdon type pressure gauges ; T_1, the copper-constantan thermocouple, which is put into the reaction vessel ; T_2 and T_3, the mercury thermometers ; the train of points denotes the electric heater ; V_1, ..., V_6, the valves. The samples, NH_3 and CO_2, are stored in A_2 or A_3 from each commercial bomb and high pressure is obtained by heating.

The procedure to carry out the experiment at a given ratio of partial pressure of NH_3 and CO_2

Fig. 1 Schematic layout of equipment.

is as follows ; gaseous CO_2 is charged into the reaction vessel until the reading of G_1 becomes equal as the partial pressure of NH_3 in the case of experiment and then until the reading of G_1 comes to a definite total pressure of experiment, then the reading of G_2 falls down from P_1 to P_2. Thus a given quantity of CO_2 is charged into the vessel in use of the reading of P_1 and P_2 in performing the reaction.

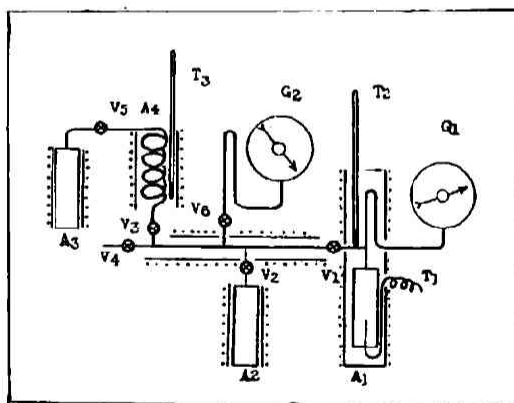The experimental procedure is as follws ; gaseous NH_3 is charged into the

reaction vessel under a constant pressure and a definite quantity of gaseous CO_2 is led into the vessel in use of G_2 as above mentioned. Afterwards the readings of G_1 against time are recorded.

The ratio of packing calculated as $NH_4CO_2NH_2$ from the pressure is $0.08 \sim 0.21$ g/cc in the range of the reaction.

Moreover, after the reaction finished, the resultants are cooled rapidly and the gravimetric analysis of urea is carried out.

The reproducibility of the experiment is within 5% of the initial pressure in the readings of G_1.

Experimental Results.

The experiments are performed in the range of pressure, $15 \sim 210$ kg/cm², temperature, $60 \sim 200°C$, under various ratioes of partial pressure. Fig. 2 ~ Fig. 6 are the pressure change curves plotted from the data of the readings of pressure gauge against time. Fig. 7 is the results of the urea conversion percent curves.
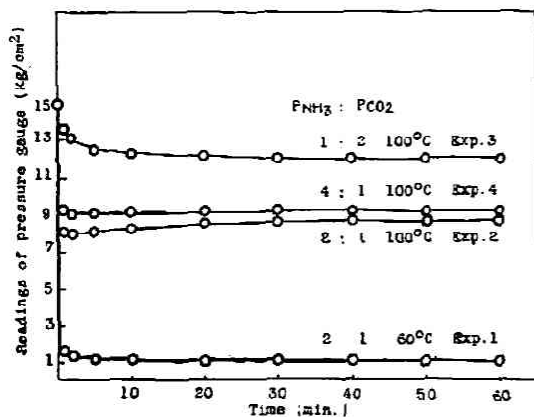

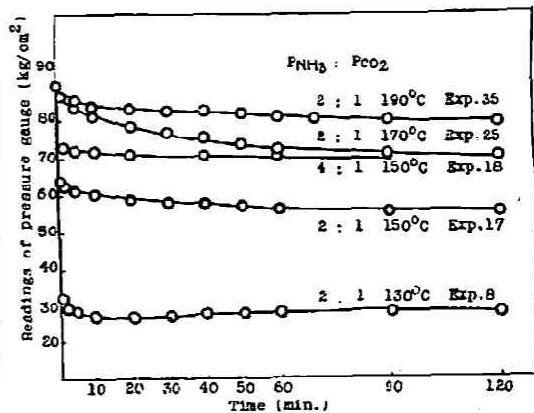Fig. 2   Pressure change curves.
Initial pressure 15 kg/cm².

Fig. 3   Pressure change curves.
Initial pressure 90 kg/cm².

Discussions.

From the pressure change curves, there are two cases; one, a rapid pressure decrease occurs, and the other does not, at the initial step of the reaction. Also, it is shown in the urea conversion percent curves, Fig. 7, that there is some difference in the forms of the reaction.

(I) The formation of $NH_4CO_2NH_2$.

From the reason discussed below it can be considered that the rapid pres-

$$\frac{d[NH_2CONH_2]}{dt} = k_3[\text{Intermediate product}]. \tag{4}$$

As K_1 is the equilibrium constant, from the step (1)

$$[\text{Intermediate product}] = K_1[NH_3]^2[CO_2]. \tag{5}$$

In such a case as $NH_4CO_2NH_2$ is not formed, accordingly, from Equations (4) and (5) the velocity of urea formation gives

$$\frac{d[NH_2CONH_2]}{dt} = K_1 k_3[NH_3]^2[CO_2] = k[NH_3]^2[CO_2], \tag{6}$$

where

$$k = K_1 k_3. \tag{7}$$

Differentiating with respect to temperature from the Equation (7),

$$\frac{d\ln k}{dT} = \frac{d\ln K_1}{dT} + \frac{d\ln k_3}{dT}. \tag{8}$$

If A is the activation energy corresponding to k, A_3, the activation energy of step (3), and Q_1, the heat of reaction in (1), the next relations are given,

$$\frac{d\ln k}{dT} = \frac{A}{RT^2}, \qquad \frac{d\ln k_3}{dT} = \frac{A_3}{RT^2}, \qquad \frac{d\ln K_1}{dT} = \frac{Q_1}{RT^2}, \tag{9}$$

where it is presumed that the endothermic heat of reaction has a positive sign. From Equations (8) and (9),

$$A = Q_1 + A_3. \tag{10}$$

The heat of reaction in the case of the formation of $NH_4CO_2NH_2$ from NH_3 and CO_2 is about -40 kcal[4]. Then, it is permitted that the heat of reaction in the step (1) takes the value nearly -40 kcal. The value of A is about -20 kcal as above described and so A_3 can take a positive value. From these considerations it can be recognized that the velocity constant, k, of this reaction in which $NH_4CO_2NH_2$ is not produced has the negative temperature coefficient.

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4) K. G. Clark and H. C. Hetherington, *J. Am. Chem. Soc.*, **49**, 1909 (1927)

sure change at the initial time of the reaction is due to the formation of $NH_4CO_2NH_2$.

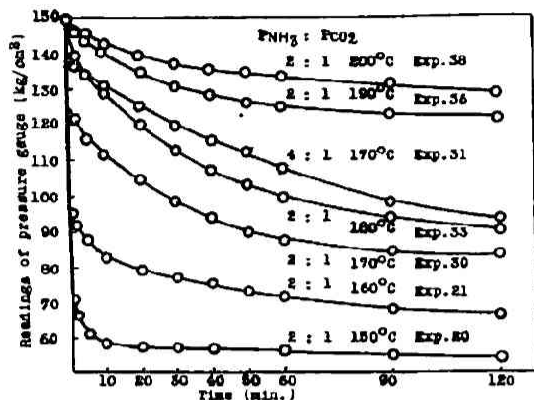Fig. 4   Pressure change curves. Initial pressure 150 kg/cm².

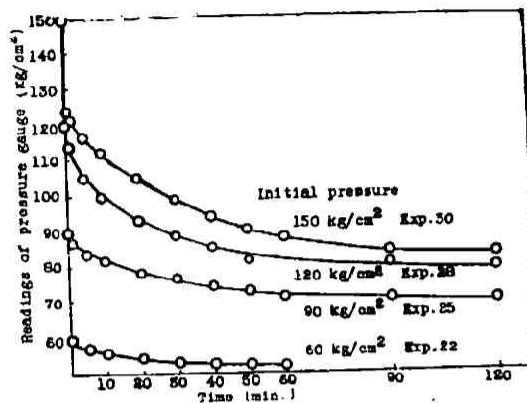Fig. 5   Pressure change curves. $P_{NH_3} : P_{CO_2} = 2 : 1$, 170°C.

1) From the dissociation pressure of $NH_4CO_2NH_2$.

In the case of Exp. 1 at 60°C in Fig. 2, the rapid pressure decrease and the heat evolution follow at the initial time, then pressure decreases to 1 kg/cm². The pressure, 1 kg/cm², is the dissociation pressure of $NH_4CO_2NH_2$ at 60°C[1] and under such condition the formation of urea does not occur. Accordingly the curve can be considered as the one of the formation of $NH_4CO_2NH_2$.

The comparison between the pressure at the inflexion point*, where the curve showing the rapid pressure decrease at the initial step crosses the following slow change curve, and the dissociation pressure of $NH_4CO_2NH_2$ extrapolated from the data of Egan et al[1]., at the same temperature, is shown in Table 1. Both pres-

Table 1

Exp. No.	Temperature (°C)	Initial press. (kg/cm²)	Press. at the inflexion pt. (kg/cm²)	Dissociation press. of $NH_4CO_2NH_2$ (kg/cm²)
2	101 (100)	15	9	9
8	136 (130)	90	36	37
20	158 (150)	150	78	82
21	165 (160)	150	100	103
30	175 (170)	150	133	141
34	183 (180)	210	177	185

($P_{NH_3} : P_{CO_2} = 2 : 1$)

1) E. P. Egan, J. E. Potts and G. D. Potts, *Ind. Eng. Chem.*, 38, 454 (1946)

* In the graphical expression of the equation concerning to the third order velocity constant, described later (Chemical kinetics in the reaction of urea formation.), two straight lines cross at the initial time. The crossing point is regarded as the inflexion point.

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sures in the comparison nearly coincide. The value shown in the parenthesis in the temperature column is the temperature before the reaction begins, but owing to the heat evolved at the initial time of the reaction, the temperature rises, and then at the inflexion point it becomes the value shown on the left hand of the temperature column. Fig. 6 shows the rapid pressure decrease at the initial time in every case of the initial pressure except 53 kg/cm², less than the dissociation pressure of $NH_4CO_2NH_2$, has the inflexion point at nearly the same point.
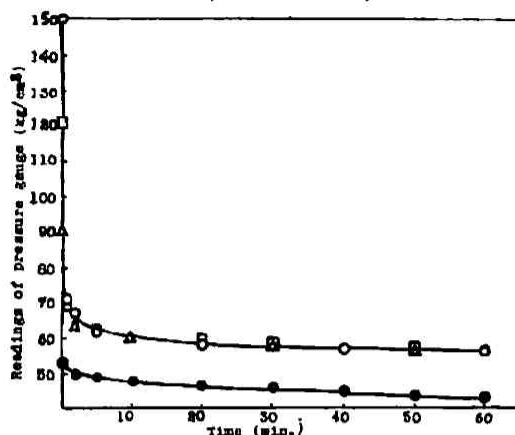

Fig. 6   Pressure change curves. 150°C.
Initial pressure
○ 150 kg/cm² Exp. 20
□ 120 kg/cm² Exp. 19
△   90 kg/cm² Exp. 17
   $P_{NH_3} : P_{CO_2} = 2 : 1$
●   53 kg/cm² Exp. 15
   $P_{NH_3} : P_{CO_2} = 3.1 : 1$

2)   From the relation of the dissociation equilibrium of $NH_4CO_2NH_2$.

The relation of the dissociation equilibrium of $NH_4CO_2NH_2$ is as follows;
$NH_4CO_2NH_2$ (solid) $\rightleftarrows 2NH_3 + CO_2$. In the case of excess of NH_3 or of CO_2, the next relations are derived from the Mass Law[2],

$$\frac{c_1}{\pi} = \frac{2}{3}\left[\left(\frac{\pi_0}{\pi}\right)^{\frac{1}{2}} - \frac{\pi}{\pi_0}\right], \quad \frac{c_2}{\pi_0} = \frac{1}{3}\left[\left(\frac{\pi_0}{\pi}\right)^2 - \frac{\pi}{\pi_0}\right],$$

where c_1, c_2 are respectively excess in pressure of NH_3 and of CO_2, π_0 is the normal dissociation pressure of $NH_4CO_2NH_2$ when the ratio of partial pressure of NH_3 and CO_2 is stoichiometric. π is the partial pressure of dissociated $NH_4CO_2NH_2$ in the vapor in the case of having excess in NH_3 or CO_2. Accordingly, the total pressures are $c_1 + \pi$ when NH_3 is in excess, $c_2 + \pi$ in excess of

Table 2

Exp. No.	Temperature (°C)	Initial press. (kg/cm²)	$P_{NH_3} : P_{CO_2}$	Press. (kg/cm²)	
				obs.	calc.
4	103 (100)	15	4 : 1	11.0	11.0
3	103 (100)	15	1 : 2	13.8	13.4
18	153 (150)	90	4 : 1	73.5	73.9
31	174 (170)	150	4 : 1	140	143

2)   T. R. Briggs and V. Migrdichian, *J. Phys. Chem.*, 28, 1121 (1924)

CO_2. It has been experimentaly proved that this relation holds in the low pressure region[2]. In Table 2 the comparisons between the observed pressure at the inflexion point and the pressure calculated from the above relation are shown and the consistency in both values is good. The parenthesis in the temperature column denotes the same as in Table 1.

$NH_4CO_2NH_2$ is not formed under the lower pressure than the pressure of dissociated $NH_4CO_2NH_2$. When the dissociation pressure is 150 kg/cm², the temperature is 176°C*. From the pressure change curves in Fig. 4, the rapid pressure decrease at the initial time occurs at the temerature below 170°C, while this rapid change does not above 180°C. From the correlation between the condition of the $NH_4CO_2NH_2$ formation and these pressure change curves, $NH_4CO_2NH_2$ is formed not above 180°C, but below 170°C. Also, in Fig. 5, $NH_4CO_2NH_2$ having the dissociation pressure of 126 kg/cm² at 170°C, in the case of the initial pressure 150 kg/cm², the pressure decreases rapidly at the initial time, while in the case of the initial pressure below 126 kg/cm², the rapid change does not occur. In other cases, the experimental results are satisfactory in consideration.

According to the above consideration, the rapid pressure decrease at the initial time of the reaction is due to the formation of $NH_4CO_2NH_2$ and the formation of $NH_4CO_2NH_2$ is dependent upon the initial pressure which is higher than the dissociation pressure of $NH_4CO_2NH_2$.

(II) The formation of urea.

1) General consideration.

From the results of the quantitative analysis of urea it may be found that it is always possible to produce urea whether $NH_4CO_2NH_2$ is formed or not. The urea conversion percent curves, Fig. 7, are the results in the same condition as the pressure change curves in Fig. 4. At 150°C and 160°C $NH_4CO_2NH_2$ is formed and at 180°C and 190°C is not, as described before. However, the formation of urea occurs in both cases. Accordingly the view that NH_4-
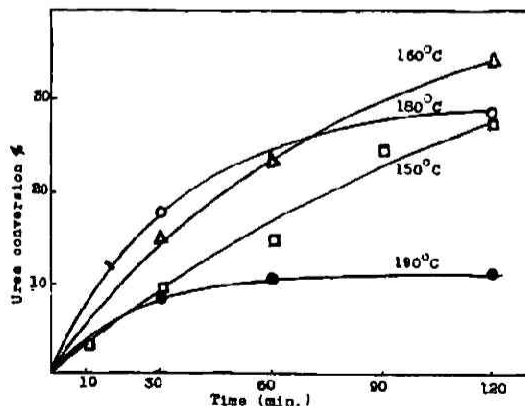

Fig. 7 Urea conversion % curves.
Initial pressure 150 kg/cm².
$P_{NH_3} : P_{CO_2} = 2 : 1$

* cf. 1)

CO_2NH_2 is the direct intermediate substance in the reaction mechanism is not generally admitted.

In the pressure change curves at the condition that $NH_4CO_2NH_2$ is not formed (*i. e.* above 180°C in Fig. 4), the pressure, in any case, decreases below the equilibrium pressure[3] in the formation of urea. From this result it may be considered that the reaction of urea at this condition goes on in the gaseous state.

In the urea conversion percent curves, Fig. 7, the temperature effect on the urea conversion is reverse between 160∼180°C, namely the limiting temperature of the existence of $NH_4CO_2NH_2$.

The effects of pressure and the ratio of partial pressure on the urea conversion percent from the results of analysis are shown in Table 3. Excess of

Table 3

Exp. No.	Temperature (°C)	Time of reaction (min.)	Initial press. (kg/cm²)	$P_{NH_3} : P_{CO_2}$	Urea conversion (%)
17₁ *	150	30	90	2 : 1	6.0
20₂ *	150	30	150	2 : 1	9.5
35₁	190	60	90	2 : 1	0.0
36₃	190	60	150	2 : 1	10.6
30 *	170	120	150	2 : 1	25.9
31 *	170	120	150	4 : 1	36.3
25	170	120	90	2 : 1	7.7
26	170	120	90	4 : 1	11.6

* The case, $NH_4CO_2NH_2$ is formed.

NH_3 and the pressure effect upon the yield of urea are recognized whether NH_4-CO_2NH_2 is formed or not.

2) Chemical kinetics in the reaction of urea formation.

The order of the reaction is obtained from the follwing relations of the reaction velocities in the two cases 1 and 2.

$$\frac{dx_1}{dt} = k\,[P_{NH_3}]_1^m[P_{CO_2}]_1^n, \qquad \frac{dx_2}{dt} = k\,[P_{NH_3}]_2^m[P_{CO_2}]_2^n,$$

when $[P_{CO_2}]_1 = [P_{CO_2}]_2$,

$$m = \frac{\log\dfrac{dx_1}{dt} - \log\dfrac{dx_2}{dt}}{\log[P_{NH_3}]_1 - \log[P_{NH_3}]_2},$$

3) M. Tokuoka, *J. Agr. Chem. Soc. Japan*, **10**, 1333 (1934)

    C. Matignon and M. Fréjacques, *Compt. rend.*, **174**, 455 (1922)

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

when $[P_{NH_3}]_1 = [P_{NH_3}]_2$,

$$n = \frac{\log\dfrac{dx_1}{dt} - \log\dfrac{dx_2}{dt}}{\log[P_{CO_2}]_1 - \log[P_{CO_2}]_2},$$

where P_{NH_3} and P_{CO_2} are the initial partial pressure of NH_3 and CO_2 respectively. Substituting the experimental results in the above relations, the values of m and n are obtained, which are shown in Table 4. From the sum of m and n the order of the reaction is regarded as the third order. Assuming that a and b are respectively the initial partial pressure of NH_3 and CO_2 and ΔP is the quantity of pressure change, the third order velocity constant is given as follows :

Table 4

Exp. No.	Initial press. (kg/cm²)	P_{NH_3}	P_{CO_2}	m	n
23	72	42	30	1.9	1.0 *
25	90	60	30	2.0	
27	100	70	30		
22	60	40	20	1.8	1.0
24	90	70	20		

(Temperature, 170°C)

* P_{NH_3}, 42, 40 of Exp. No. 23, 22 are regarded as the same pressure.

$$k = \frac{1}{t(a-2b)^2}\left\{ \frac{\dfrac{2\Delta P}{3}(2b-a)}{a\left(a-\dfrac{2\Delta P}{3}\right)} + 2.303\log\frac{b\left(a-\dfrac{2\Delta P}{3}\right)}{a\left(b-\dfrac{\Delta P}{3}\right)} \right\},$$

but when $a = 2b$,

$$k = \frac{9}{8t}\{(3b-\Delta P)^{-2}-(3b)^{-2}\}.$$

Accordingly, the values of the bracket in the former equation or $(3b-\Delta P)^{-2}$ in the latter against time are plotted as linear relations and also the tangents are proportional to the velocity constants. The time range satisfied with linearity in the case of $P_{NH_3}:P_{CO_2}=2:1$, is shorter than in the case of $P_{NH_3}:P_{CO_2}=4:1$.

Table 5

Exp. No.	Temperature (°C)	Initial press. (kg/cm²)	$P_{NH_3}:P_{CO_2}$	Velocity constant 10⁶ (cm⁴/kg². min)
25	170	90	2 : 1	1.4 ⎫
26	170	90	4 : 1	1.8 ⎬ mean 1.6
28	170	120	2 : 1	1.6 ⎭
33	180	150	2 : 1	1.0
36	190	150	2 : 1	0.5
38	200	150	2 : 1	0.3

It may be considered that the continuation of linearity is due to the opposite reaction that is prevented by excess of NH_3. The velocity constants obtained from the above relations are shown in Table 5. That is, the velocity constants have the negative temperature coefficient and the activation energy calculated from the relation of $\log k - \dfrac{1}{T}$ is about -20 kcal.

The velocity constants shown in Table 5 are the values obtained when $NH_4CO_2NH_2$ is not formed. The yields of urea calculated from the velocity constants and the observed yields in the case of the formation of $NH_4CO_2NH_2$ are shown in Table 6. The calculation is as follows;

Table 6

Exp. No.	Temperature (°C)	Velocity constant 10^6 (cm⁴/kg². min)	Weight of urea (g)	
			calc.	obs.
33₁	180	1.0	—	0.838
30₂	170	1.6	0.8	0.720
21₁	160	3.1 *	0.7	0.803
20₂	150	4.3 *	0.4	0.524

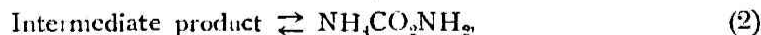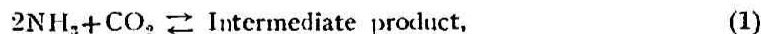(Initial pressue, 150 kg/cm²; P_{NH_3} : $P_{CO_2} = 2 : 1$; time of reaction, 30 min.)
 * extrapolated value.

$$\text{yield of urea (in weight)} \fallingdotseq ak \sum_{t=0}^{30} [P_{NH_3}]^2 [P_{CO_2}] = ak \sum_{t=0}^{30} \left(\frac{2P}{3}\right)^2 \left(\frac{P}{3}\right),$$

where P is the reading of pressure gauge, a is the proportional constant determined by substituting the values at 180'C ($NH_4CO_2NH_2$ is not formed) in Table 6. The calculated weight of urea and the observed are the values at 30 minutes. Accordingly, it can be considered that the reaction of urea formation almost proceeds in the gaseous state, even in such a case as $NH_4CO_2NH_2$ is formed; at least in the initial state of the reaction.

3) The reaction mechanism.

From the reason above described the following mechanism is proposed.

$$2NH_3 + CO_2 \rightleftarrows \text{Intermediate product,} \tag{1}$$

$$\text{Intermediate product} \rightleftarrows NH_4CO_2NH_2, \tag{2}$$

$$\text{Intermediate product} \rightarrow NH_2CONH_2 + H_2O. \tag{3}$$

The step (2) is possible only when the initial pressure is higher than the dissociation pressure of $NH_4CO_2NH_2$. Assuming the equilibrium relation is always established in the steps of (1) and (2) and k_3 is the velocity constant of (3), the velocity of urea formation reduces to