

窒酸암모니움의 熱分解 反應速度(Ⅱ)

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(접수 72. 11. 9.)

Thermal Decomposition Rate of Ammonium Nitrate(Ⅱ)

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Abstract

A relatively small amount of ammonium nitrate was thermally decomposed on a stainless steel hot plate maintained at constant temperatures ranging from 240°C to 320°C. The hot plate is a part of the reactor kettle with the closure atop of it. The reactor holds the decomposed gas whose pressure is measured by means of a pressure transducer.

The reaction mechanism and the rate were determined by using the gas composition data and the recorded kinetic curves.

Beyond 318°C. it was found that ammonium nitrate decomposes explosively.

요 약

밀폐된 반응기에 비교적 적은양의 질산암모늄을 넣고, 240°C—320°C의 온도범위에서 등은 열분해를 시켰다.

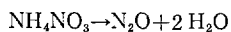
pressure transducer를 이용하여, 반응진행에 따른 반응기의 압력변화를 측정하고, gas chromatography를 사용하여, 생성기체의 조성을 구했다.

위의 두가지 data를 이용해서 질산암모늄의 열분해 반응기구와 반응속도를 구했다.

또한, 318°C 이상에서는 폭발적인 분해반응이 일어남을 확인했다.

following reaction among many possible reactions.

Introduction



Many investigators in the past have concentrated their efforts on the thermal decomposition of ammonium nitrate for the production of nitrous oxide from this reaction⁽¹⁻¹²⁾. Therefore, their effort was limited to the reaction mechanism and kinetics of the

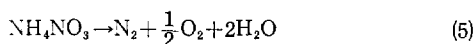
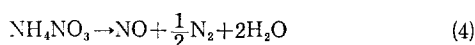
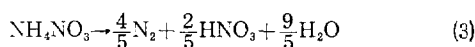
Although considerable attempts have been made to develop catalysts for the production of nitrous oxide, it was reported that chromates, dichromates, or chlorides used as catalyst accelerated the side reaction producing too much nitrogen⁽¹⁴⁻¹⁸⁾.

Here we considered only two main decomposition reactions producing N_2O and N_2 in determining the decomposition rate of ammonium nitrate, because considerable amount of N_2 gas was detected by gas chromatographic analysis in the thermal decomposition of ammonium nitrate conducted without a catalyst at the temperature range from 240°C to 330°C (13), and other decomposition reactions producing negligible amount of NO , O_2 and NO_2 were not considered.

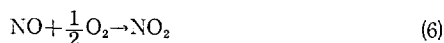
The thermal decomposition rate of the main reactions can be calculated from the total pressure increase due to the formation of gas products in the hermetically sealed reactor and the results of analyses of the gas products by assuming the order of the reaction, since each reaction produces equal moles of gas products per mole of ammonium nitrate.

Decomposition Mechanism and Kinetics

When ammonium nitrate is heated, it is believed that following reactions including dissociation reaction are possible.



NO and O_2 produced by reaction (4) and (5) combines into NO_2 as follows;



As the amount of NO , NO_2 and O_2 produced by reaction (4), (5), and (6) is negligible in comparison with that of N_2O and N_2 , reactions (4), (5) and (6) are not considered here.

Feik⁽¹⁾ and Wise⁽¹⁰⁾ reported that ammonium nitrate decomposes only after the dissociation equilibrium, attained rapidly, is established.

According to Feick and Hainer⁽¹⁹⁾, the disso-

ciation vapor pressure of ammonium nitrate is expressed by the following empirical correlation within the range from 250°C to 350°C .

$$\log_{10} P_d (\text{cmHg}) = 8.503 - \frac{4109}{T}$$

If the ideal gas law is applied to the gas products, the number of moles of ammonium nitrate dissociated is $P_d V/2RT$ and the number of moles of ammonium nitrate that is to be decomposed after the dissociation equilibrium has been attained is;

$$A_0 = A (\text{initial feed}) - P_d V/2RT$$

Assuming reactions (2) and (3) are first order, the decomposition rate of ammonium nitrate by (2) and (3) becomes $-dA/dt = (k_1 + k_2) A$ and integrating this equation, we obtain the following equation:

$$A = A_0 \text{Exp} \{ -(k_1 + k_2) t \}$$

where t is the time elapsed after the dissociation equilibrium has been reached.

Denoting the total moles of products from reaction (2) and (3) by B and C , respectively, the rate of reaction (2) and (3) becomes

$$\frac{dB}{dt} = 3k_1 A_0 \text{Exp} \{ -(k_1 + k_2) t \}$$

$$\frac{dC}{dt} = 3k_2 A_0 \text{Exp} \{ -(k_1 + k_2) t \}$$

Integrating these equations, we obtain

$$B = \frac{3k_1 A_0}{k_1 + k_2} (1 - \text{Exp} \{ -(k_1 + k_2) t \}) \quad (7)$$

$$C = \frac{3k_2 A_0}{k_1 + k_2} (1 - \text{Exp} \{ -(k_1 + k_2) t \}), \quad (8)$$

and total moles of all products formed by reaction (2) and (3) are

$$B + C = 3A_0 (1 - \text{Exp} \{ -(k_1 + k_2) t \}). \quad (9)$$

The partial pressure exerted by all the decomposition products is

$$p_{B+C} = \frac{(B+C) RT}{V} \quad (10)$$

$$p_{B+C} = p_t - p_d \quad (11)$$

where p_t is total pressure in the reactor and p_d is the dissociation pressure.

we obtain, from equation (9), (10) and (11),

$$(p_t - p_d) V = 3A_0 (1 - \exp(-(k_1 + k_2)t) RT.$$

Rearranging this equation results in

$$\ln(1 - (p_t - p_d) \frac{V}{3A_0 RT}) = -(k_1 + k_2)t. \quad (12)$$

From equation (7) and (8), the ratio of B to C is

$$\frac{B}{C} = \frac{k_1}{k_2}. \quad (13)$$

On the other hand, B and C , from the stoichiometric point of view, can be expressed as

$$B = 3n_{\text{N}_2\text{O}} \quad (14)$$

$$C = \frac{15}{4}n_{\text{N}_2} \quad (15)$$

From equation (13), (14), and (15), we obtain

$$\frac{k_1}{k_2} = \frac{4n_{\text{N}_2\text{O}}}{5n_{\text{N}_2}} \quad (16)$$

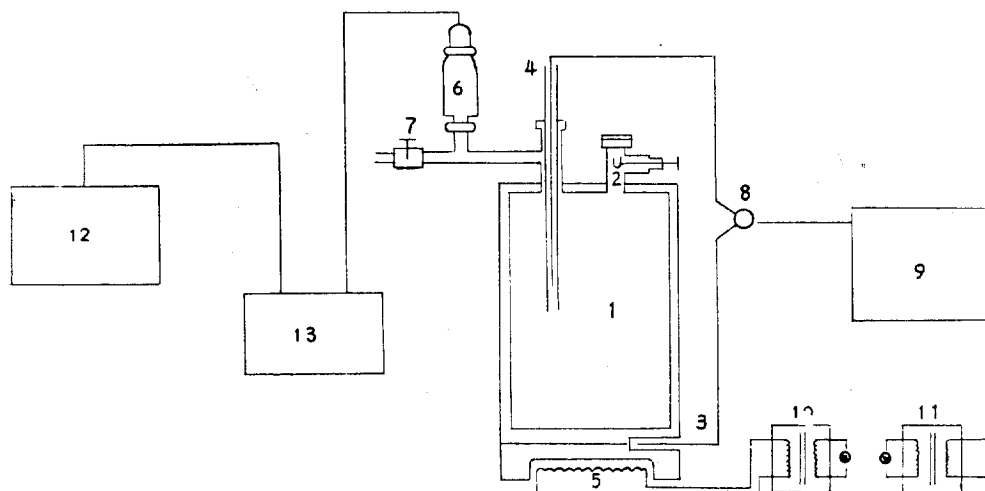
Therefore, decomposition rate of reaction (2) and (3) can be determined from equation (12) and (16) by measuring the total pressure change in the reactor

and analyzing the final gas compositions.

Experiment

A schematic diagram of the experimental apparatus is shown in Fig. 1.

To maintain the constant reaction temperature in an exothermic decomposition reaction of ammonium nitrate, 0.6 g of ammonium nitrate dried for 4 hours at 110°C was introduced onto a hot stainless steel reactor bottom with a large heat capacity. Since heat capacity of steel is about 1.2 Kcal/(°C), heat liberated from 0.6 g of ammonium nitrate raises the reactor bottom temperature by 0.1°C. The details of reactor is shown in Fig. 2. An electrical heater was held from the bottom in close contact with the reactor bottom, and its temperature was controlled with a variable transformer. The temperature difference between the bottom and interior of the reactor was reduced by controlling the input voltage to another heater which was wound around the reactor wall and attachments. The reactor was insulated with asbestos and glass wool. The temperature of reactor was measured with 2 copper constantan thermocouples inserted into the bottom, through a hole drilled



- | | | |
|---------------------|---------------------|------------------------|
| 1. Reactor | 2. Sample Container | 3. Thermocouple-1 |
| 4. Thermocouple-2 | 5. Heater | 6. Pressure Transducer |
| 7. Gas Outlet Valve | 8. Switching Device | 9. Potentiometer |
| 10. Transformer-1 | 11. Transformer-2 | 12. Gas-chromatography |
| 13. Recorder | | |

Fig. 1 Schematic Diagram of Experimental Apparatus

horizontally, and the interior of the reactor.

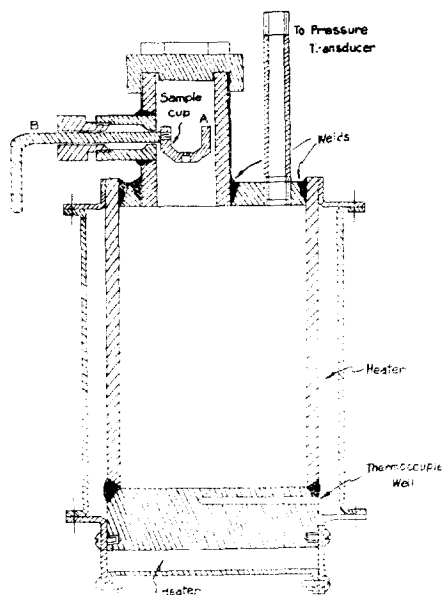


Fig. 2 Decomposition Reactor

The procedure of introducing the solid ammonium nitrate into the reactor is as follows, after the reactor temperature reaches a desired one, 0.6 g of ammonium nitrate is charged into cup A attached to the end of spindle B of the stuffing box shown in Fig. 2, and the cap of the reactor is closed. By rotating the handle of valve B, the solid sample is dropped onto the reactor bottom.

Table 1. Operating Conditions of Gas Chromatography

Column	
column 1	stainless steel tube 4 mm ϕ \times 2 m
column 2	copper tube 4 mm ϕ \times 3 m
Column material	
column 1	0.5–0.7 mm Active Carbon
column 2	60–80 mesh Molecular Sieve 5A
column oven temperature	90°C
detector oven temperature	110°C
sample	2 ml
carrier gas	Helium, 25 ml/min.
chart speed	40 mm/min.

Final gas composition was analyzed by gas chromatography. Active carbon was used as the column material for the separation of N₂O, NO, NO₂ and air, and molecular sieve 5A for N₂ and O₂ separation.

The operating condition of the gas chromatography is shown in table 1.

Pure N₂, O₂, and N₂O were used for an absolute calibration of the gas chromatographic analysis of the product gases

NO used for the absolute calibration was prepared by heating the mixture of ferrous sulfate (FeSO₄), conc. H₂SO₄ and conc. HNO₃ (25).

NO was oxidized by pure oxygen to NO₂ for the absolute calibration of this compound.

The result of absolute calibration of each compound is shown in table 2.

Table 2. Results of the Absolute Calibration

column Material	Compound	g-mole/cm ²
molecular sieve 5A	O ₂	4.56×10^{-9}
	N ₂	4.50×10^{-9}
Active Carbon	N ₂ O	4.56×10^{-9}
	NO	4.54×10^{-9}
	NO ₂	4.72×10^{-9}

The pressure in the reactor was measured by pressure transducer by converting the pressure into electrical signal.

Result and Discussion

The total pressure changes in the reactor with time at selected temperatures are shown in Fig. 3. In Fig. 4 the total pressure changes are replotted against log t.

Fig. 5-a and Fig. 5-b show plots of $\log (1 - (pt - pd)/v/3A_0RT)$ versus reaction time at the temperature range from 245°C to 270°C and from 278°C to 309°C, respectively.

The values of $(k_1 + k_2)$, calculated from the slope of each line in Fig. 5-a and Fig. 5-b, were given in Table 3.

Fig. 6 is a gas-chromatogram of the final gas product obtained at 320°C. The molar ratio of N₂O to N₂ at each temperature was calculated from the gas chromatographic analysis and given in Table 3.

The values of k_1 and k_2 , calculated from equation (12) and (16), were also presented in Table 3.

In Fig. 7, $\log k_1$ and $\log k_2$ were plotted against

1/T. Since both lines are straight as shown in the figure, previous assumptions are found to be reasonable.

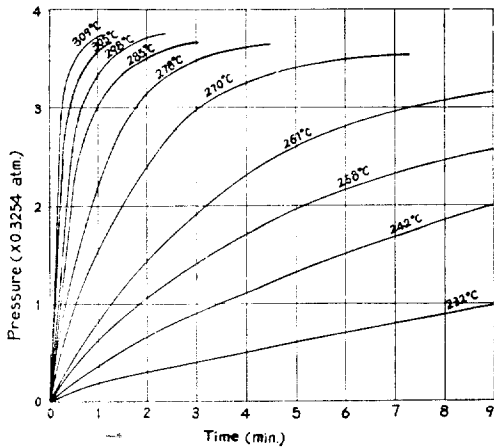


Fig. 3 Pressure vs. Reaction Time

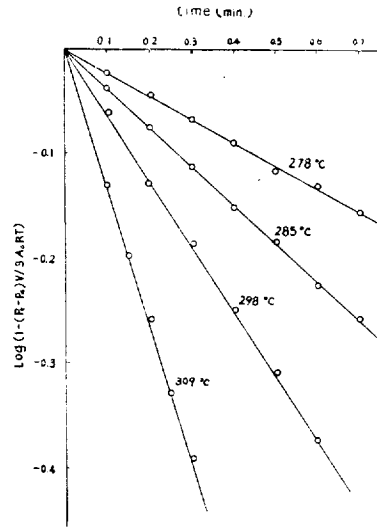
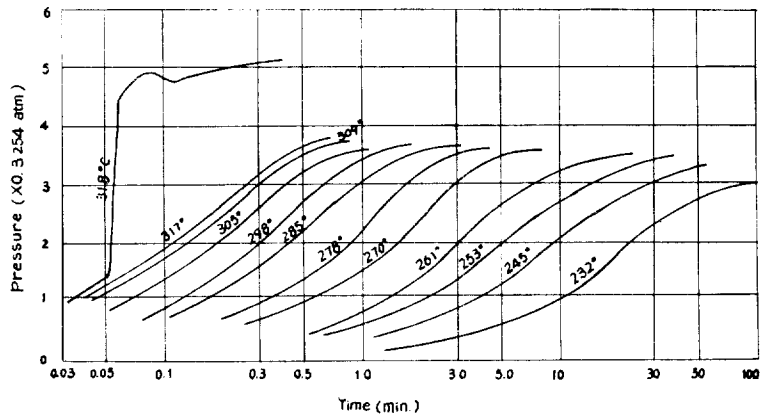
Fig. 5-b $\text{Log}(1 - (P_t - P_d) V / 3A_0 RT)$ vs. time

Fig. 4 Pressure vs. Reaction Time

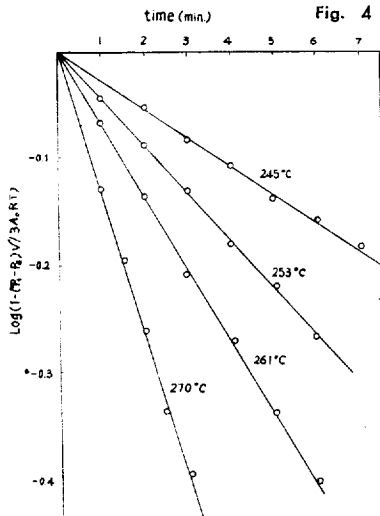
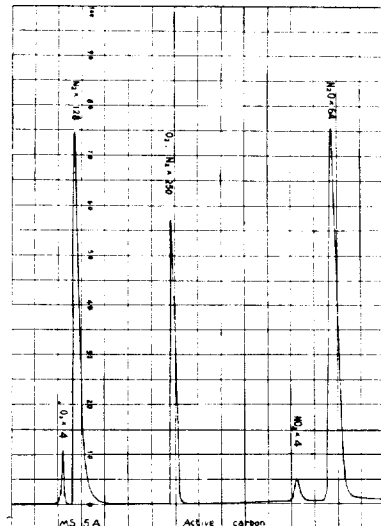
Fig. 5-a $\text{Log}(1 - (P_t - P_d) V / 3A_0 RT)$ vs. time

Fig. 6 Gas-chromatogram of the Product at 320°C

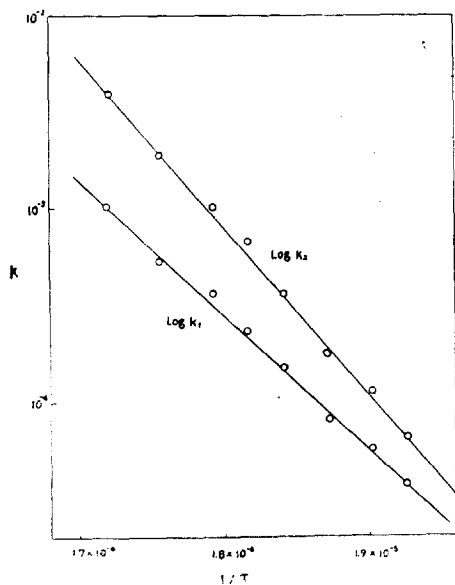


Fig. 7 Arrhenius Plot

Table 3. Reaction Rate Constants

Temperature (°C)	$k_1 + k_2$	n_{N_2}/n_{N_2O}	k_1 (1/sec)	k_2 (1/sec)
245	1.02×10^{-3}	1.43	3.66×10^{-4}	6.54×10^{-4}
253	1.70×10^{-3}	1.60	5.66×10^{-4}	1.13×10^{-3}
261	2.59×10^{-3}	1.77	8.12×10^{-4}	1.79×10^{-3}
270	5.10×10^{-3}	1.97	1.47×10^{-3}	3.63×10^{-3}
278	8.67×10^{-3}	2.22	2.29×10^{-3}	6.38×10^{-3}
285	1.36×10^{-2}	2.31	3.50×10^{-3}	1.01×10^{-2}
298	2.40×10^{-2}	2.78	5.36×10^{-3}	1.84×10^{-2}
309	4.98×10^{-2}	3.17	1.01×10^{-2}	3.97×10^{-2}

The values of p_d and A_0 at selected reaction temperatures were listed in Table 4.

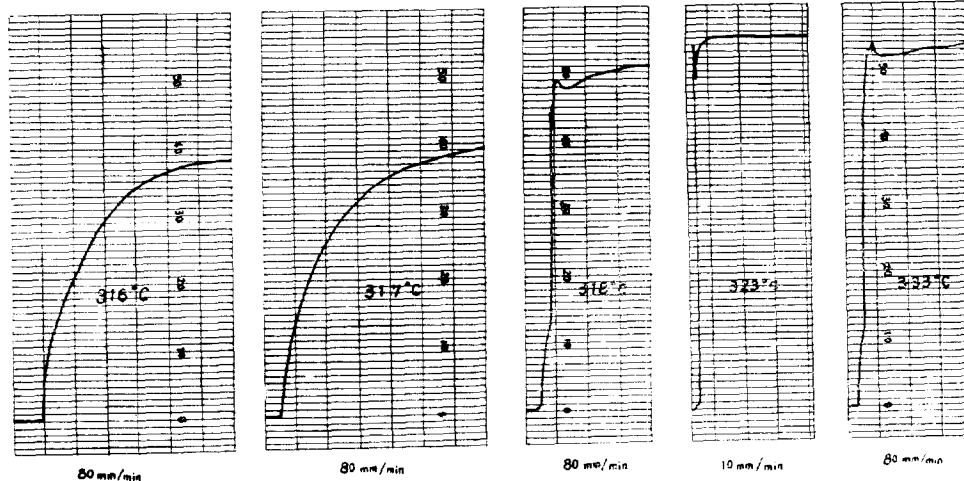


Fig. 8 Kinetic Curves of Thermal Decomposition of Ammonium Nitrate Near Explosion Temperature

Final pressure in the reactor after all ammonium nitrate reacted may be predicted by adding the equilibrium pressure p_d to the partial pressure (p_{B-C})_{final} exerted by all the decomposition products and this was also listed in Table 4.

Table 4. Predicted End Pressure

Temperature (°C)	p_d (atm)	A_0 (moles)	p_{B-C} (atm)	p_t (atm)
245	0.0489	7.15×10^{-3}	1.475	1.524
253	0.0644	7.04×10^{-3}	1.476	1.540
261	0.0835	6.91×10^{-3}	1.470	1.554
270	0.1127	6.72×10^{-3}	1.456	1.569
278	0.1420	6.53×10^{-3}	1.436	1.578
285	0.1804	6.29×10^{-3}	1.396	1.580
298	0.2645	5.76×10^{-3}	1.312	1.577
309	0.3640	5.15×10^{-3}	1.193	1.557

The equations of k_1 and k_2 formulated from Fig. 7 are expressed by;

$$\log k_1 = 9.757 - 31,300/2.303 RT$$

$$\log k_2 = 13.155 - 38,780/2.303 RT$$

At 318°C and higher temperatures, explosive decomposition reaction was found to take place as shown in Fig. 4 and Fig. 8.

Conclusion

- 1) The yield of N_2O decreases as the reaction temperature increases.

- 2) Between 240°C and 317°C, each decomposition reaction producing N_2O and N_2 is first order, and the rate is expressed by;

$$k_1 = 10^{9.757} \exp(-31,300/RT)$$

$$k_2 = 10^{13.155} \exp(-38,780/RT)$$

- 3) Above 318°C, an explosive reaction occurs.

Nomenclature

- p_t : the total pressure of the reactor.
 p_d : the dissociation pressure of ammonium nitrate.
 T : absolute temperature (°K).
 A : moles of ammonium nitrate at any time.
 A (initial feed): moles of ammonium nitrate initially introduced into the reactor.
 A_0 : moles of ammonium nitrate to be decomposed after the dissociation equilibrium is established.
 V : reactor volume.
 R : gas constant.
 k_1 : reaction rate constant of reaction (2).
 k_2 : reaction rate constant of reaction (3).
 t : the time elapsed after the dissociation equilibrium is established.
 B : total moles of products from reaction (2).
 C : total moles of products from reaction (3).
 p_{B+C} : the partial pressure exerted by all the decomposition products.
 n_{N_2O} : moles of N_2O produced.
 n_{N_2} : moles of N_2 produced.

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