Studies on the Decomposition of Ammonia and Hydrazine by High Frequency Discharge

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The chemical reaction under high frequency discharge has been studied and it has been found that the energy consumed in the reaction is roughly proportional to the frequency of the applied electric current[1]. However, from the standpoint of reaction rate, it is highly questionable whether the rate of reaction under high frequency discharge would be affected by the frequency of the applied electric current or not. In order to obtain information concerning the reactions under high frequency discharge, the selectivities of frequencies to the reactions in the decomposition of both ammonia and hydrazine vapour have been studied.

Experimental Procedures

The decomposition of ammonia and also of hydrazine under high frequency discharge were carried out in a closed vessel shown in Fig. 1. The volume of the glass vessel, cylindrical in shape, of which the diameter was 7 cm., was approximately 1000 cc. A single electrode was inserted into this vessel at the bottom and high frequency electric current was applied to this electrode. The electric discharge occurred at the top of this electrode.

The frequencies of electric current used in these experiments were 100 and 250 MC. For the purpose of keeping their power applied on these reactions at a definite value, all the electric conditions of a generator were constantly fixed in every case.

The ammonia, hydrazine, nitrogen and hydrogen used in these experiments were purified by ordinary methods. The quantities of ammonia and hydrazine in the reaction vessel were expressed by the partial pressures in the reaction vessel at 25°C. The initial pressure of ammonia was from 50 to 250 mmHg and that of hydrazine was from 3 to 10 mmHg.

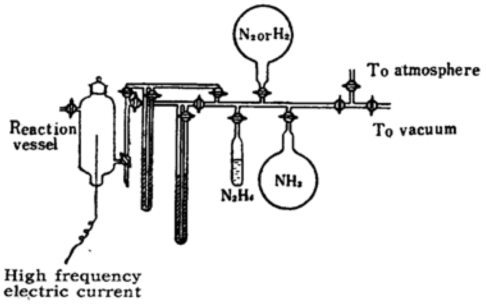

Fig. 1. Apparatus

Results and Discussion

In these experiments, the amounts of reactant were plotted against the reaction time. Several experiments with additional hydrogen or nitrogen were also carried out. From these results, the rate of the reaction was expressed with the amount of the reactant decomposed in a certain reaction time.

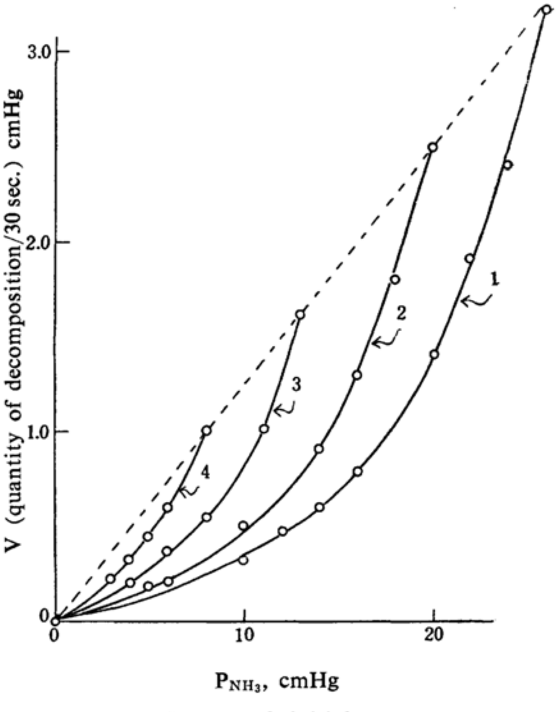

Fig. 2. Influence of initial pressure on reaction rate under 100 MC frequency discharge. Showing that the initial reaction rate is proportional to the amount of ammonia and the decomposition products retard the reaction.

NO.	$[P_{NH_3}]_0$, cmHg
1	26.0
2	20.0
3	13.0
4	8.0

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[1] E. Briner et al., *Helv. Chim. Acta*, **14**, 534 (1931); **18**, 1468 (1935); **19**, 287 (1936); **28**, 714 (1945); **30**, 105 (1947).

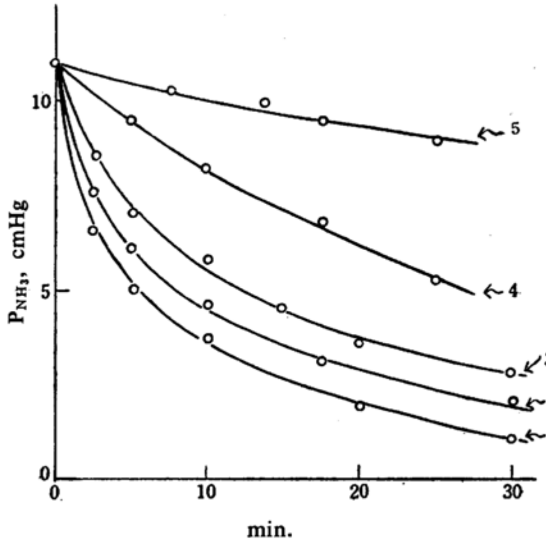

Fig. 3. Effect of hydrogen on decomposition of ammonia under 100 MC frequency discharge. Plots of amount of ammonia against reaction time.

$[P_{NH_3}]_0$; 11.0 cmHg

NO.	$[H_2]_0$, cmHg
1	0
2	3.50
3	14.30
4	25.80
5	32.80

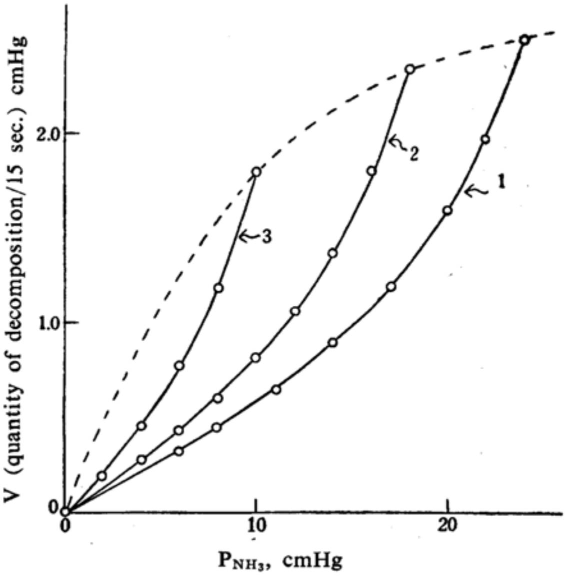

Fig. 5. Influence of initial pressure on reaction rate under 250 MC frequency discharge. Showing that the initial reaction is an intermediate type between the zero and the 1st order reaction and the reaction is retarded by the decomposition products.

NO.	$[P_{NH_3}]_0$, cmHg
1	24.0
2	18.0
3	10.0

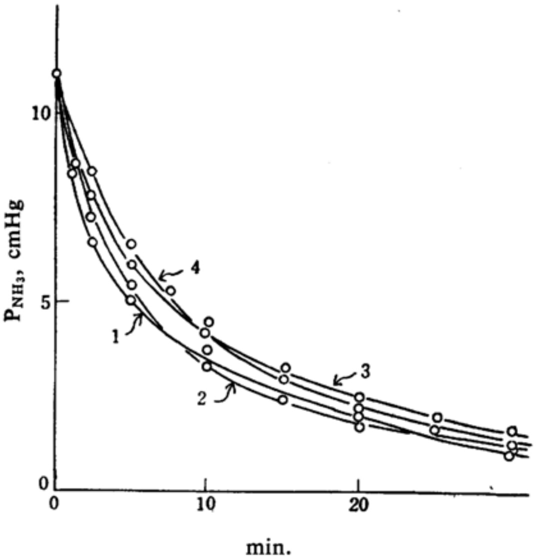

Fig. 4. Effect of nitrogen on decomposition of ammonia under 100 MC frequency discharge. Plots of amount of ammonia against reaction time.

$[P_{NH_3}]_0$; 11.0 cmHg

NO.	$[N_2]_0$, cmHg
1	0
2	3.10
3	11.80
4	33.80

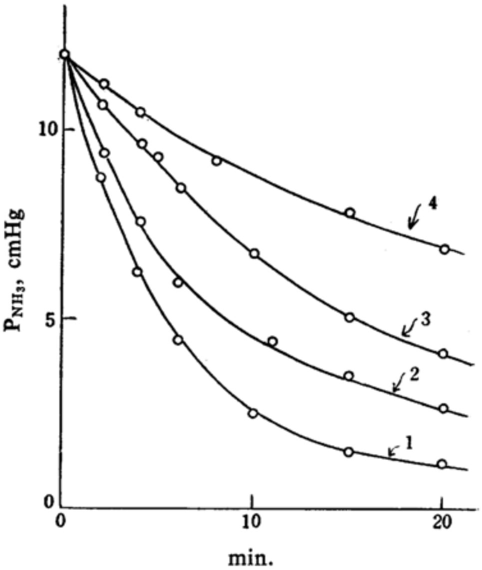

Fig. 6. Effect of hydrogen on decomposition of ammonia under 250 MC frequency discharge. Plots of amount of ammonia against reaction time.

$[P_{NH_3}]_0$; 12.0 cmHg

NO.	$[P_{H_2}]_0$, cmHg
1	0
2	3.0
3	9.0
4	12.0

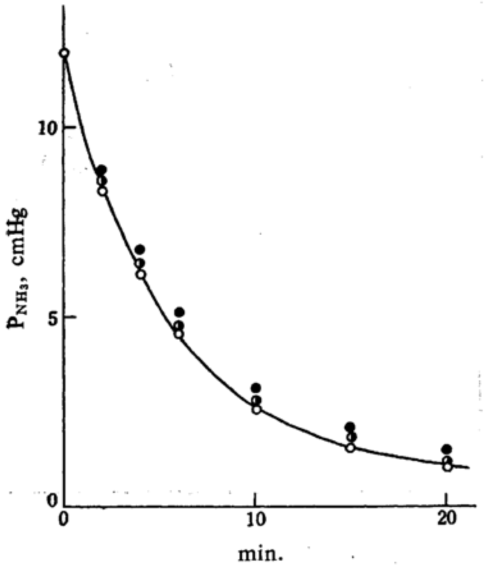

Fig. 7. Effect of nitrogen on decomposition of ammonia under 250 MC frequency discharge. Plots of amount of ammonia against reaction time.
$[P_{NH_3}]_0$; 12.0 cmHg
$[P_{N_2}]_0$, cmHg
○…… 0
◑…… 6.00
●……10.50

Decomposition of Ammonia.—The decomposition products were analysed by gas chromatogrophy. They were nitrogen, hydrogen and hydrazine. The main products were nitrogen and hydrogen. The amount of hydrazine produced was so small that the effect caused by the hydrazine on this reaction may be ignored.

On the decomposition under 100 MC frequency discharge, it is shown in Fig. 2 that the initial stage of the reaction was of the 1st order and that the retardation by both nitrogen and hydrogen was observed. Comparing Fig. 3 with Fig. 4, it is seen that the amount of ammonia decomposed in a definite time decreases according to the quantity of hydrogen added, while the nitrogen added exhibits no effects on the rate of ammonia decomposition. Under 250 MC frequency discharge, it is known from Fig. 5 that the initial reaction is not of the 1st order, but it is an intermediate type between the zero and 1st order reactions, and comparing Fig. 6 with Fig. 7, it may be seen that the overall reaction is retarded by hydrogen.

The molecules in electric discharge are excited by a collision with an impacting electron and change to an excited molecule or a positive ion. It is considered that both a positive ion and an excited molecule are possible agents in the chemical reaction. If excited molecules were responsible, the reaction should be pressure sensitive, for it may be expected that the concentration of excited molecules would decrease with pressure. The outstanding feature of the experiment in electric discharge is that the reaction is directly proportional to the discharge current and it is independent of pressure over a large range of values. Furthermore, it has been observed in the studies[2] with electrons of controlled speed that the reaction hardly occurs below the ionization potential of the gas. These experimental results favor an ionic reaction in electric discharge. Upon neutralization of a positive ion, the entire energy of ionization available may serve as activation energy for chemical processes or else the molecule will return to the normal state after a short average life with the emission of radiation[3]. In a spectroscopic investigation[4], on high frequency discharge, it has been noticed that, in a discharge tube, a molecule with one charge comes to be clearly observed as the frequency of electric current increases. This phenomenon shows one of the specific properties of high frequency discharge and from this fact it is presumed that the life-time and number of positive charge moleculs produced in a discharge tube tend to increase with the frequency of the electric current.

Thus, one accounts for the kinetics of reactions by the following series of reactions:

$$NH_3 \xrightarrow{k_1} NH_3^+ \quad \text{(in electric discharge)}$$

$$NH_3^+ \xrightarrow{k_2} NH_3^*$$

$$NH_3^* \xrightarrow{k_3} \frac{1}{2}N_2+\frac{3}{2}H_2$$

$$NH_3^+ \xrightarrow{k_4} NH_3+E$$

$$NH_3^+ + H_2 \xrightarrow{k_5} [NH_3^+ \cdot H_2] \longrightarrow NH_3+H_2+E_1$$

$$NH_3^+ + NH_3 \xrightarrow{k_6} [NH_3^+ \cdot NH_3] \longrightarrow NH_3+NH_3+E_2$$

In these reactions, it is difficult to understand strictly the behaviour of hydrogen molecules, but from the results obtained in this experiment it is supposed that hydrogen has the greatest probability of deactivation of all ionized molecules. If the life-time of NH_3^+ is long, it is known that, as the results of several collisions between hydrogen and the ionized

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[2] C. H. Kunsman, *Phys. Rev.*, **31**, 307 (1928).

[3] G. Glockler, "The Electrochemistry of Gases and other Dielectrics", John Wiley & Sons, Inc., New York (1939), p. 430.

[4] W. Jones, *Proc. Roy. Soc.*, **A127**, 511 (1930); L. Henry, *J. Phys. Chem.*, **34**, 2792 (1930).

molecule, the ionized molecule loses its excessive energy and becomes a normal molecule, while hydrogen becomes an activated molecule. Applying the steady state assumption, one arrives at expression 1 for the rate of decomposition.

$$\frac{\mathrm{d}[\mathrm{NH_3}^+]}{\mathrm{d}t}=k_1[\mathrm{NH_3}]-k_2[\mathrm{NH_3}^+]-k_4[\mathrm{NH_3}^+]$$

$$-k_5[\mathrm{NH_3}^+][\mathrm{H_2}]-k_6[\mathrm{NH_3}^+][\mathrm{NH_3}]=0$$

$$[\mathrm{NH_3}^+]=\frac{k_1[\mathrm{NH_3}]}{k_2+k_4+k_5[\mathrm{H_2}]+k_6[\mathrm{NH_3}]}$$

$$\frac{\mathrm{d}[\mathrm{NH_3}^*]}{\mathrm{d}t}=k_2[\mathrm{NH_3}^+]-k_3[\mathrm{NH_3}^*]=0$$

$$[\mathrm{NH_3}^*]=\frac{k_2}{k_3}[\mathrm{NH_3}^+]$$

$$V=k_3[\mathrm{NH_3}^*]=k_2[\mathrm{NH_3}^+]$$

$$=\frac{k_1k_2[\mathrm{NH_3}]}{k_2+k_4+k_5[\mathrm{H_2}]+k_6[\mathrm{NH_3}]} \qquad (1)$$

When a hydrogen molecule does not exist in a reaction vessel, the rate of reaction is expressed as follows and this formula expresses the relation between the initial rate V_0 and the concentration of ammonia.

$$V_0=k_3[\mathrm{NH_3}^*]=k_2[\mathrm{NH_3}^+]$$

$$=\frac{k_1k_2[\mathrm{NH_3}]}{k_2+k_4+k_6[\mathrm{NH_3}]} \qquad (2)$$

Using expressions 1 and 2, the following relations are obtained.

$$\frac{V_0-V}{V}=\frac{k_5[\mathrm{H_2}]}{k_2+k_4+k_6[\mathrm{NH_3}]}=\Theta$$

$$\frac{k_2+k_4}{k_5}+\frac{k_6}{k_5}[\mathrm{NH_3}]=\frac{[\mathrm{H_2}]}{\Theta} \qquad (3)$$

If the life-time of $\mathrm{NH_3}^+$ is short, the k_6 process may be neglected and the rate of decomposition is approximated as follows:

$$V=\frac{k_1k_2[\mathrm{NH_3}]}{k_2+k_4+k_5[\mathrm{H_2}]} \qquad (4)$$

$$\frac{k_2+k_4}{k_1k_2}+\frac{k_5}{k_1k_2}[\mathrm{H_2}]=\frac{[\mathrm{NH_3}]}{V} \qquad (5)$$

Using the results shown in Figs. 2 and 5, the plots of $\mathrm{NH_3}/V$ vs. $\mathrm{H_2}$ and $\mathrm{H_2}/\Theta$ vs. $\mathrm{NH_3}$ are shown in Figs. 12 and 13, respectively. A linear relation between $\mathrm{NH_3}/V$ and $\mathrm{H_2}$ or $\mathrm{H_2}/\Theta$ and $\mathrm{NH_3}$ is clearly shown in these figures, being independent of the initial concentration of ammonia, and the agreement between the experiment and the calculation is reasonable.

Decomposition of Hydrazine.—The decomposition products of this reaction are nitrogen and hydrogen and ammonia is not produced. In this reaction, comparing Fig. 8 with Fig. 9

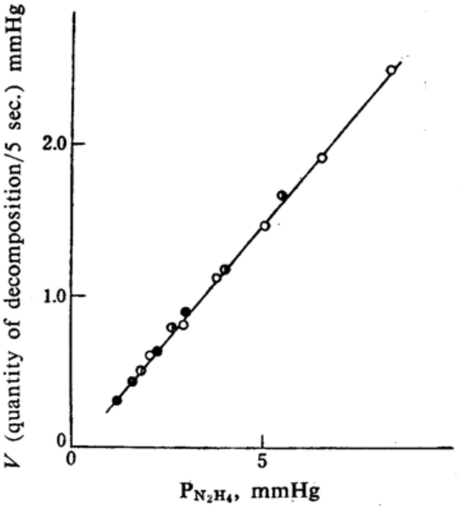

Fig. 8. Decomposition of hydrazine under 100 MC frequency discharge. Plots of reaction rate against hydrazine concentration.

$[P_{N_2H_4}]_0$, mmHg
○……8.40
◑……5.50
●……3.00

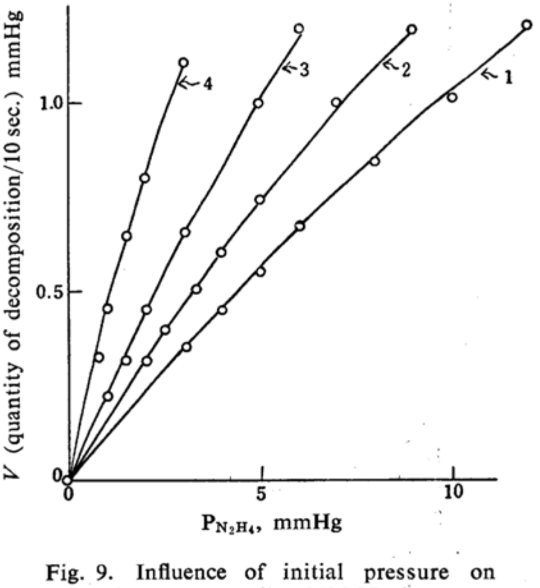

Fig. 9. Influence of initial pressure on reaction rate under 250 MC frequency discharge. Showing that the initial reaction is zero order and the reaction is retarded by the decomposition products.

NO.	$[P_{N_2H_4}]_0$, mmHg
1	12.0
2	9.0
3	6.0
4	3.0

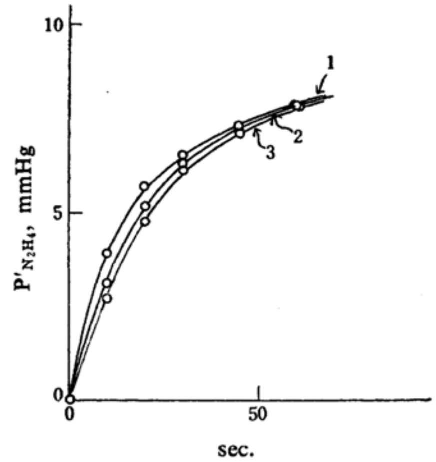

Fig. 10. Effect of nitrogen and hydrogen on decomposition of hydrazine under 100 MC frequency discharge. Plots of amount of hydrazine decomposed against reaction time.

$[P_{N_2H_4}]_0$; 8.40 mmHg

NO.	$[P_{H_2}]_0$, mmHg	$[P_{N_2}]_0$, mmHg
1	0	0
2	15.0	0
3	0	15.0

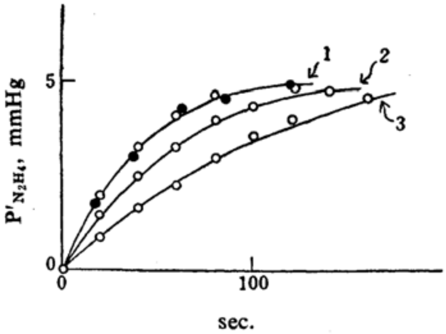

Fig. 11. Effect of nitrogen and hydrogen on decomposition of hydrazine under 250 MC frequency discharge. Plots of amount of hydrazine decomposed against reaction time.

$[P_{N_2H_4}]_0$; 5.0 mmHg

NO.	$[P_{N_2}]_0$, mmHg	$[P_{H_2}]_0$, mmHg
1 ○	0	0
1 ●	0	6.0
2	6.0	0
3	9.0	0

it can be shown that the rate of decomposition under high frequency discharge varies with the values of frequencies of the applied electric current. The reaction under the frequency 100 MC is a 1st order reaction, but under the frequency 250 MC the initial rate of decomposition is of zero order. Moreover, as is seen in Figs. 10 and 11, the hydrogen produced in the course of the decomposition does not retard the rate of decomposition under the former condition, but it moderately retards the rate of reaction under the latter condition. From these results, it is possible to explain the reaction processes as follows:

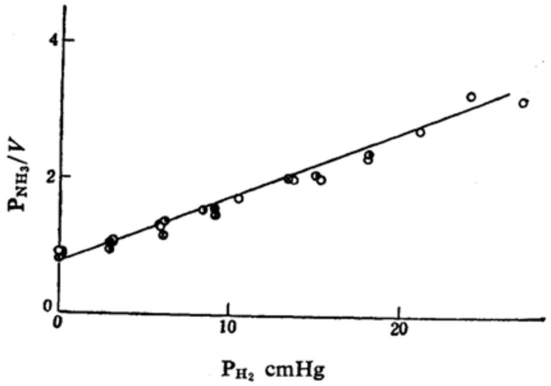

Fig. 12. Plots of P_{NH_3}/V vs. P_{H_2}.

$[P_{NH_3}]_0$, cmHg	$[P_{NH_3}]_0$, cmHg
○……26.0	◑……20.0
⊗……13.0	●…… 8.0

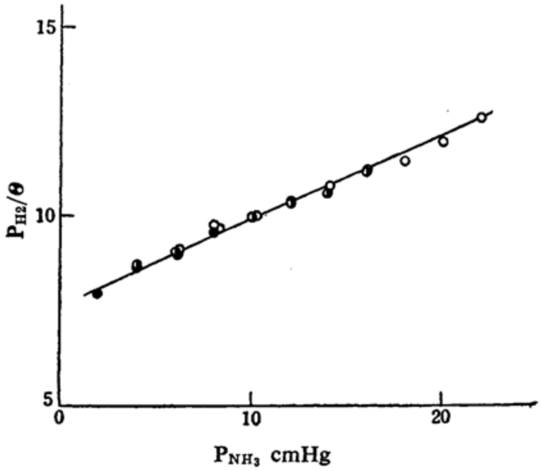

Fig. 13. Plots of P_{H_2}/Θ vs. P_{NH_3}.

$[P_{NH_3}]_0$, cmHg	$[P_{NH_3}]_0$, cmHg
○……24.0	◑……18.0
●……10.0	

$$N_2H_4 \xrightarrow{k_1} N_2H_4^+ \text{ (in electric discharge)}$$

$$N_2H_4^+ \xrightarrow{k_2} N_2H_4^*$$

$$N_2H_4^* \xrightarrow{k_3} N_2+2H_2$$

$$N_2H_4^+ \xrightarrow{k_4} N_2H_4+E$$

$$N_2H_4^+ + H_2 \xrightarrow{k_5} [N_2H_4^+ \cdot H_2] \longrightarrow N_2H_4+H_2+E_1$$

$$N_2H_4^+ + N_2H_4 \xrightarrow{k_6} [N_2H_4^+ \cdot N_2H_4] \longrightarrow N_2H_4+N_2H_4+E_2$$

Under the frequency 100 MC, if the lifetime of $N_2H_4^+$ is short, it is supposed that $N_2H_4^+$ cannot be deactivated by the collision with H_2 or N_2H_4. In this case, applying the usual steady state assumption, expression 6 for the rate of decomposition is obtained.

$$\frac{d[N_2H_4^+]}{dt}=k_1[N_2H_4]-k_2[N_2H_4^+]$$

$$-k_4[N_2H_4^+]=0$$

$$[N_2H_4^+]=\frac{k_1[N_2H_4]}{k_2+k_4}$$

$$\frac{d[N_2H_4^*]}{dt}=k_2[N_2H_4^+]-k_3[N_2H_4^*]=0$$

$$[N_2H_4^*]=\frac{k_2}{k_3}[N_2H_4^+]$$

$$V=k_3[N_2H_4^*]=\frac{k_1k_2}{k_2+k_4}[N_2H_4] \qquad (6)$$

Under the frequency 250 MC, if the lifetime of $N_2H_4^+$ becomes longer with the increase of frequency of electric current, it is supposed that $N_2H_4^+$ comes to be deactivated by each molecule of hydrogen and hydrazine. In this case, the following equations are obtained:

$$\frac{d[N_2H_4^+]}{dt}=k_1[N_2H_4]-k_2[N_2H_4^+]$$

$$-k_4[N_2H_4^+]-k_5[N_2H_4^+][H_2]$$

$$-k_6[N_2H_4^+][N_2H_4]=0$$

$$[N_2H_4^+]=\frac{k_1[N_2H_4]}{k_2+k_4+k_5[H_2]+k_6[N_2H_4]}$$

$$\frac{d[N_2H_4^*]}{dt}=k_2[N_2H_4^+]-k_3[N_2H_4^*]=0$$

$$[N_2H_4^*]=\frac{k_2}{k_3}[N_2H_4^+]$$

$$V=k_3[N_2H_4^+]=\frac{k_1k_2[N_2H_4]}{k_2+k_4+k_5[H_2]+k_6[N_2H_4]} \qquad (7)$$

In this decomposition, as the value of hydrogen produced in the course of the decomposition is equal to $2([N_2H_4]_0-[N_2H_4])$ the following equations are derived.

$$V=\frac{k_1k_2[N_2H_4]}{k_2+k_4+2k_5[N_2H_4]_0+(k_6-2k_5)[N_2H_4]}$$

$$\frac{[N_2H_4]}{V}=\frac{1}{k_1k_2}\{(k_2+k_4+2k_5[N_2H_4]_0)$$

$$+(k_6-2k_5)[N_2H_4]\} \qquad (8)$$

where, $[N_2H_4]_0$ is the initial concentration of hydrazine. Using the results shown in Fig. 9, N_2H_4/V is plotted against N_2H_4 as shown in Fig. 14. As is obvious from these figures, the agreement between the experiment and the calculation is satisfactory.

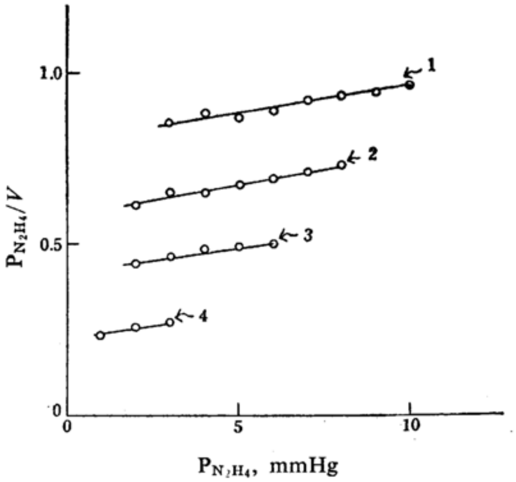

Fig. 14. Plots of $P_{N_2H_4}/V$ vs. $P_{N_2H_4}$.

NO.	$[P_{N_2H_4}]_0$, mmHg
1	12.0
2	9.0
3	6.0
4	3.0

Summary

1) The decomposition of both ammonia and hydrazine were carried out under high frequency discharge and the effects of frequency on the chemical reactions were investigated. The frequencies of electric current were 100 and 250 MC.

2) The effects of frequency appeared clearly on the decomposition of hydrazine: under 100 MC frequency discharge the decomposition was a 1st order reaction, while under 250 MC it was approximately zero order reaction, and the overall reaction was retarded moderately by the hydrogen produced in the course of the reaction.

3) As for the decomposition of ammonia, in any case, the reactions were retarded by hydrogen. Under 100 MC frequency discharge the reaction was 1st order, while under 250 MC it was a fractional order reaction.

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