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Kinetic Studies of Ammonia Oxidation in Shock Waves. II. The Rate of Ammonia Consumption*

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An investigation was made of ammonia oxidation in shock waves at temperatures from 2100 to 2600°K by monitoring the ultraviolet absorption of ammonia at 2245 Å. The absorption coefficient of ammonia was measured at various temperatures; the rate constant of the decomposition reaction at higher temperatures with a mixture of 1% NH_3 and 99% Ar was found to be in good agreement with the results of other studies. By using several mixtures of ammonia and oxygen highly diluted with argon, the rate of ammonia consumption immediately after an induction period was found to be expressed by:

$$-\left(\frac{d[NH_3]}{dt}\right)_0 = k_0[NH_3]^{1.5}[O_2]^{0.5}[Ar]^{0.5}$$

where: $\log k_0(l^{1.5}\text{mole}^{-1.5}\text{sec}^{-1}) = 12.77 \pm 0.10 + (-8488 \pm 573)/T$. This corresponds to an apparent activation energy of 38.8±2.6 kcal./mole.

In a preceding paper[1] on the ammonia-oxygen reaction, we reported the results obtained from measurements of the induction periods and time histories of various intermediate species, and a reaction mechanism for the induction period was proposed.

Now, a challenging problem is to study the early stage of the reaction which follows the induction period. We will describe here results obtained from measurements of ammonia absorption at 2245 Å over the range of conditions $2100 \leq T \leq 2600$°K, $2.1 \leq p \leq 5.4$ atm., $0.5 < [NH_3]/[O_2] \leq 2$, and $1.0 \times 10^{-4} \leq [O_2]$, $[NH_3] \leq 4.1 \times 10^{-4}$ mol./l.

Experimental

The experimental details have been described previously.[2] In brief, the velocity of an incident shock wave was measured with two thin-film thermometers, which were placed at a distance of 139.0 mm. from each other, and with an electronic counter. One of the thermometers was placed 5.0 mm. from the endplate where the observation windows of quartz were set.

An ultraviolet absorption of ammonia was measured at 2245 Å.[3] The slit width of a monochrometer was set at 0.6 mm., which allowed a band pass of 7 Å.

The procedures of preparing reaction mixtures as well as the materials used were the same as those described in a previous paper.[1]

Results and Discussion

The Extinction Coefficients of Ammonia at 2245 Å.—The extinction coefficient at room temperature was determined from the decrease in photocurrent when the shock tube (7.6 cm. in internal diameter) was filled with pure ammonia. The absorption of ammonia agreed well with Beer's law up to a pressure of 700 mmHg, which was the upper limit of our glass gas-handling system. The decadic extinction coefficients found were 3.42 and 4.15 l. mole^{-1}, at 295 and 300°K respectively.

The extinction coefficients at high temperatures were determined from the initial decreases in photocurrent immediately after the passage of the incident and reflected shock waves, by using mixtures of 1, 2, or 3% ammonia and argon. The absorption increased linearly with the concentration of ammonia up to about a 90% absorption. The extinction coefficients as a function of the temperature are plotted in Fig. 1, which shows a rather definite decrease in their value above 3000°K. This may be due to a rapid decomposition of ammonia at these high temperatures. The solid line in the figure was obtained by a multiple regression analysis, while the dashed line was obtained by Michel and Wagner[4] at 2300 Å. The latter line was calculated from their Arrhenius-type expression up to 3000°K, though its effective temperature range was not explicit in their paper. The difference between these two data is large at lower temperatures;

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[1] T. Takeyama and H. Miyama, This Bulletin, **38**, 1670 (1965).

[2] T. Takeyama and H. Miyama, ibid., **38**, 936 (1965).

[3] R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," Chapman & Hall, London (1950), p. 180.

[4] K. W. Michel and H. Gg. Wagner, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1965), p. 353.

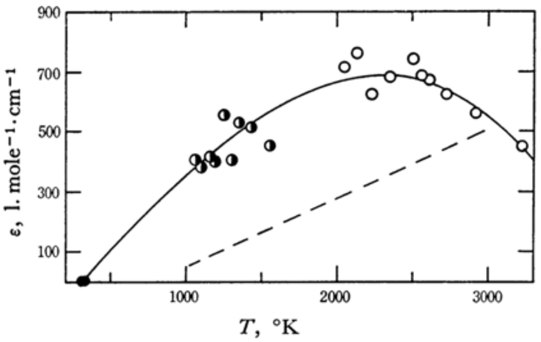

Fig. 1. Temperature dependence of the NH_3 extinction coefficient at 2245Å.
●, measured by static method at room temperature; ◑, measured in incident shock waves, ○, measured in reflected shock waves. Solid line is the best fit to the points by multiple regression analysis. Dashed line is a result of Michel and Wagner⁴⁾ at 2400A.

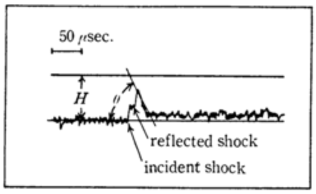

Fig. 2. Typical oscillogram showing NH_3 absorption vs. time.
1%NH_3-99%Ar; p_1, 51.0 mmHg: w_r, 1122 m./sec.; T_5, 2790°K; P_5, 7.3 atm.; [NH_3], 2.05×10^{-4} mole/l.

they differ by a factor of ten at 1000°K. This can be attributed to the strong wavelength dependence of extinction coefficients at lower temperatures.⁵⁾

The Pyrolysis of Ammonia.—Oscillographic records obtained in the measurements of the extinction coefficients of ammonia showed that a detectable amount of decomposition started only after a temperature-dependent induction period at lower temperatures (<2400°K). Therefore, the initial rates of the decomposition of ammonia were determined for higher-temperature runs, in which no induction period was observed, as is shown in Fig. 2. Here, mixture of 1% ammonia and argon were used. The equation used was⁶⁾:

$$-\frac{d[NH_3]}{dt}=\frac{\tan\theta\exp(\varepsilon l[NH_3])}{Hw\varepsilon l} \tag{1}$$

where ε donotes the extinction coefficient in l. mole⁻¹ cm⁻¹; l, the optical length (7.6 cm.), and w, the sweep velocity on the record (sec. cm⁻¹). The height, H, is assumed to be the deflection for 100% absorption, since the room temperature absorption of ammonia is negligibly small, as was described above. The tangent of the angle θ gives the initial rate of change of absorption by ammonia. θ was estimated within a range not exceeding a 10% decomposition of ammonia. Therefore, as an approximation, the authors did not include in Eq. 1 such corrections brought about by the reaction as the temperature decrease, the density increase, and the change in the extinction coefficient.

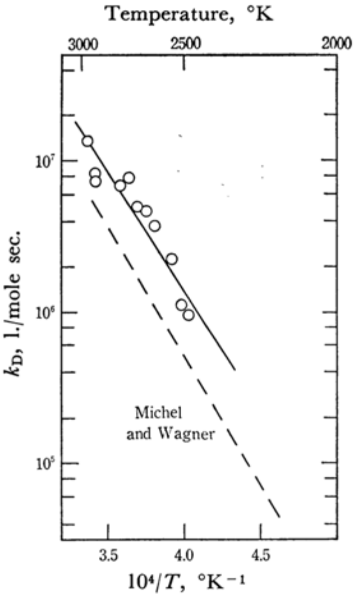

Fig. 3. Second-order rate constants for decomposition of ammonia.

Thus, the decomposition rate constant, k_D, of the first order with respect to ammonia and argon,* was determined from the initial rate. The results are presented in Fig. 3 as an Arrhenius plot. The solid line obtained by a least-squares calculation is expressed by:

$$\log k_D\ (\text{l. mole}^{-1}\,\text{sec}^{-1})=(12.36\pm0.15) \\ -(71100\pm9200)/2.303\boldsymbol{R}T \tag{2}$$

For the purposes of comparison, the results of Michel and Wagner⁴⁾ obtained from the measurement of the ultraviolet absorption of ammonia at 2300 Å are also shown in the figure. There exists a good agreement among the data of the two groups; this confirms the reliability of the present measurements.

The Rate of Ammonia Consumption in the Oxidation Reaction.—The oxidation of ammonia was studied over the temperature range from 2100

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5) H. Gg. Wagner, private communication.
6) H. B. Palmer and D. F. Hornig, *J. Chem. Phys.*, **26**, 98 (1957).

* Michel and Wagner⁴⁾ used the second-order expression, $k_D[NH_3][Ar]$, though Jacob⁷⁾ obtained $k_D[NH_3]^{1.5}[Ar]^{0.5}$. Although our data are not enough to determine which of these expressions is right, the former expression was used for the sake of simplicity. Even when the latter is applied, however, our data agree well with those of Jacob.

7) T. A. Jacob, *J. Phys. Chem.*, **67**, 665 (1963).

TABLE I. INITIAL RATES OF AMMONIA CONSUMPTION DETERMINED AT 2255±10°K WITH VARIOUS REACTION MIXTURES

Reaction mixture	Number of runs	Composition %			P_4 atm.	P_1 mmHg	T_5 °K	$[NH_3]$ 10^{-4} mole/l.	$[O_2]$ 10^{-4} mole/l.	[Ar] 10^{-2} mole/l.	v_0 mole $l^{-1}\cdot sec^{-1}$
		NH_3	O_2	Ar							
I	5	2.0	1.0	97.0	5.0	50.3±0.1	2255±10	3.91±0.01	1.96±0.00	1.90±0.00	19.0±2.6
II	6	1.0	1.0	98.0	5.0	53.3±0.3	2255±15	2.01±0.01	2.01±0.01	1.97±0.01	4.9±0.7
III	2	0.5	1.0	98.5	5.0	54.3±0.1	2260± 0	1.01±0.00	2.01±0.00	1.98±0.00	1.9±0.0
IV	4	1.0	2.0	97.0	5.0	53.6±0.1	2265±15	2.05±0.00	4.10±0.01	1.99±0.00	7.1±0.5
V	5	1.0	0.5	98.5	5.0	53.4±0.2	2255±15	2.00±0.01	1.00±0.00	1.97±0.01	3.5±0.3
VI	7	0.8	0.8	98.4	7.3	78.7±0.3	2250± 0	2.40±0.01	2.40±0.01	2.88±0.01	7.6±2.0
VII	5	1.0	1.0	98.0	6.0	63.8±0.4	2250±15	2.40±0.02	2.40±0.02	2.35±0.02	10.2±1.1
VIII	7	1.2	1.2	97.6	5.0	52.2±0.1	2250± 0	2.38±0.01	2.38±0.01	1.93±0.00	7.1±1.2
IX	9	2.0	2.0	96.0	3.0	29.2±0.4	2260± 0	2.31±0.03	2.31±0.03	1.11±0.02	5.9±1.2

Note; P_4, P_1, and T_5 are pressure of driver section, initial pressure of test section, and temperature immediately behind reflected shock wave respectively.

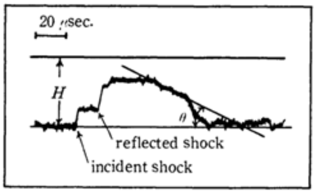

Fig. 4. Oscillographic record showing the change in NH_3 absorption during oxidation reaction. 0.82%NH_3-0.82%O_2-98.36%Ar; P_1, 97.1 mmHg; w_r, 978.9 m./sec.; T_5, 2160°K; P_5, 5.14 atm.; $[NH_3]$ and $[O_2]$, 2.38×10^{-4} mole/l.

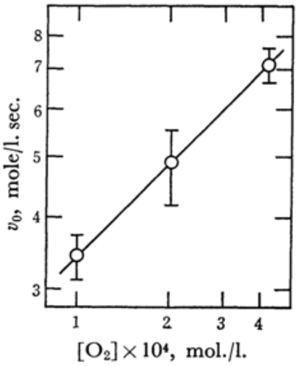

Fig. 6. Dependence of rate on oxygen concentration.
T_5, 2260±15°K;
$[NH_3]$, (2.01±0.02)×10^{-4} mole/l.
[Ar], (1.97±0.01)×10^{-2} mole/l.

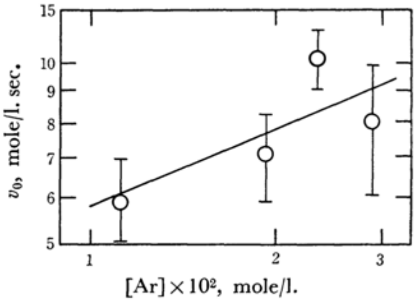

Fig. 7. Dependence of rate on argon concentration.
T_5, 2255±10°K;
$[NH_3]$ and $[O_2]$, (2.28±0.10) ×10^{-4} mole./l.

to 2600°K. A typical oscillogram is shown in Fig. 4. An appreciable amount of reaction starts after an induction period, which becomes shorter at higher temperatures, with an initial rate of v_0. Then, the rate increases to a final rate, v, as the reaction proceeds further. As the temperature increases, the v_0 rate becomes greater until finally it coalesces with v. The initial rates were calculated by the procedure used in the preceding section. The order of reaction was determined in the following manner; for example, for the determination of the order with respect to ammonia, the initial rates were measured by using different mixtures, in which only the ammonia content was varied, keeping those of oxygen and argon unchanged, and by adjusting the pressures of the driving helium and of the reaction mixtures so that a constant temperature was obtained. The results obtained at 2255±10°K are summarized in Table I and shown graphically in Figs. 5, 6, and 7. The reaction orders with respect to ammonia, oxygen, and argon were found

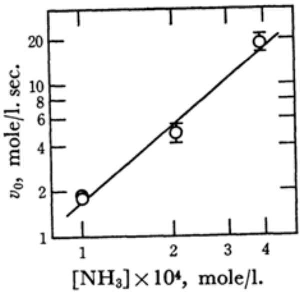

Fig. 5. Dependence of rate on ammonia concentration.
T_5, 2255±10°K; $[O_2]$, (1.99±0.02)×10^{-4} mole/l.
[Ar], (1.94±0.03)×10^{-2} mole/l.

from least-squares calculation to be 1.70 ± 0.06, 0.51 ± 0.01, and 0.42 ± 0.08* respectively. Thus, the initial rate of ammonia consumption may approximately be expressed by the following equation:

$$v_0 = -\left(\frac{d[NH_3]}{dt}\right)_0 = k_0[NH_3]^{1.5}[O_2]^{0.5}[Ar]^{0.5} \qquad (3)$$

Next, the rate constant, k_0, was determined over the 2100—2600°K temperature range and the 2.1—5.4 atm. pressure range by using mixtures of 1% ammonia, 1% oxygen, and 98% argon, on the assumption that the rate equation (3) is valid. The results are shown in Fig. 8 as an Arrhenius plot. The solid line calculated by a least-squares method is expressed as follows:

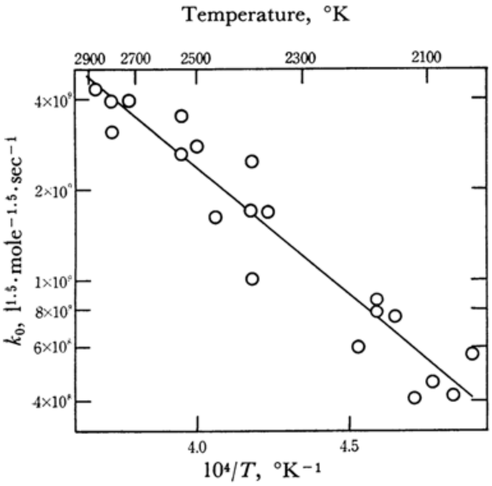

Fig. 8. Arrhenius plot for the rate constants of ammonia consumption in 1%NH_3-1%O_2-98%Ar mixture.

$$\log k_0\ (l.^{1.5}mole^{-1.5}sec^{-1}) = (12.77\pm0.10) + (-8488\pm573)/T \qquad (4)$$

The temperature dependence corresponds to an apparent activation energy of 38.8 ± 2.6 kcal./mole. On the other hand, the values of activation energy obtained at lower temperatures[8-10] were in the range of 30—50 kcal./mole. However, a comparison of the present value with those at lower temperatures is useless because the rate expressions in the latter cases are more complicated due to the wall effect.

Also, we were not successful in finding a reasonable chain-branching mechanism to fit the rate expression (3) by using the present and other available data. However, concerning the thermal decomposition of ammonia in shock waves, Jacob[7] obtained the following relation:

$$-d[NH_3]/dt = k[NH_3]^{1.5}[Ar]^{0.5} \qquad (5)$$

Here, $k = 2.5\times10^{13}\exp(-77\ \text{kcal.}/\boldsymbol{R}T)$ l. mole^{-1}· sec^{-1}. In order to explain this relation, Avery and Bradley[11] proposed this reaction scheme:

$$NH_3 + Ar \xrightarrow{k_1} R_1 + \cdots + Ar \qquad (I)$$

$$R_1 + NH_3 \xrightarrow{k_2} [R_2 + \cdots] \rightarrow R_1 + \cdots \qquad (II)$$

$$R_1 + R_1 \xrightarrow{k_3} \text{stable products,} \qquad (III)$$

The assumption of a stationary-state concentration of the R_1 radical leads to a corresponding kinetic expression with $k = k_2k_1^{1/2}/k_3^{1/2}$. If the initiation step I is replaced with the following steps in the case of ammonia oxidation, the rate expression (6) is easily derived by a stationary-state assumption:

$$NH_3 + O_2 \rightleftarrows [NH_3\cdots O_2]$$

equilibrium constant K

$$[NH_3\cdots O_2] + Ar \xrightarrow{k_1'} R_1 + \cdots$$

$$-d[NH_3]/dt = \frac{k_2k_1'^{1/2}K^{1/2}}{\sqrt{2}\,k_3^{1/2}} \times [NH_3]^{1.5}[O_2]^{0.5}[Ar]^{0.5} \qquad (6)$$

This agrees with experimental equation (3). However, the scheme described above is one of many possibilities of explaining the present results; the actual situation in the high-temperature oxidation of ammonia will not be so simple.

In order to explain the present experimental results, it is desirable to compare them with the theoretical rate law and the activation energy, which can be predicted by an analytical solution of several linear differential equation for an appropriate chain-branching scheme. However, no detailed data on elementary reactions are available for this purpose, and so the solution of this problem must be postponed.

The authors wish to express their thanks to Messrs. Kazutoshi Sugiyama and Akio Sawa for their help in the experiment.

[*2] Least-squares calculation by using all the data in Table I also gives a reaction order of about 0.5 with respect to argon. However, for the sake of simplicity, typical runs, all conducted under almost the same conditions, except for the argon concentration, in order to keep the effect of the ammonia and oxygen concentrations as small as possible, are shown in Fig. 7.

8) E. R. Stephens and R. H. Pease, *J. Am. Chem. Soc.*, **74**, 3480 (1952).

9) E. R. Stephens and R. H. Pease, ibid., **72**, 1188 (1950).

10) J. Vervimp and A. Van Tiggelen, *Bull. Soc. Chim. Belg.*, **62**, 205 (1953).

11) H. E. Avery and J. N. Bradley, *Trans. Faraday Soc.*, **60**, 857 (1964).