BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1761—1765 (1968)

Kinetic Studies of Ammonia Oxidation in Shock Waves. IV. Comparison of Induction Periods for the Ignition of NH_3-O_2-N_2 with Those for NH_3-O_2-Ar Mixtures

Hajime Miyama

Basic Research Loboratories, Toyo Rayon Company, Ltd., Tebiro, Kamakura, Kanagawa

(Received August 14, 1967)

Induction periods for ammonia oxidation in the NH_3-O_2-Ar and NH_3-O_2-N_2 mixtures were measured by monitoring an ultraviolet absorption of ammonia in reflected shock waves. For the NH_3-O_2-Ar mixtures, induction periods in the temperature range of 1450—2730°K were found to be expressed by

$$\log \tau_i[O_2]\ (\mathrm{mol}\cdot l^{-1}\mu\mathrm{sec}) = -(16.24\pm0.17) + (10080\pm320)/T$$

when oxygen content is in the range of 4—10%, and by

$$\mathrm{long}\ \tau_i(\mu\mathrm{sec}) = -(2.55\pm0.14) + (8810\pm220)/T$$

when the oxygen content is less than 1%. Values of induction periods for the 0.5% NH_3-0.5% O_2-99% N_2 and 1% NH_3-1% O_2-98% N_2 mixtures were also measured and compared with those for the NH_3-O_2 mixtures highly diluted with argon. Both results agreed well by taking into account vibrational relaxation of the reacting system if appropriate values of vibrational relaxation times for N_2 dilute in NH_3 is assumed. Therefore, possibility of coupling of vibrational relaxation of N_2 and oxidation reaction was considered to be small.

In the first paper of this series[1,2] we found a linear relationship between $\log\tau_i[O_2]$ and $1/T$ for the shock-heated NH_3-O_2-Ar mixtures where τ_i was induction period determined by the reaction between NH_2 and O_2. Thereafter, we[3] measured induction periods for the mixtures of 90% N_2-6% NH_3-4% O_2 and 90% N_2-4% NH_3-6% O_2, and made Arrhenius plots by assuming two possible cases; (a) nitrogen is relaxed translationally, rotationally and vibrationally, and (b) nitrogen is relaxed translationally and rotationally. Comparison of these plots with a plot for the NH_3-O_2-Ar mixtures showed that data calculated for the case (b) are very close to the plot for the NH_3-O_2-Ar mixtures at higher temperatures but those for the case (a) approach to the latter plot at lower temperatures. This phenomenon was attributed to the effect of vibrational relaxation of nitrogen which became comparable to the induction period of ammonia oxidation in certain temperature range. Also, it was considered that the coexistence of NH_3 and O_2 might shorten the vibrational relaxation time of N_2.

In order to minimize the effect of these additives and to examine the effect of vibrational relaxation of N_2 on the oxidation reaction, measurement of induction periods was performed for the NH_3-O_2 mixtures highly diluted with nitrogen and compared with those for the NH_3-O_2 mixtures highly diluted with argon.

Experimental

The experimental details have been described previously.[1-4] Induction periods were measured in reflected shock waves by monitoring the absorption of NH_3 at 2245 Å, 2300 Å or 2400 Å. One of these wavelengths was chosen depending on the NH_3 concentration because the extinction coefficient of NH_3 was higher at shorter wavelength. The mixtures used and experimental conditions were summarized in Table 1, where data for the mixtures VIII and X were taken from the previous report.[1]

Results and Discussion

The Induction Periods for NH_3-O_2-Ar Mixtures. Arrhenius plots of $\tau_i[O_2]$ for the mixtures I—XI are shown in Fig. 1. Here, data for the mixtures containing more than 4% oxygen are expressed by a straight line, a least-squares expressions of which is as follows:

$$\log\tau_i[O_2](\mathrm{mol}\cdot l^{-1}\cdot\mu\mathrm{sec}) = -(16.24\pm0.17) + (10080\pm320)/T \quad (1)$$

This indicates that the linear relation between

---

[1] T. Takeyama and H. Miyama, This Bulletin, **39**, 2352 (1966).

[2] T. Takeyama and H. Miyama, *ibid.*, **39**, 2609 (1966).

[3] H. Miyama and R. Endoh, *J. Chem. Phys.*, **46**, 2011 (1967).

[4] T. Takeyama and H. Miyama, *J. Chem. Phys.*, **42**, 3737 (1965); This Bulletin, **38**, 1670 (1965).

TABLE 1. EXPERIMENTAL CONDITIONS

Reaction mixture	Composition (%)				T_5 (°K)	P_5 (atm)	$[O_2]$ (10^{-3} mol/l)	τ_t (μsec)
	NH_3%	O_2%	Ar%	N_2%				
I	0.5	0.5	99	0	1560—2230	2.61—7.41	0.0851—0.264	50—1250 (NH_3 2245 Å)
II	1	0.5	98.5	0	2160—2370	3.63—3.92	0.094 —0.111	16— 37 (NH_3 2245 Å)
III	0.5	1	98.5	0	2140—2320	3.64—3.97	0.196 —0.220	11— 38 (NH_3 2245 Å)
IV	1	1	98	0	1560—2730	1.89—7.48	0.113 —0.555	4—1230 (NH_3 2245 Å)
V	2	1	97	0	2100—2580	3.41—4.05	0.161 —0.229	7— 36 (NH_3 2245 Å)
VI	2	2	96	0	1580—2320	1.98—7.75	0.222 —1.12	13— 950 (NH_3 2245 Å or 2300 Å)
VII	3	3	94	0	1530—2130	4.74—8.33	0.814 —1.84	50—1280 (NH_3 2400 Å)
VIII	6	4	90	0	1600—2300	3.49—4.51	0.741 —1.32	28—1360 (OH 3067 Å)
IX	5	5	90	0	1490—2320	3.73—7.66	0.980 —2.81	12—1850 (NH_3 2400 Å)
X	4	6	90	0	1550—2110	3.54—5.52	1.23 —2.47	37—1026 (OH 3067 Å)
XI	10	10	80	0	1450—2120	3.62—7.31	2.08 —6.06	12—1400 (NH_3 2400 Å)
XII	0.5	0.5	0	99	1530—2190 (1670—2490)	1.52—4.75 (1.47—4.66)	0.0504—0.184 (0.0439—0.165)	17—1580 (NH_3 2245 Å)
XIII	1	1	0	98	1530—2300 (1660—2600)	1.49—4.55 (1.45—4.47)	0.0956—0.364 (0.0804—0.328)	6—1600 (NH_3 2245 Å)

Note: Shock parameters calculated for mixtures XII and XIII correspond to case (a), and those corresponding to case (b) are shown in parentheses. T_5 and P_5 are temperature and pressure behind reflected shock waves.

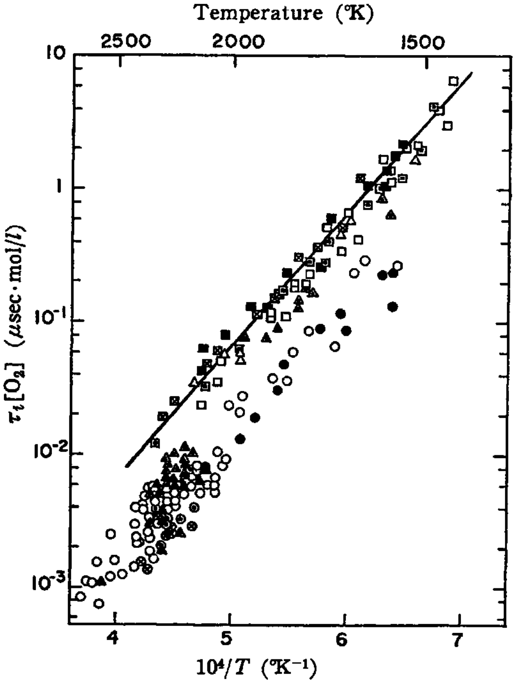

Fig. 1. Arrhenius plot for $\tau_t[O_2]$.

Marks ●, ⊗, ⊙ ○, ▲, ◬, △, ⊠, ⊡, ■, and □ refer to mixtures I, II, III, IV, V, VI, VII, VIII, IX, X, and XI respectively.

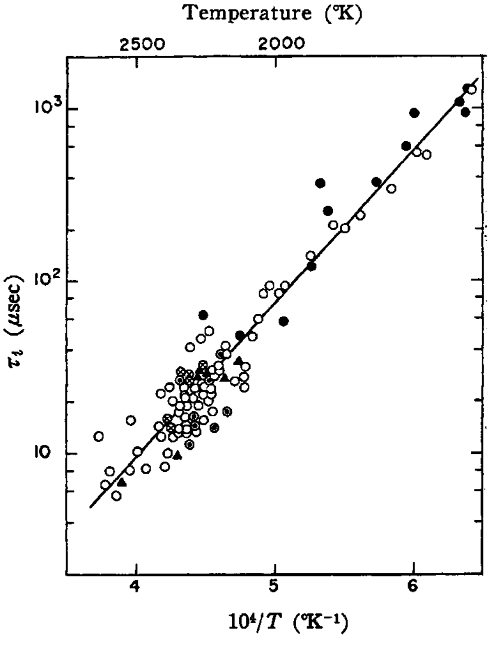

Fig. 2. Arrhenius plot for τ_t.

Marks are the same as in Fig. 1.

log $\tau_i[O_2]$ and $1/T$ obtained previously[1] holds over a wide range of oxygen concentration (4—10%).

However, when the oxygen content is less than 3%, log $\tau_i[O_2]$ decreases as the former decreases. Especially, when the oxygen content is less than 1%, the result is well expressed by a linear plot of log τ_i *via* $1/T$ as shown in Fig. 2, where the solid line obtained by a least-squares calculation is expressed by:

$$\log \tau_i(\mu\text{sec}) = -(2.55\pm0.14) + (8810\pm220)/T \qquad (2)$$

In order to explain this relationship from the viewpoint of chemical kinetics, available experimental data are not enough.

The Induction Periods for NH_3-O_2-N_2 Mixtures and Vibrational Relaxation of Nitrogen. According to the preliminary experiment, the dependence of τ_i on the oxygen content observed for NH_3-O_2-N_2 was similar in tendency to that for NH_3-O_2-Ar. In order to examine the effect of vibrational relaxation of nitrogen, it is desirable to use mixtures of small ammonia and oxygen contents. Therefore, detailed measurments were performed for the mixtures XII and XIII. The results are shown in Fig. 3, where a solid line is calculated by Eq. (2) and open and closed marks correspond to cases (a) and (b), respectively. These two cases were assumed to calculate reflected shock temperatures and oxygen concentrations from the initial pressures and incident shock velocities. As described previously,[4] nitrogen is considered to be relaxed translationally, rotationally, and vibrationally for (a), and to be relaxed translationally and rotationally for (b). In both cases, it was assumed that the internal degrees of freedom of ammonia and oxygen are completely relaxed. From the figure, it is obvious that data calculated for the case (b) agree with the plot for the NH_3-O_2-Ar mixtures at higher temperatures and those for the case (a) at lower temperatures.

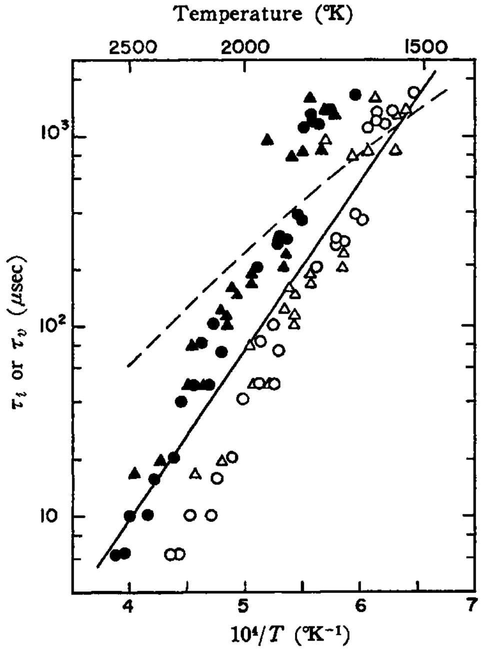

Fig. 3. Arrhenius plot for τ_i and $\tau_{N_2\text{-}N_2}$.

Triangles and circles refer to mixtures XII and XIII, respectively, open marks correspond to case (a) and closed marks to case (b), and a solid and a broken line were calculated from Eqs. (2) and (3).

Vibrational relaxation time of nitrogen, $\tau_{N_2\text{-}N_2}$, is given by the expression of Milliken and White[5] as follows.

$$\log P\tau_{N_2\text{-}N_2}(\text{atm}\cdot\text{sec}) = 102T^{-1/3} - 11.24 \qquad (3)$$

Values of $\tau_{N_2\text{-}N_2}$ calculaletd by substituting $P=3.0$ atm, which is an average of pressures behind reflected shock waves for the mixtures XII and XIII, are also shown in Fig. 3 by a broken line. From the figure, it is seen that $\tau_{N_2\text{-}N_2}$ is equal to τ_i for the NH_3-O_2-Ar mixtures at 1570°K, and that $\tau_{N_2\text{-}N_2}<\tau_i$ below this temperature and $\tau_{N_2\text{-}N_2}>\tau_i$ above it. Therefore, it is expected that the case (a) is applicable at lower temperatures and (b) at higher temperatures. However, the crossover temperature from (a) to (b) in Fig. 3 is higher than that expected. This is considered to be due to the effect of NH_3 and O_2 in shortening the vibrational relaxation time.[3]

It is well known[6] that translational temperature of polyatomic gas behind the shock wave decreases exponentially with time t as follows.

$$\frac{T-T_a}{T_b-T_a} = \exp\left(-\frac{C_p t}{C_p'\tau_v}\right) \qquad (4)$$

Here, T_a and T_b are shock wave temperatures corresponding to the cases (a) and (b), C_p is average specific heat at constant pressure, C_p' is C_p minus vibrational contribution, and τ_v is vibrational relaxation time. For the system diluted with argon, the temperature behind shock front is almost constant during the induction period. However, for the system diluted with nitrogen, the temperature decreases from T_b and approaches to T_a during the induction period according to Eq. (4). Therefore, instead of constant temperature in the case of argon dilution, average temperature must be adopted to define temperature of the system diluted with nitrogen. Thus, temperature T of the reaction system during the induction period τ_i is given as follows by using Eq. (4).

$$T=\frac{1}{\tau_i}\int_0^{\tau_i} T dt$$

---

5) R. C. Millikan and D. R. White, *J. Chem. Phys.*, **39**, 98 (1963).

6) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London (1961), p. 54.

$$= \frac{\tau_v}{\tau_i}\cdot\frac{C_p'}{C_p}(T_b-T_a)\left\{1-\exp\left(-\frac{C_p\tau_i}{C_p'\tau_v}\right)\right\} + T_a \qquad (5)$$

Therefore, if τ_v is known, it is possible to calculate temperature of the system from Eq. (5). According to the empirical expression of Millikan and White[7] (which is not correct theoretically but very useful) where only translation-to-vibration energy conversion was assumed, τ_v of the present system is expressed as follows.

TABLE 2. PARAMETERS USED FOR THE CALCULATION OF TEMPERATURES OF THE REACTION SYSTEM

Reaction mixture	T_a (°K)	T_b (°K)	P (atm)	C_p/C_p'	τ_i (μ sec)	T (°K)
XII	1550	1700	3.68	1.20	1320	1562
	1570	1720	4.71	1.20	1300	1579
	1590	1750	3.61	1.20	850	1608
	1640	1800	1.32	1.21	1580	1657
	1660	1830	4.66	1.21	800	1674
	1680	1860	3.13	1.22	790	1700
	1710	1890	3.57	1.22	240	1761
	1710	1890	1.93	1.22	210	1775
	1730	1920	1.78	1.22	970	1758
	1780	1980	2.86	1.22	170	1858
	1780	1980	3.50	1.22	190	1842
	1840	2050	1.50	1.22	160	1956
	1840	2050	2.75	1.23	105	1945
	1840	2050	4.30	1.23	110	1917
	1840	2050	3.31	1.23	170	1968
	1860	2080	3.15	1.23	130	1947
	1920	2160	2.65	1.23	50	2078
	1950	2190	3.07	1.23	50	2097
	1980	2230	2.51	1.24	80	2051
	2080	2350	2.41	1.25	20	2298
	2190	2490	2.29	1.25	17	2434
XIII	1550	1690	3.68	1.20	1600	1555
	1590	1740	3.61	1.20	1350	1596
	1610	1760	3.50	1.20	1200	1616
	1630	1790	1.62	1.21	1400	1642
	1630	1790	3.33	1.21	1250	1637
	1650	1820	3.11	1.21	1140	1658
	1650	1820	3.89	1.21	350	1670
	1680	1840	3.71	1.21	380	1698
	1700	1870	4.90	1.21	270	1719
	1730	1900	3.04	1.21	280	1758
	1730	1900	4.73	1.21	270	1749
	1780	1960	2.60	1.21	200	1823
	1780	1960	4.67	1.21	200	1805
	1890	2100	2.59	1.22	70	1987
	1910	2130	2.39	1.23	50	2034
	1910	2130	2.65	1.23	100	1987
	1940	2170	3.40	1.23	50	2045
	1940	2170	4.08	1.23	80	2006
	2010	2240	3.22	1.23	40	2127
	2040	2280	2.35	1.23	20	2218
	2110	2370	2.17	1.24	15	2315
	2140	2410	3.18	1.25	10	2352
	2220	2500	2.04	1.26	10	2454
	2260	2550	1.73	1.26	6	2523
	2300	2600	2.19	1.26	6	2564
	2300	2600	2.67	1.26	6	2557

$$(P\tau_v)^{-1} = \phi_{N_2}(P\tau_{N_2\text{-}N_2})^{-1} + \phi_{NH_3}(P\tau_{N_2\text{-}NH_3})^{-1} + \phi_{O_2}(P\tau_{N_2\text{-}O_2})^{-1} \qquad (6)$$

Here, relaxation times with two subscripts refer to relaxation of the first species when it is present at high dilution in the second-named gas at a total pressure of P atm, and ϕ_s' are mole fractions of components. Although $\tau_{N_2\text{-}O_2}$ is not known, this can be estimated by using an empirical formula of Millikan and White[7] and was found to be comparable to $\tau_{N_2\text{-}N_2}$. Since $\phi_{N_2} \gg \phi_{O_2}$ in the present experimental conditions, the third term in Eq. (6) can be neglected. Therefore, Eq. (6) is expressed as follows.

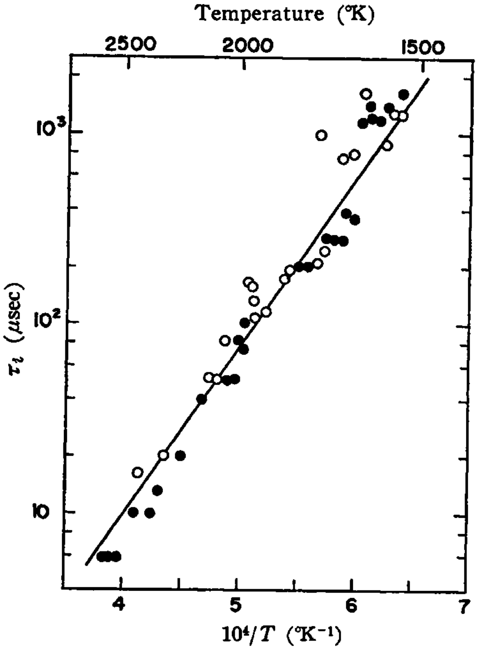

Fig. 4. Arrhenius plot for τ_i.

Marks ○ and ● refer to mixtures XII and XIII respectively and a solid line was calculated from Eqs. (2).

$$(P\tau_v)^{-1} = \phi_{N_2}(P\tau_{N_2\text{-}N_2})^{-1} + \phi_{NH_3}(P\tau_{N_2\text{-}NH_3})^{-1} \qquad (7)$$

Here, $\tau_{N_2\text{-}N_2}$ is given by Eq. (3), but no information about $\tau_{N_2\text{-}NH_3}$ is available. How-

---

[7] R. C. Millikan and D. R. White, *J. Chem. Phys.*, **39**, 3209 (1963).

ever, recently, White[8] found that $\tau_{N_2\text{-}He}$, $\tau_{N_2\text{-}C_2H_2}$, and $\tau_{N_2\text{-}CH_4}$ are approximately double, equal to, and 60% of $\tau_{N_2\text{-}H_2}$ in the range of 1600 to 2500°K. Since vibrational frequencies of NH_3 are not close to those of N_2, much more rapid vibration-to-vibration exchange between N_2 and NH_3 compared with that between N_2 and C_2H_2 or CH_4 is not expected and $\tau_{N_2\text{-}NH_3}$ may be comparable to $\tau_{N_2\text{-}C_2H_2}$ or $\tau_{N_2\text{-}CH_4}$, that is, to $\tau_{N_2\text{-}H_2}$. Therefore, as a rather reasonable approximation, let us assume

$$\tau_{N_2\text{-}NH_3} \doteqdot \tau_{N_2\text{-}H_2} \tag{8}$$

By using an expression for $\tau_{N_2\text{-}H_2}$ given by White,[9] $\tau_{N_2\text{-}NH_3}$ is expressed as follows.

$$\log P\tau_{N_2\text{-}NH_3} \doteqdot 35.0(T^{-1/3} - 0.0176) - 8.00 \tag{9}$$

From Eqs. (3), (5), (7), and (9), temperature of the present system can be calculated with a computor by using known values of T_a, T_b, P, C_p/C_p' and τ_i as shown in Table 2, where reflected shock pressure P is an average of those for (a) and (b) since difference between them is less than 0.5% at maximum. Also, calculated values of the temperature T are shown in the table. Thus, in Fig. 4, values of τ_i is plotted against newly obtained values of T. Here, excellent agreement between both polts for NH_3-O_2-N_2 and NH_3-O_2-Ar is observed. This agreement suggests that τ_i for the NH_3-O_2-N_2 is the same as that for NH_3-O_2-Ar and possibility of coupling of vibrational relaxation and oxidation reaction is small. However, we cannot say that it is conclusive unless $\tau_{N_2\text{-}NH_3} \doteqdot \tau_{N_2\text{-}H_2}$ is proved. It is a very challenging problem to measure vibrational relaxation times for N_2 dilute in NH_3 and to obtain more detailed informations about kinetics of NH_3-O_2-N_2 system.

The author wishes to express his thanks to Dr. Soji Tsuchiya for his helpful advice, to Mr. Kazutoshi Sugiyama for his help in the experiment, and to Mr. Takashi Suzuki for reviewing the manuscript.

---

[8] D. R. White, *ibid.*, **48**, 525 (1968).
[9] D. R. White, *ibid.*, **46**, 2016 (1967).