

THERMAL DECOMPOSITION OF NITROUS OXIDE
BY SINGLE-PULSE SHOCK TUBE
—THE EFFECT OF H_2O ADDITION AND
THE RELIABILITY OF MAGIC HOLE TYPE SHOCK
TUBE AS A TOOL FOR KINETIC STUDY—

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I. *Summary*

The effect of water vapour on the thermal decomposition of nitrous oxide was examined using magic hole type single-pulse shock tube. Temperature range was 1270–1600 K and total gas concentration behind reflected shock wave was about 2.5×10^{-5} mol/cc. Nitrous oxide was largely diluted to about 6000 ppm with argon. For addition experiments, water was added to the mixture gas so that the water concentration was 200 ppm and 1000 ppm. Addition of water showed no significant effect on the nitrogen formation rate.

The temperature elevation during reflected shock heating was observed unfortunately due to the generation of compressive wave caused by the interaction between boundary layer and reflected shock wave. Temperature decreased rather rapidly after arrival of rarefaction fan. Consequently, temperature was not constant behind the reflected shock wave. The correction was made for such temperature changes. The rate constant obtained after correction showed a reasonable value.

II. *Introduction*

Magic hole type single-pulse shock tube of small size is one of the most convenient tool for high temperature gaseous reaction study because it can be easily operated to reach thousands degree of temperature with only small amount of sample gas. The kinetic data from the tool, however, is often accompanied by less reliability mainly because the gaseous system is too small to prevent the boundary layer influence.

In the present report, the effect of addition of water vapour to the reaction system and the possible improvement in the kinetic data obtained are major interest. Since water vapour can be a most probable impurity in a reaction sample due to the desorption from glass wall, its effect on rate constants should be clarified. It is advantageous to choose the decomposition reaction of nitrous oxide as a test gas because its kinetics has been extensively studied and established by many authors.

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III. Experimental

The shock tube used was made of pyrex glass with 4 cm i.d.. The 277cm long driven section consisted of three parts: brass tube to which the damp tank was attached; the pyrex tube; and a brass end block. Three piezoelectric pressure transducers were mounted in a line on the side wall of the end block. The distances between the neighbouring two transducers were set to be equal each other (23.1 cm). The signals from transducers were fed into the pulse counter with two channels through pulse trimmig circuits. The speed of incident shock wave at the tube end was calculated from the time intervals measured by the counter. The pressure profile at the end wall was measured by the high frequency pressure transducer (Sundstrand 601B) located at the center of end plate.

Nitrous oxide was obtained from Takachiho Co. Ltd.. It was purified by trap to trap distillation using liquid nitrogen and dryice-acetone refrigerants. After the purification nitrogen and oxygen were less than 3 ppm. Water vapour was obtained from distilled water which was evacuated at dryice-acetone temperature in advance.

For the water free experiments two kinds of mixture were used: 6100 and 6400 ppm. N_2O in Ar, respectively. For the water added experiments the following two mixtures were used: the ratio of N_2O to H_2O in Ar were 6740 ppm/180 ppm and 5570 ppm/1080 ppm.

It was somewhat troublesome to determine the water vapour content in a reaction gas mixture because of the adsorption of water on wall. Metal tank of 20 l volume plated with chromium was used as a reservoir of reaction gas mixture. The water sensor (Panametrics Hygrometer Model 2000) whose operation principle is based on impedance change of porous aliminum oxide with absorbing water vapour, was mounted on the wall of the tank. It required about 30 minutes for the meter reading of the water sensor to reach at equilibrium. Since metal tank was so strong that pressurized gas mixture was stored. The higher partial pressure of water vapour enabled the determination to be more accurate. In order to complete mixing, reaction gas mixture was kept more than one day before use. After measuring the water vapour level, reaction gas mixture was introduced into the driven section through pneumatic valve. After flushing the driven section two or three times with reaction mixture gas itself, it was charged and instantly shock heated.

Immediately after shock heating, products gas mixture was taken through pneumatically actuated valve into a glass vessel evacuated in advance.

IV. Results and Discussion

Effect of Water Vapour Addition

Dwell time was considered practically constant (1 ± 0.1 ms) during all runs. Fig. 1 shows the plots of $\log(A[N_2]/[N_2O]_0)$ vs. $1/T$ where $[N_2O]_0$ denotes initial concentration of nitrous oxide. It can be seen from the figure that the difference in the rate was not significant between water added (200 ppm and 1000 ppm water vapour) and water free systems. The ratio $[O_2]/[N_2]$ in the product gas was shown in Fig. 2. No effect of water vapour addition on the ratio was also recognized.

FIG. 1 COMPARISON OF DECOMPOSITION RATE BETWEEN H_2O FREE AND H_2O ADDED SYSTEMS

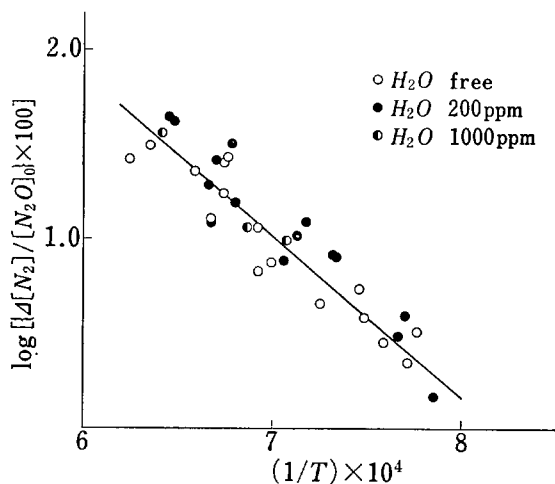
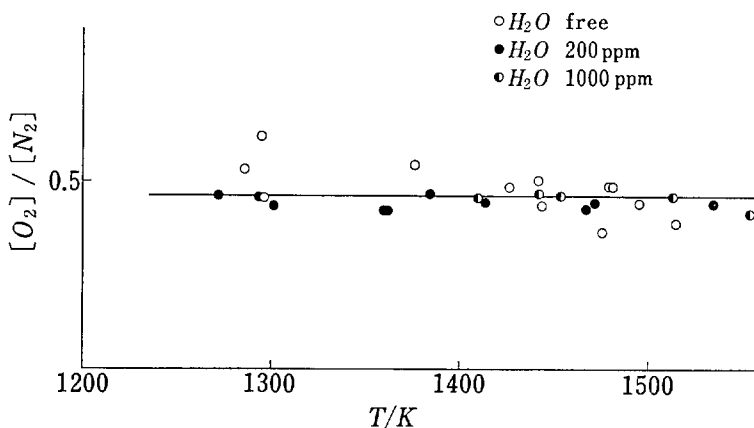
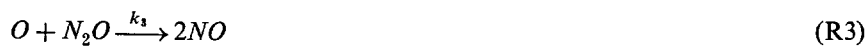


FIG. 2 COMPARISON OF THE PRODUCTS RATIO BETWEEN H_2O FREE AND H_2O ADDED SYSTEMS

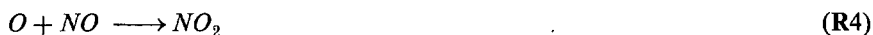


Thermal Decomposition Mechanism and Rate Expression

The rate of N_2 formation obtained were analyzed on the basis of steady state condition for oxygen atom concentration. There is an agreement among many authors that the following three reactions are major processes of N_2O decomposition at high temperature,



An estimation of the rate constant of reaction **R1** would depend upon whether the steady state approximation for the concentration of oxygen atom produced as an intermediate was valid or not. Gutman et al [1] has studied nitrous oxide decomposition using reflected shock wave with mass spectrometer attached to the tube over the temperature range 1800–3500 K and concluded that the steady state approximation could be made for the oxygen atom. Lipkea et al [2] reported the overall N_2O decomposition rate constant, k_{obs} , was two times larger than the rate constant k_1 using single-pulse shock tube over the temperature range 1300–1950 K. The result is consistent with the steady state assumption. Validity of steady state is further supported when the relative importance of reaction **R2** and **R3** increase in lower temperature range as in the present work because the activation energy of reaction **R1** is higher than the others. This assumption can be more fortified considering the following points. If the rate of **R1** should be much faster than the rates of **R2** and **R3**, then the concentration of oxygen atom would continue to increase during high temperature just after reflected shock wave. But when the cooling process starts to begin, **R1** becomes slower and unstable oxygen atom has to react by some chemical reactions and to change to stable products. Possible competitive reaction with reaction **R2** and **R3** at lower temperature are the following reactions according to the photo-decomposition study [3] of nitrous oxide at room temperature,



By comparison of rate constants, however, it is found that reaction **R2** and **R3** should be predominant over the reactions **R4** or **R5** at 800 K or above. Therefore oxygen atoms accumulated during high temperature period would be consumed via only reactions **R2** and **R3** and the products distribution might be expected to be the same as in steady state condition.

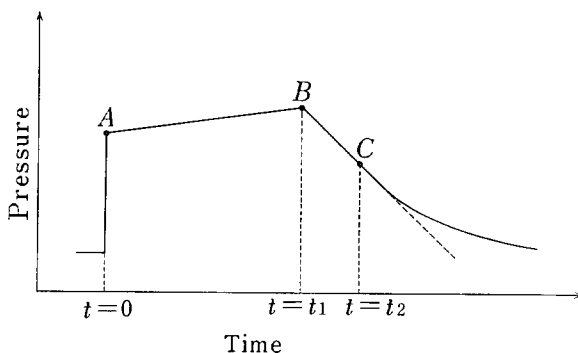
On the basis of steady state approximation, the rate constant of nitrogen formation, k_{N_2} , can be related with k_{obs} . The assumption of $k_2 = k_3$ is adopted after many authors and then the relation is expressed as follows,

$$k_{N_2} = (3/4)k_{obs} \quad (\text{Eq. 1})$$

The Correction of Rate Constant

The theory of shock wave predicts that the pressure behind reflected shock wave increases almost immediately to a constant value and keep it until rarefaction fan comes. We call this period " T_5 " region. Shock tube with small diameter like ours, however, unfortunately does not show such typical " T_5 " region. In our case the pressure behind reflected shock wave continues to increase till the arrival of rarefaction fan and after then it begins to decrease. This small increase of pressure is considered to be due to the compressive wave [4] caused by the interaction between reflected shock wave and boundary layer formed during the propagation of incident shock wave. Our pressure profile can be adequately approximated linearly with time as shown in Fig. 3. By assuming the adiabatic and reversible process for such pressure changes, the resultant rates of temperature change were calculated to be 1×10^5 deg/sec for increasing and -4×10^5 deg/sec for decreasing, respectively. In order to correct apparent decomposition rates affected by the temperature change, we employed

FIG. 3 SCHEMATIC PRESSURE PROFILE BEHIND REFLECTED SHOCK WAVE



a method similar to that used by *E. Tschuikow-Roux et al* [5] in a cooling region. That is to say, we assumed that the pressure change process was simply adiabatic and reversible and that the reaction in problem was the first order reaction. So far as the latter assumption there is an agreement among many authors that overall rate expression of the decomposition is represented as follows,

$$\frac{d[N_2O]}{dt} = k[M][N_2O]. \quad (\text{Eq. 2})$$

Since the total concentration, $[M]$, can be regarded as approximately constant through our experimental runs, the following pseud first order rate expression is effective,

$$\frac{d[N_2O]}{dt} = k_{obs}[N_2O]. \quad (\text{Eq. 3})$$

As shown precisely in the Appendix, the corrected rate constant, k_c , is related to the observed rate constant, k_{obs} , as follows,

$$k_c = \frac{1}{-(\epsilon/t_1 + \theta\epsilon'/t_1)} k_{obs} \quad (\text{Eq. 4})$$

where

$$\epsilon = \frac{R(T_0^0)^2}{Em} \left\{ 1 - \exp\left(-\frac{E\Delta T}{R(T_0^0)^2}\right) \right\}$$

$$\epsilon' = \frac{R(T_0^1)^2}{Em'} \left\{ 1 - \exp\left(-\frac{E\Delta T'}{R(T_0^1)^2}\right) \right\}.$$

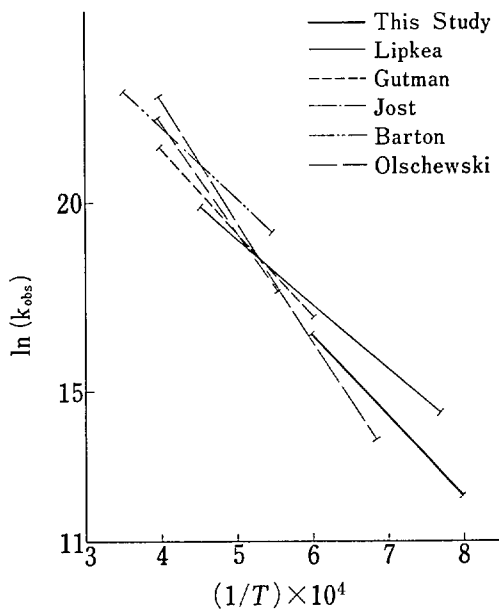
If putting $m=0$ in Eq. 4, then it becomes Eq. 5 which is identical with the one derived by *E. Tschuikow-Roux*.

$$k_c = \frac{1}{1 - \epsilon'/t_1} k_{obs}. \quad (\text{Eq. 5})$$

In Table 1, $k_c/[M]$ and correction factor f defined as the ratio of k_c/k_{obs} , are shown. The factor f varies rather widely and it requires the correction necessarily. The temperature dependence of the corrected rate constants is in Fig. 4 together with the literature values. It seems to be quite reasonable and significant in the lowest temperature range.

TABLE 1 CORRECTED RATE CONSTANT AND CORRECTION FACTOR

Run	H ₂ O (ppm)	T/K	{ <i>k_c</i> /[<i>M</i>]} × 10 ⁻⁶ *	<i>f</i>
1	0	1287	0.49	2.80
2	0	1296	0.44	1.99
3	0	1378	0.59	2.47
4	0	1428	1.05	2.98
5	0	1478	5.68	1.81
6	0	1482	4.67	1.31
7	0	1483	3.65	2.80
8	0	1602	5.84	1.58
9	200	1273	0.16	3.26
10	200	1296	0.72	1.74
11	200	1303	0.41	2.65
12	200	1345	1.38	1.95
13	200	1364	1.07	2.71
14	200	1393	1.51	3.23
15	200	1402	1.98	2.18
16	200	1415	1.45	1.90
17	200	1469	1.60	3.93
18	200	1474	5.34	2.65
19	200	1486	3.09	2.29
20	200	1501	3.81	1.67
21	200	1503	2.14	3.45
22	200	1537	3.25	4.11
23	200	1543	2.91	1.85
24	200	1549	3.93	4.68

* Unit is cc·mol⁻¹·s⁻¹.FIG. 4 COMPARISON OF THE *k_{obs}* WITH THAT OF OTHER WORKERS

Conclusively saying, a Single-Pulse Shock Tube Technique gives a reasonable kinetic data, if an appropriate correction is made. Though data shows comparatively large scattering as seen also in the result of Lipkea et al. This type of simple apparatus, therefore, is suitable for the purpose of elucidation of reaction mechanism and the rough estimation of reaction rate.

V. Appendix

The pressure profile behind reflected shock wave is assumed to be essentially the one illustrated in Fig. 3. Then the following Eqs. represent pressure increasing region A-B and decreasing region B-C respectively,

$$P(t) = P_5^0 + \left(\frac{dP}{dt}\right)_{01} t \quad \text{for } 0 \leq t \leq t_1 \quad (\text{Eq. 1})$$

$$P(t) = P_5' + \left(\frac{dP}{dt}\right)_{12} (t - t_1) \quad \text{for } t_1 \leq t \leq t_2 \quad (\text{Eq. 2})$$

where the thermodynamic state at $t=0$ is assumed to be just same as the one calculated from the observed shock speed. The coefficients $(dp/dt)_{01}$, $(dp/dt)_{12}$ are the slopes of the pressure-time plot in each region. Apparently $(dp/dt)_{01}$ has positive sign $(dp/dt)_{12}$ has negative. For adiabatic and reversible process, the following equation holds,

$$\frac{P(t)}{P(t')} = \left[\frac{T(t)}{T(t')}\right]^{\frac{\gamma}{\gamma-1}} \quad (\text{Eq. 3})$$

where γ denotes the ratio of C_p to C_v . From Eqs. 1, 2 and 3, the differential coefficients of temperature in each region are represented as follows,

$$m_{01} = \left(\frac{dT}{dt}\right)_{01} = \frac{\gamma-1}{\gamma} \left(\frac{T_5^0}{P_5^0}\right) \left(\frac{dP}{dt}\right)_{01} \quad \text{for } 0 \leq t \leq t_1 \quad (\text{Eq. 4})$$

$$m_{12} = \left(\frac{dT}{dt}\right)_{12} = -\frac{\gamma-1}{\gamma} \left(\frac{T_5'}{P_5'}\right) \left(\frac{dP}{dt}\right)_{12} \quad \text{for } t_1 \leq t \leq t_2 \quad (\text{Eq. 5})$$

where T_5' and P_5' are temperature and pressure at maximum point B in the profile. On the other hand, Eq. 6 is effective for the first order reaction,

$$-\frac{dN(t)}{dt} = N(t)A \exp\left(\frac{-E}{RT(t)}\right). \quad (\text{Eq. 6})$$

Then term $T(t)$, temperature at time t , in Eq. 6 can be obtained from Eq. 3 in the region $0 \leq t \leq t_1$. Thus,

$$T(t) = T_5^0 \left\{ 1 + \frac{1}{P_5^0} \left(\frac{dP}{dt}\right)_{01} t \right\}^{\frac{\gamma-1}{\gamma}}. \quad (\text{Eq. 7})$$

The reciprocal expression of Eq. 7 is,

$$\frac{1}{T(t)} = \frac{1}{T_5^0} \left\{ 1 + \frac{1}{P_5^0} \left(\frac{dP}{dt}\right)_{01} t \right\}^{-\frac{\gamma-1}{\gamma}}. \quad (\text{Eq. 7'})$$

Taylor expansion can be done with respect to the term $(1/P_5^0)(dP/dt)_{01}t$ in the parenthesis of Eq. 7. As the pressure change, $(dP/dt)_{01}t$, is always much smaller than the initial pressure P_5^0 experimentally, the higher terms more than second order can be neglected and we obtain the Eq. 8,

$$\frac{1}{T(t)} \simeq \frac{1}{T_5^0} \left\{ 1 - \left(\frac{m}{T_5^0} \right) t \right\}. \quad (\text{Eq. 8})$$

Now we can integrate Eq. 8 analytically,

$$- \int_{N_0}^{N_1} \frac{1}{N} dN = A \int_0^{t_1} \exp \left\{ - \frac{E}{RT_5^0} \left(1 - \frac{m}{T_5^0} t \right) \right\} dt.$$

Thus,
$$\ln \left(\frac{N_0}{N_1} \right) = A \exp \left(- \frac{E}{RT_5^0} \right) \int_0^{t_1} \exp \left(\frac{Em}{R(T_5^0)^2} t \right) dt$$

$$= -k_c \frac{R(T_5^0)^2}{Em} \left\{ 1 - \exp \left(\frac{Em}{R(T_5^0)^2} t_1 \right) \right\} \quad (\text{Eq. 9})$$

where N_0 and N_1 are the total number of the reactant molecule at $t=0$ and $t=t_1$, respectively. Similar treatment can be done in the time region $t_1 \leq t \leq t_2$, provided that t_2 value is characterized as following. We defined the time as t_2 when the pressure change rate decreases to one hundredth of it at time t_1 . As the corresponding pressure change $\Delta p' = p'_5 - p(t_2)$ is also smaller than p'_5 , then similar expression as Eq. 9 is derived,

$$\ln \left(\frac{N_1}{N_2} \right) = -k'_c \frac{R(T'_5)^2}{Em'} \left\{ 1 - \exp \frac{Em'}{R(T'_5)^2} (t_2 - t_1) \right\} \quad (\text{Eq. 10})$$

where $k'_c = A \exp \left(- \frac{E}{RT'_5} \right)$.

By introducing ΔT and $\Delta T'$, Eqs. 9 and 10 become Eqs. 11 and 12 respectively,

where $\Delta T = T'_5 - T_5^0 = T(t_1) - T_5^0 = mt_1$ and

$$\Delta T' = T'_5 - T(t_2) = T(t_1) - T(t_2) = -m'(t_2 - t_1),$$

$$\ln \left(\frac{N_0}{N_1} \right) = -k_c \frac{R(T_5^0)^2}{Em} \left\{ 1 - \exp \left(\frac{E \Delta T}{R(T_5^0)^2} \right) \right\} \quad (\text{Eq. 11})$$

$$\ln \left(\frac{N_1}{N_2} \right) = -k'_c \frac{R(T'_5)^2}{Em'} \left\{ 1 - \exp \left(\frac{-E \Delta T'}{R(T'_5)^2} \right) \right\}. \quad (\text{Eq. 12})$$

The rate constant k'_c can be related with k_c as follows,

$$k'_c = A \exp \left(- \frac{E}{RT'_5} \right) = A \exp \left\{ - \frac{E}{R(T_5^0 + \Delta T)} \right\} \simeq A \exp \left\{ - \frac{E}{RT_5^0} \left(1 - \frac{\Delta T}{T_5^0} \right) \right\}$$

$$= k_c \exp \left(\frac{E \Delta T}{R(T_5^0)^2} \right) = k_c \theta \quad (\text{Eq. 13})$$

where $\theta = \exp \left(\frac{E \Delta T}{R(T_5^0)^2} \right)$.

Equation 12 can be rewritten by using Eq. 13,

$$\ln\left(\frac{N_1}{N_2}\right) = -k_c\theta \frac{R(T'_5)^2}{Em'} \left\{1 - \exp\left(-\frac{E\Delta T'}{R(T'_5)^2}\right)\right\}. \quad (\text{Eq. 14})$$

By adding Eq. 11 and Eq. 14, we obtain the next,

$$\ln\left(\frac{N_0}{N_2}\right) = -k_c\varepsilon - k_c\theta\varepsilon' \quad (\text{Eq. 15})$$

$$\text{where } \varepsilon = \frac{R(T_5^0)^2}{Em} \left\{1 - \exp\left(-\frac{E\Delta T}{R(T_5^0)^2}\right)\right\} \text{ and } \varepsilon' = \frac{R(T'_5)^2}{Em'} \left\{1 - \exp\left(-\frac{E\Delta T'}{R(T'_5)^2}\right)\right\}.$$

As the observable quantities are N_1 , N_2 and dwell time t_1 , the following expression holds,

$$\ln\left(\frac{N_0}{N_2}\right) = k_{obs}t_1 \quad (\text{Eq. 16})$$

where k_{obs} denotes the apparent first order rate constant. By Eqs. 15 and 16 we obtain the final result.

$$k_c = \frac{-1}{\frac{\varepsilon}{t_1} + \frac{\theta\varepsilon'}{t_1}} k_{obs} \quad (\text{Eq. 17})$$

when we put $\Delta T = 0$, in other words, there is no temperature rise in the time region $0 \leq t \leq t_1$ then,

$$\lim_{\Delta T \rightarrow 0} \varepsilon \longrightarrow -\frac{\Delta T}{m} = -t_1.$$

Therefore,

$$\lim_{\Delta T \rightarrow 0} k_c = \frac{1}{1 - \frac{\theta\varepsilon'}{t_1}} k_{obs}.$$

As k'_c equals to $k_c(\theta = 1)$ at $\Delta T = 0$, next relation is derived,

$$k_c = \frac{1}{1 - \frac{\varepsilon'}{t_1}} k_{obs}. \quad (\text{Eq. 18})$$

This equation is just identical with the one reported by E. Tschuikow-Roux et al.

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