

Shock-tube Studies of N₂O Decomposition and N₂O–H₂ Reaction

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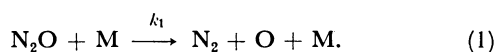
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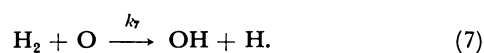
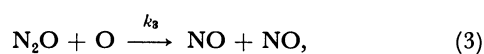
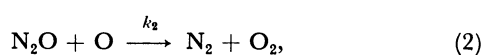
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N₂O decomposition and N₂O–H₂ reaction were studied behind incident and reflected shock waves in the temperature range 1450–2200 K and pressure range 0.6–3.5 atm using both single-pulse and time-resolve techniques. A computer-simulation study was performed to determine the rate-constant expressions of important elementary reactions. Computer calculations showed that the values of the rate constant for N₂O+O $\xrightarrow{k_2}$ N₂+O₂ and N₂O+O $\xrightarrow{k_3}$ NO+NO (cited in current papers) are too low. The rate-constant expressions were found to be $k_2=7.0\times 10^{14} \exp(-28 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_3=5.6\times 10^{14} \exp(-28 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rate constant expression for N₂O+H $\xrightarrow{k_4}$ N₂+OH, was found to be $k_4=1.5\times 10^{14} \exp(-15 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

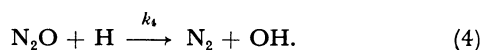
The decomposition of N₂O and the reaction of N₂O–H₂ have been extensively studied at high temperatures (above 1000 K) by many workers.^{1–18} Previous experimental studies have shown that an initiation step in both the N₂O decomposition and the N₂O–H₂ reaction is the breaking of the nitrogen-oxygen bond.



The values of k_1 reported are in agreement within a factor of approximately 2 to 3. However, the reported activation energies (E_1 's) scatter between 61 and 40 kcal/mol. Even in recent years, Sulzmann *et al.*,¹⁸ Endo *et al.*,¹⁷ Dean *et al.*¹⁶ and Roth and Just¹⁵ have reported $E_1=56$, 57.6, 51.7, and 61 kcal/mol, respectively. The oxygen atoms generated by reaction (1) react with N₂O or H₂ as follows,



Values of the rate constants published for reactions (2) and (3) are widespread. The reported ratios of k_3/k_2 separate almost into two groups over the same temperature range; one is $k_3/k_2=0.9\text{--}1.2$,^{5,6,8,13,18} other is $k_3/k_2=0.3\text{--}0.5$.^{3,10} The reported values of the rate constant of reaction (4) are also scattered.



In this study, we wish to report the rate constants k_1 , k_2 , k_3 , and k_4 , with which we can interpret both the N₂O decomposition and the N₂O–H₂ reaction over the temperature range 1450–2200 K.

Experimental

The apparatus and procedures have already been de-

scribed in detail,^{19,20} so only a brief description is given here. Infrared emission through two 0.8 mm slits and an interference filter ($\lambda_{\text{max}}=4.68 \mu\text{m}$, half-width=0.1 μm) was observed with a Fujitsu IV-200C4 InSb detector to study the time variation of the N₂O concentration. In runs using reflected shock waves, reacted gas mixtures were introduced to a pre-evacuated container made of Aluminum (25 cc in volume) through a valve near an end-plate after about 20 s from the infrared-emission measurements. The reacted mixtures were analyzed on a mass spectrometer (Nihondenshi-JMS-01SG-2). In the analysis, the isotope ³⁶Ar (0.34%), which was included in ⁴⁰Ar, was used as a reference material. Since the concentration of ³⁶Ar was comparable to NO and O₂ concentrations produced in our experiment, it was possible to accurately determine these concentrations. The energy of the ionizing electron beam was 12 eV. The use of such a relatively low voltage has a major advantage. The formation of fragment ions was almost completely eliminated, thus simplifying the interpretation of the mass spectra. A measurement of absolute concentrations is possible using relative sensitivity factors. These factors were determined under conditions as close as possible to those used in the determination of the product concentration during the N₂O decomposition and the N₂O–H₂ reaction. The analyzed peaks of the reacted gases were of mass numbers, 44, 32, and 30, corresponding to N₂O, O₂, and NO, respectively. No peak was found at a mass number of 46 (NO₂). In the determination of the O₂ concentration, the background signal at a mass number of 32 was subtracted from the O₂ signal.

Data interpretation was achieved by computer simulation. The computer calculations^{20,21} and the effective heating time used²⁰ were essentially the same as described previously. The temperature of the reaction system increases as the reaction progressed because the decomposition of N₂O and N₂O–H₂ reaction are exothermic. This temperature change might affect the N₂O emission intensity greatly. Hence, simulations of time-variations were carried out with programs that considered the dependence of the emission-intensity on temperature.

The compositions of employed reaction mixtures were as follows: (A) 2.0% N₂O, 98.0% Ar; (B) 2.0% N₂O, 1.0% H₂, 97.0% Ar; (C) 1.0% N₂O, 0.5% H₂, 98.5% Ar; (D) 0.5% N₂O, 1.0% H₂, 98.5% Ar. The N₂O decomposition with mixture (A) and N₂O–H₂ reaction with mixtures (B)–(D) were studied behind incident (1500 K < T_2 < 2200 K, 0.6 atm < P_2 < 1.1 atm) and reflected (1500 K < T_5 < 2100 K, 2.0 atm <

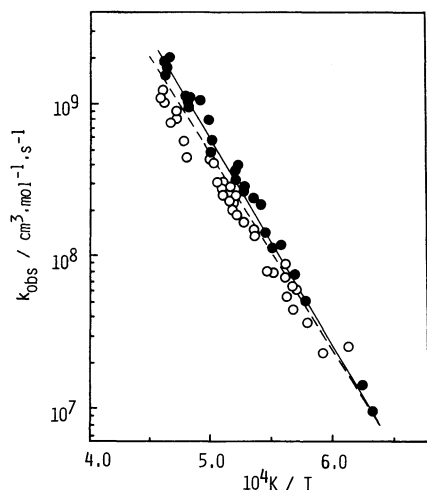


Fig. 1. Arrhenius plot showing comparison of the present results with data of other works.

●: Observed behind incident shock waves with mixture (A); ○: Observed behind reflected shock waves with mixture (A); —: $2k_1$ reported by Roth and Just; - - - -: $2k_1$ observed by Olschewski *et al.* and Endo *et al.*

$P_5 < 3.5$ atm) shock waves with both single-pulse and time-resolve techniques. H_2 and Ar, specified to be 99.9 and 99.99% pure, respectively, were obtained from commercial cylinders and were used without further purification. The N_2O gas obtained from a commercial cylinder was purified by trap-to-trap distillations. The purity (99.9% or higher) was confirmed by a gas-chromatographic analysis.¹⁹⁾

Results and Discussion

The time variation of the N_2O concentration at $4.68 \mu m$ was observed behind incident and reflected shock waves with mixture (A). The observed rate constant, k_{obsd} , for N_2O decomposition was calculated from the initial slope (within $20 \mu s$) of the time variation. The values of $k_{obsd} = 2.6 \times 10^{15} \exp(-60.7 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ obtained with incident shock waves are in good agreement with the values of the $2k_1$ reported by Roth and Just,¹⁵⁾ and are similar to the $2k_1$ reported by Olschewski *et al.*⁴⁾ and Endo *et al.*¹⁷⁾ as shown in Fig. 1. The values of $k_{obsd} = 6.24 \times 10^{14} \exp(-56.9 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ obtained with reflected shock waves, however, are slightly lower than those obtained with incident shock waves. The deviation between the two is larger at high temperatures than at low temperatures. This shows that the initial temperatures (within $20 \mu s$) behind reflected shock waves are somewhat lower than those calculated from incident shock speeds. The real gas temperatures at the reflected shock front are considered to be $70 \pm 40 \text{ K}$ lower than those calculated. This finding is consistent with that reported by Tsuchiya and Kuratani.²⁵⁾ This phenomenon has also been reported by several workers,^{22–25)} who showed that the pressure and temperature slowly increased with time after the arrival of re-

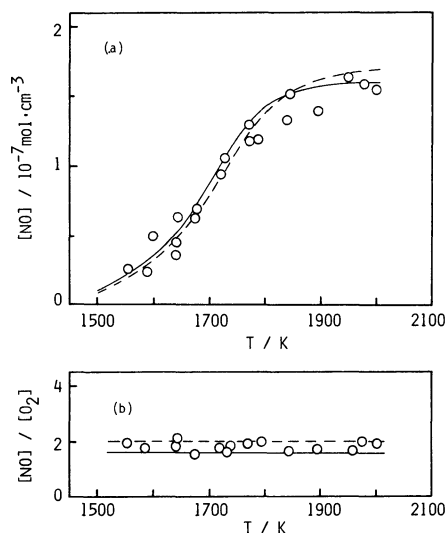


Fig. 2. Relationship between $[N_2O]$ or $[NO]/[O_2]$ and temperature.

○: Observed with mixture (A); —: computed with Table 1; - - - -: computed with the mechanism and rate constant expressions reported by Baulch *et al.*

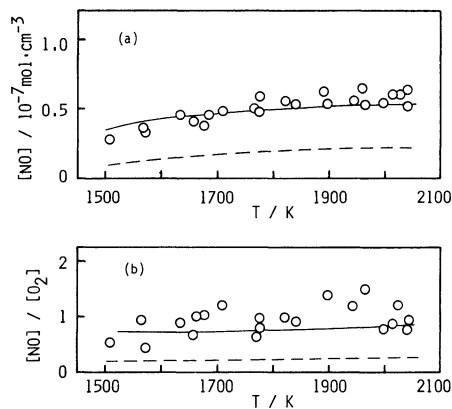


Fig. 3. Relationship of $[NO]$ or $[NO]/[O_2]$ and temperature.

○: Observed with mixture (B); —: computed with Table 1; - - - -: computed with the mechanism and rate constant expressions reported by Baulch *et al.*

flected shock waves. The average temperature during the reaction time (about $1000 \mu s$) was also shown to be comparable to the temperature calculated from the incident shock speed.²⁵⁾ The temperature under our experimental condition, however, should be examined, since the temperature parameter is very important in calculating the rate constants. Since the mechanism and rate constant expressions of the H_2-O_2 reaction are known very well, it is possible to check the average temperature behind reflected shock waves by comparing the observed results with the calculated ones. By using the same method as mentioned in a previous paper,²¹⁾ the temperatures behind reflected shock waves were examined. The average temperature during $100-1200 \mu s$ was shown to be almost the same as that

TABLE 1. ELEMENTARY REACTIONS AND RATE CONSTANT EXPRESSIONS^{a)}

	Reaction	<i>A</i>	<i>n</i>	<i>E</i>	Ref. ^{b)}
1	N ₂ O+M=N ₂ +O+M	1.4×10 ¹⁵	0.0	61200	15
2	N ₂ O+O=N ₂ +O ₂	7.0×10 ¹⁴	0.0	28000	This work
3	N ₂ O+O=NO+NO	5.6×10 ¹⁴	0.0	28000	This work
4	N ₂ O+H=N ₂ +OH	1.5×10 ¹⁴	0.0	15000	This work
5	H ₂ +M=H+H+M	2.2×10 ¹²	0.5	92600	
6	O ₂ +M=O+O+M	1.8×10 ¹¹	0.5	95700	
7	H ₂ +O=OH+H	2.2×10 ¹⁴	0.0	13700	
8	H ₂ +OH=H ₂ O+H	5.2×10 ¹³	0.0	6500	
9	O ₂ +H=OH+O	1.2×10 ¹⁷	-0.9	16630	
10	O ₂ +H+M=HO ₂ +M	2.5×10 ¹⁵	0.0	0	
11	HO ₂ +H=OH+OH	2.5×10 ¹⁴	0.0	1900	
12	HO ₂ +OH=H ₂ O+O ₂	5.0×10 ¹³	0.0	1000	
13	OH+OH=H ₂ O+O	5.5×10 ¹³	0.0	7000	
14	OH+H+M=H ₂ O+M	7.5×10 ²³	-2.6	0	

a) Rate constants in the form, $AT^n \exp(-E/RT)$, in cm, mol, cal, and K units. b) The reference for reactions 5—14 is Ref. 20.

calculated from the incident shock speed. Hence, the temperature T calculated from incident shock speeds was employed for the analysis of quenched reactant and product concentrations. The product distribution was determined by analyzing the product concentration on a mass spectrometer. The relationships of $[\text{NO}]$ and $[\text{NO}]/[\text{O}_2]$ vs. T with mixture (A) are shown in Figs. 2(a) and (b), respectively. The ratio $[\text{NO}]/[\text{O}_2]$ is about 2 over the temperature range 1600—2000 K. This also shows $k_2/k_3 \approx 1$. This result is in agreement with those of Gutman *et al.*,⁵⁾ Borisov,⁶⁾ Barton and Dove,⁸⁾ Dean,¹³⁾ and Sulzmann *et al.*¹⁸⁾ The relationships $[\text{NO}]$ and $[\text{NO}]/[\text{O}_2]$ vs. T with mixture (B) are shown in Figs. 3(a) and (b), respectively. In mixture (A), $[\text{NO}]$ and $[\text{NO}]/[\text{O}_2]$ observed at each temperature can be interpreted using the mechanism and rate-constant expressions recommended by Baulch *et al.*²⁶⁾ However, the results calculated with Table 1 are better than those. While, in mixture (B), $[\text{NO}]$ and $[\text{NO}]/[\text{O}_2]$ observed at each temperature are bigger than those obtained by using their mechanism and rate constant expressions as shown in Figs. 3(a) and (b). The findings show that the values of k_2 and k_3 are too small to interpret these. When $k_2 = 7.0 \times 10^{14} \exp(-28 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_3 = 5.6 \times 10^{14} \exp(-28 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ are employed, the computed results are in good agreement with those measured as may be shown in Figs. 3(a) and (b). Our k_2 and k_3 values are about six, four, six and nineteen times those recommended by Baulch *et al.*²⁶⁾ and recently reported Monat *et al.*,¹⁴⁾ Sulzmann *et al.*¹⁸⁾ and Dean *et al.*,¹⁶⁾ respectively, as may be shown in Fig. 4. While our values of k_2 and k_3 are found (Fig. 4) to be similar to and about one half of those reported by Lin and Bauer²⁷⁾ and Henrici and Bauer,⁷⁾ respectively. Henrici and Bauer evaluated the k_3 value from a study with a N₂O-H₂ mixture and reported that the k_2 and k_3 values estimated in the study of N₂O decomposition were too low to account for the rate of formation of NO in the shock-heated reaction of N₂O with H₂. It is found that the values of k_2 and k_3

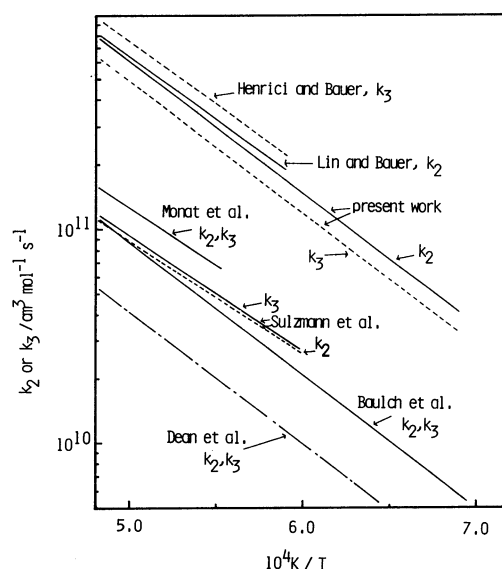


Fig. 4. Comparison of our k_2 or k_3 value with those reported in recent years. ---: Extrapolated value of Dean *et al.*

reported in the study of N₂O decomposition are fairly smaller than those estimated with the N₂O-H₂ mixture.

The values of k_2 and k_3 reported by several workers except for Henrici and Bauer⁷⁾ and Lin and Bauer²⁷⁾ have been estimated from results regarding the N₂O decomposition: The rate constants were obtained from measurements of the N₂O or NO concentration. When values between Dean's value¹⁶⁾ and ours are used as the rate constants of k_2 and k_3 , the product concentrations calculated for the N₂O decomposition scarcely vary as may be seen in Figs. 2(a) and 2(b). The values of k_2 and k_3 between these are found to be insensitive regarding N₂O decomposition. If the values of k_2 and k_3 were estimated from the study of N₂O decomposition, one might always find smaller values for k_2 and k_3 than the real values. Thus, it is difficult to estimate reliable values of k_2 and k_3 from the study of N₂O decomposition. However, in the N₂O-H₂ reaction, the values of k_2 and k_3 are sensitive to

TABLE 2. ELEMENTARY REACTION AND RATE CONSTANT EXPRESSIONS

Reaction	A	n	E
$\text{NO} + \text{OH} = \text{NO}_2 + \text{H}$	1.0×10^{14}	0.0	1200
$\text{NO} + \text{N}_2\text{O} = \text{NO}_2 + \text{N}_2$	2.0×10^{14}	0.0	50000
$\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$	1.0×10^{12}	0.0	45000
$\text{H} + \text{NO} + \text{M} = \text{HNO} + \text{M}$	3.1×10^{15}	0.0	-7000
$\text{OH} + \text{HNO} = \text{NO} + \text{H}_2\text{O}$	8.5×10^{13}	0.0	0
$\text{H} + \text{NO}_2 = \text{NO} + \text{OH}$	5.4×10^{14}	0.0	1740
$\text{N}_2\text{O} + \text{H} = \text{NO} + \text{NH}$	1.0×10^{11}	0.0	30000
$\text{NO}_2 + \text{M} = \text{NO} + \text{O} + \text{M}$	1.0×10^{16}	0.0	65000

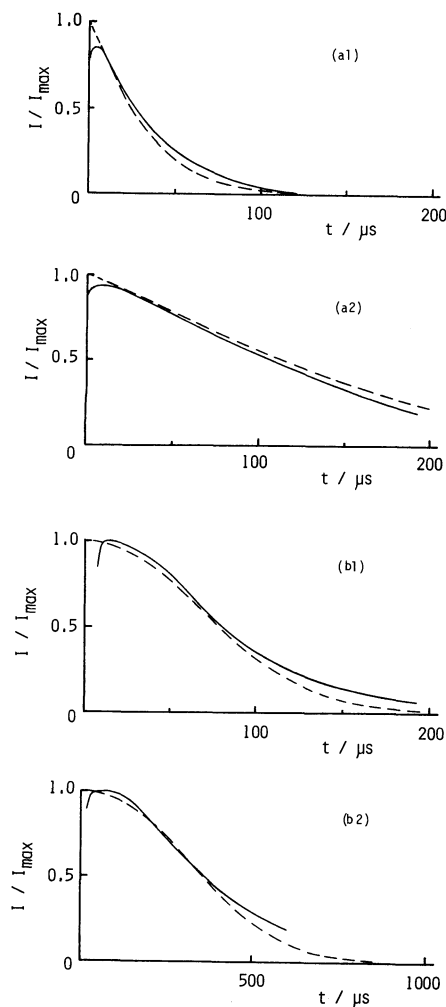


Fig. 5. Comparison of N_2O profiles computed using Table 1 with observed emissions. The broken and solid lines show values computed with Table 1 and observed, respectively.

(a1) Mixture (A), $T_2=2151$ K; (a2) mixture (A), $T_2=1923$ K; (b1) mixture (D), $T_5=1774$ K; (b2) mixture (D), $T_5=1559$ K.

product concentrations. In the $\text{N}_2\text{O}-\text{H}_2$ reaction, therefore, we can estimate reliable values for k_2 and k_3 . Using these values, one can also interpret the results in the N_2O decomposition well, as shown in Fig. 2(a) and 2(b), Fig. 5(a) and Fig. 6(a).

The k_2 and k_3 expressions may be accurate to within

$\pm 20\%$ under our experimental conditions. Systematic errors in the instrumentation and kinetic model may contribute this much again. We therefore, suggest that our k_2 and k_3 expressions are probably accurate to within $\pm 50\%$.

Reaction (4) is also important for the interpretation of the $\text{H}_2-\text{N}_2\text{O}$ reaction. The value of the rate constant k_4 strongly influences the N_2O consumption. When the expression $k_4=1.5 \times 10^{14} \exp(-15 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was employed, the calculated results were in good agreement with the observed ones. This value is about one half of that reported by Fenimore and Jones¹⁾ and is about twice that reported by Dixon-Lewis and Williams²⁸⁾ or by Baulch *et al.*²⁶⁾ The value of k_4 is also considered to be probably accurate to within $\pm 50\%$.

Several reactions for the production and consumption of NO have been reported. They are shown in Table 2. The calculations with mechanism including reactions of Table 2 were carried out and the influence of these reactions on the NO concentration produced was examined. These reactions were found to be unimportant under our experimental conditions.

A comparison of the observed emission profiles with the computed N_2O profiles with mixtures (A) and (D) is shown in Figs. 5(a1)—(b2). In both the N_2O decomposition and the $\text{H}_2-\text{N}_2\text{O}$ reaction, the curves calculated with Table 1 are in good agreement with the observed ones within experimental accuracy. t_{80} , t_{50} , and t_{20} were defined as the elapsed times between the shock arrival and the 80, 50, and 20% consumptions of the maximum $[\text{N}_2\text{O}]$, respectively. τ was also defined as the elapsed time between the shock arrival and the onset of the rapid decrease in the N_2O concentration.²⁹⁾ Plots of τ , t_{80} , and t_{50} or t_{20} vs. $1/T$ for mixtures (A), (B), and (D) are shown in Figs. 6(a)—(c). The calculated τ , t_{80} , t_{50} , and t_{20} are in good agreement with experimental ones.

Henrici and Bauer⁷⁾ have measured the concentration profiles of OH in the reaction of H_2 with N_2O over the temperature range 1700—2600 K and over a total density 0.7×10^{-5} — $1.4 \times 10^{-5} \text{ mol cm}^{-3}$. These are similar to our experimental conditions. Hence, we selected their results in order to check the OH concentration in the modeling. A comparison of calculated $[\text{OH}]_{\text{max}}/P_1$ with $[\text{OH}]_{\text{max}}/P_1$ measured by Henrich and Bauer⁷⁾ is shown in Fig. 7. The values computed using Table 1 explain their results well, as shown in Fig. 7. Hence, the values of k_2 and k_3 , which are about six times those recommended by Baulch *et al.*,²⁶⁾ are considered to be appropriate for an interpretation of the OH concentration in the $\text{N}_2\text{O}-\text{H}_2$ reaction.

Conclusion

N_2O decomposition and $\text{N}_2\text{O}-\text{H}_2$ reactions were studied behind incident and reflected shock waves in

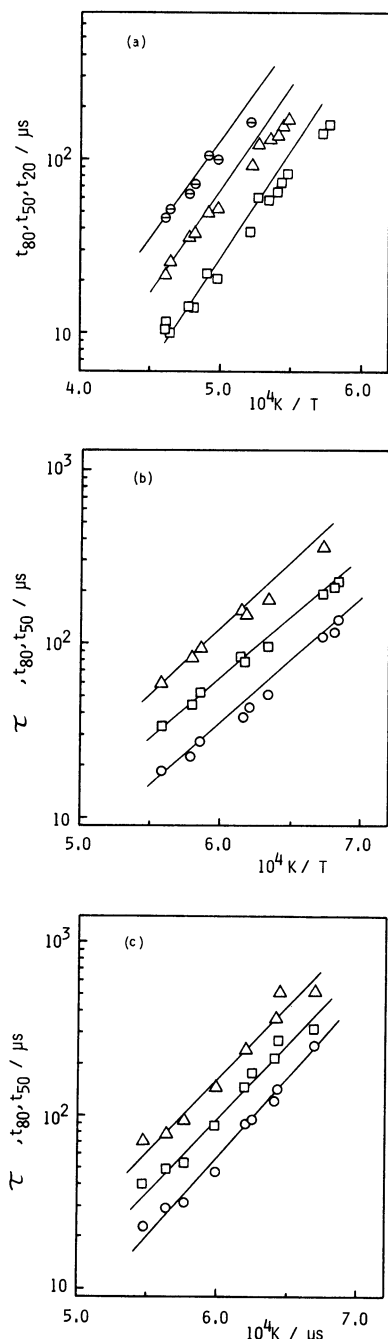


Fig. 6. Comparison of $\log t_{80}$, $\log t_{50}$, and $\log \tau$ or $\log t_{20}$ computed using Table 1 with observed ones. The observed values at t_{20} , t_{50} , t_{80} , and τ are shown with symbols Θ , Δ , $\square$, and $\circ$, respectively. (a) results for mixture (A) behind incident shock waves; (b) results for mixture (B) behind incident shock waves; (c) results for mixture (D) behind reflected shock waves.

the temperature range 1450–2200 K with both single-pulse and time-resolve techniques. Our results support the value reported by Roth and Just¹⁵⁾ as the k_1 value. The rate constant expressions $k_2 = 7.0 \times 10^{14} \exp(-28 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_3 = 5.6 \times 10^{14} \exp(-28 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_4 = 1.5 \times 10^{14} \exp(-15 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reactions $\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$,

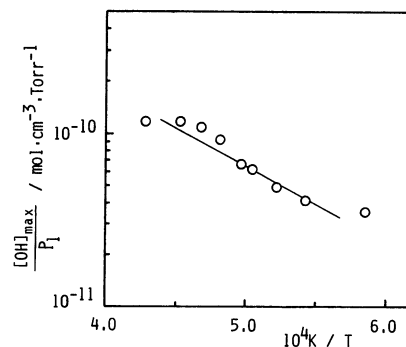


Fig. 7. Comparison of $[\text{OH}]_{\text{max}}/P_1$ calculated using Table 1 with $[\text{OH}]_{\text{max}}/P_1$ measured by Henrich and Bauer. $\circ$: Observed by Henrich and Bauer; —: computed with Table 1.

$\text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO}$ and $\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}$ were derived, respectively.

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