

**Resonance absorption measurements of atom concentrations in reacting gas mixtures. VIII. Rate constants for  $\text{O}+\text{H}_2\rightarrow\text{OH}+\text{H}$  and  $\text{O}+\text{D}_2\rightarrow\text{OD}+\text{D}$  from measurements of O atoms in oxidation of  $\text{H}_2$  and  $\text{D}_2$  by  $\text{N}_2\text{O}$**

Krishna M. Pamidimukkala and Gordon B. Skinner

Citation: *The Journal of Chemical Physics* **76**, 311 (1982); doi: 10.1063/1.442779

View online: <http://dx.doi.org/10.1063/1.442779>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/76/1?ver=pdfcov>

Published by the AIP Publishing

---

**Articles you may be interested in**

Rate constants for the reactions  $\text{H}+\text{O}_2\rightarrow\text{OH}+\text{O}$  and  $\text{D}+\text{O}_2\rightarrow\text{OD}+\text{O}$  over the temperature range 1085–2278 K by the laser photolysis–shock tube technique

*J. Chem. Phys.* **95**, 262 (1991); 10.1063/1.461483

Shock tube studies of rate constant for  $\text{H}+\text{O}_2\rightarrow\text{O}+\text{OH}$  by measuring O and OH absorption in rich  $\text{H}_2\text{O}_2$  mixtures

*AIP Conf. Proc.* **208**, 456 (1990); 10.1063/1.39374

Resonance absorption measurements of atom concentrations in reacting gas mixtures. VI. Shapes of the vacuum ultraviolet oxygen (3 S–3 P) resonance triplet from microwave sources and empirical calibration in a shock tube

*J. Chem. Phys.* **75**, 1116 (1981); 10.1063/1.442184

Resonance absorption measurements of atom concentrations in reacting gas mixtures. II. Calibration of microwave sources over a wide temperature range

*J. Chem. Phys.* **70**, 5614 (1979); 10.1063/1.437438

Resonance absorption measurements of atom concentrations in reacting gas mixtures. I. Shapes of H and D Lyman $\alpha$  lines from microwave sources

*J. Chem. Phys.* **70**, 5607 (1979); 10.1063/1.437437

---



# Resonance absorption measurements of atom concentrations in reacting gas mixtures. VIII. Rate constants for $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ and $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ from measurements of O atoms in oxidation of $\text{H}_2$ and $\text{D}_2$ by $\text{N}_2\text{O}$

Krishna M. Pamidimukkala and Gordon B. Skinner

Department of Chemistry, Wright State University, Dayton, Ohio 45435  
(Received 2 July 1981; accepted 8 September 1981)

Resonance absorption spectroscopy has been used to measure O atom concentration in shock treated  $\text{H}_2\text{-N}_2\text{O-Ar}$  and  $\text{D}_2\text{-N}_2\text{O-Ar}$  mixtures. Four compositions were studied over the temperature range 1919–2781 K for the  $\text{H}_2$ -containing mixtures and 2097–2481 K for those containing  $\text{D}_2$ . Only a few elementary reactions exerted any appreciable influence on the total oxidation process so that the rate coefficients of those reactions could be deduced. Primary sensitivity under all conditions was to the rate coefficients of the reactions directly responsible for the formation and removal of oxygen atoms. We find  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ ,  $k = 2.3E14 \exp(-57.5 \text{ kJ/RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ ,  $k = 1.6E14 \exp(-59.6 \text{ kJ/RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Under our conditions the reaction of H or D atoms with  $\text{N}_2\text{O}$  was insignificant, in contrast to the observations of Dean at higher concentrations. The isotope effect for this reaction is close to 1.6 throughout our temperature range.

## INTRODUCTION

During the past few years, several papers, such as those of Appel and Appleton,<sup>1</sup> Dean,<sup>2</sup> and Roth and Just,<sup>3</sup> have shown the utility of  $\text{N}_2\text{O}$  dissociation as a source of O atoms in shock tube experiments. At moderate concentration<sup>2</sup> the overall process involves several elementary steps:



At lower concentrations (<100 ppm) and moderate total pressures (<5 atm), it can be shown by numerical computation that Reactions (2) to (4) are insignificant.

We have recently<sup>4</sup> used the dissociation of  $\text{N}_2\text{O}$  as a stoichiometric source of O atoms for calibration of an absorption spectrometric system for measuring atom concentrations, and in the process also obtained new data on rate constants for Reaction (1) which turned out to be in good agreement with data obtained using another shock tube method by Olschewski, Troe, and Wagner<sup>5</sup> and adopted by Baulch *et al.*<sup>6</sup> in their review.

When  $\text{H}_2$  is added to the reaction mixture, the reaction



occurs, leading to a reduction in the concentration of O atoms. While other reactions also participate, as described below, the largest part of the change in O atom concentration is due to Reaction (5), so that our experiments lead directly to rate coefficients for that reaction.

## EXPERIMENTAL

All the data were obtained behind reflected shock waves in a 7.6 cm diam stainless steel shock tube.<sup>7</sup>

The atomic resonance absorption spectroscopic technique was used for measuring O atom concentrations. The source of resonance radiation was a microwave discharge flow lamp (source B of Ref. 7) operated at 40 W power. The gas mixture, 0.1%  $\text{O}_2$  in He, was used at a constant lamp pressure of 2.5 Torr. A 0.3 m, McPherson model 218 scanning vacuum monochromator mounted opposite the discharge lamp was used to isolate the oxygen components. All experiments were performed with 1 mm slits centered at  $1305 \text{ \AA}$  so that all three components were passed by the monochromator. The lamp was calibrated previously<sup>4</sup> for analysis of oxygen atoms by producing known concentrations of O atoms and relating these to the fraction of light absorbed, and also by measuring profiles of the spectral lines.

Gas mixtures were made from Airco Research Grade argon having total hydrocarbon, hydrogen and oxygen impurities less than 2 ppm, Airco  $\text{N}_2\text{O}$  (99.995%) and Matheson Ultra High Purity hydrogen (99.999%) containing less than 1 ppm hydrocarbons. Deuterium was also from Matheson, 99.5% pure. The argon was further purified by allowing it to pass through a trap containing molecular sieves of type 4A and 5A cooled to dry ice temperature. These sieves were expected to remove trace amounts of hydrocarbon and other impurities. The gas samples were prepared by dilution of more concentrated mixtures. Test samples were introduced into the shock tube near the end plate so as to push impurities, if present, down the shock tube to the diaphragm so as to obtain pure gases as much as possible near the field of view of the detector.

In each experiment, the intensity of the lamp and reflected shock pressure were recorded on a storage oscilloscope as a function of time, then transferred to a strip chart recorder. Reflected shock pressures were constant within a few per cent during the test time. Temperatures, calculated from incident shock speeds, were expected to be within  $\pm 20 \text{ K}$ .

TABLE I. Summary of experimental results.

Temperature K	Pressure atm	Test Time s × 10 <sup>3</sup>	Maximum [O] × 10 <sup>11</sup> mol cc <sup>-1</sup>		t <sup>a</sup> max s × 10 <sup>3</sup>	[O] × 10 <sup>11</sup> toward end <sup>b</sup> mol cc <sup>-1</sup>		t <sub>e</sub> <sup>b</sup>	Ratio <sup>c</sup>
			Observed	Calculation		Observed	Calculation		
Mixture 1. 100 ppm H <sub>2</sub> , 20 ppm N <sub>2</sub> O									
1919	1.46	2	2.9	2.7	0.60	2.2	1.9	1.2	1.08
2014	1.61	2	4.4	4.1	0.30	1.3	1.3	1.4	0.99
2078	1.55	2	5.2	4.8	0.20	1.1	1.3	1.2	1.00
2079	1.58	2	4.8	4.8	0.20	1.4	1.3	1.2	1.07
2146	1.58	2	5.6	5.6	0.16	0.9	1.4	1.0	0.85
2157	1.61	1	5.6	5.8	0.16	2.3	2.4	0.6	0.91
2249	1.28	1	6.0	5.6	0.12	1.7	1.8	0.6	0.99
2260	1.54	2	7.1	6.8	0.12	1.8	1.8	0.6	0.98
2349	1.40	1	7.0	7.0	0.08	1.5	1.5	0.6	0.91
2372	1.47	1	8.0	7.5	0.08	0.8	1.4	0.6	0.94
2419	1.48	1	8.4	7.8	0.08	0.7	1.4	0.6	0.85
2638	1.75	1	10.0	10.4	0.04	1.4	2.0	0.3	0.83
2781	1.27	1	6.0	7.9	0.04	1.9	1.7	0.3	1.05
Mixture 2. 100 ppm H <sub>2</sub> , 30 ppm N <sub>2</sub> O									
2070	1.47	2	7.4	6.7	0.20	2.5	2.8	1.2	0.98
2138	1.33	1	9.2	7.1	0.20	3.7	3.3	0.8	1.18
2147	1.45	2	9.2	7.7	0.20	3.4	3.4	0.8	1.10
2198	1.35	1	8.8	8.1	0.16	3.8	3.3	0.7	1.20
2208	1.38	1	7.8	8.3	0.12	3.9	3.6	0.6	0.87
2327	1.22	2	8.2	8.8	0.12	4.1	2.9	0.6	1.14
2494	1.49	1	11.0	10.5	0.10	3.4	3.2	0.5	0.80
Average ratio for mixtures 1 and 2									0.99
Mixture 3. 100 ppm D <sub>2</sub> , 20 ppm N <sub>2</sub> O									
2097	1.71	2	5.7	7.0	0.24	1.3	1.3	1.2	0.82
2196	1.67	2	8.8	8.0	0.20	0.7	0.8	1.2	0.96
2228	1.51	2	8.1	7.6	0.20	0.8	1.0	1.1	1.03
2238	1.59	2	9.0	8.0	0.20	0.9	1.1	1.0	0.92
2292	1.51	2	9.0	8.4	0.14	0.7	0.9	1.0	1.03
2315	1.49	1	9.2	8.6	0.14	0.2	0.2	0.6	1.07
2316	1.48	2	8.3	8.3	0.14	1.7	2.2	0.6	0.89
2372	1.62	2	10.0	9.7	0.10	1.9	1.9	0.6	0.97
2383	1.44	1	8.2	8.5	0.10	2.3	1.9	0.6	0.99
2455	1.46	1	12.0	9.3	0.08	1.5	1.6	0.6	1.07
2480	1.43	1	10.0	9.3	0.06	1.8	2.0	0.5	0.96
2481	1.37	1	9.1	8.9	0.06	2.1	2.1	0.5	1.00
Mixture 4. 100 ppm D <sub>2</sub> , 10 ppm N <sub>2</sub> O									
2032	1.67	2	3.5	3.1	0.24	0.8	0.6	1.2	1.15
2061	1.71	2	3.2	3.3	0.24	0.6	0.5	1.2	1.10
2070	1.68	2	3.6	3.3	0.20	0.7	0.5	1.2	1.26
2177	1.63	1	3.6	3.9	0.18	1.2	1.2	0.6	0.92
2208	1.59	1	3.7	3.8	0.12	1.3	1.5	0.5	0.84
2249	1.59	1	5.3	4.2	0.12	1.9	1.3	0.5	1.21
2305	1.60	1	4.5	4.4	0.12	1.1	1.1	0.5	0.96
2315	1.43	1	4.6	4.1	0.12	1.2	1.2	0.5	1.06
2339	1.30	1	5.4	3.9	0.10	2.3	1.6	0.4	1.38
2373	1.38	1	5.9	4.3	0.10	1.3	0.9	0.5	1.38
2419	1.22	1	5.8	4.2	0.08	1.4	1.3	0.4	1.22
2610	1.44	1	8.2	4.4	0.06	0.9	0.8	0.4	1.44
Average ratio for Mixtures 3 and 4									1.07

<sup>a</sup>Time to reach [O] max.<sup>b</sup>[O] and time when 65% or more of the reaction was assumed to be complete.<sup>c</sup>Ratio is the average of ratios, [O] observed/[O] calculation, calculated over 16 places throughout the [O] vs  $t$  graph.

## RESULTS

Reaction mixtures of  $H_2-N_2O-Ar$  and  $D_2-N_2O-Ar$  were shock heated to different temperatures and the O atom concentrations were measured as a function of time. The test time varied from 1 to 2 ms depending on

temperature. The details of individual experiments are given in Table I for  $H_2/N_2O$  and  $D_2/N_2O$  mixtures. To illustrate a typical experiment, the transmitted intensity as attenuated by oxygen atoms in the shock tube for 100 ppm  $H_2$ , 20 ppm  $N_2O$  at 2157 K is shown in Fig. 1. Since the pressure transducer and the optical window are at

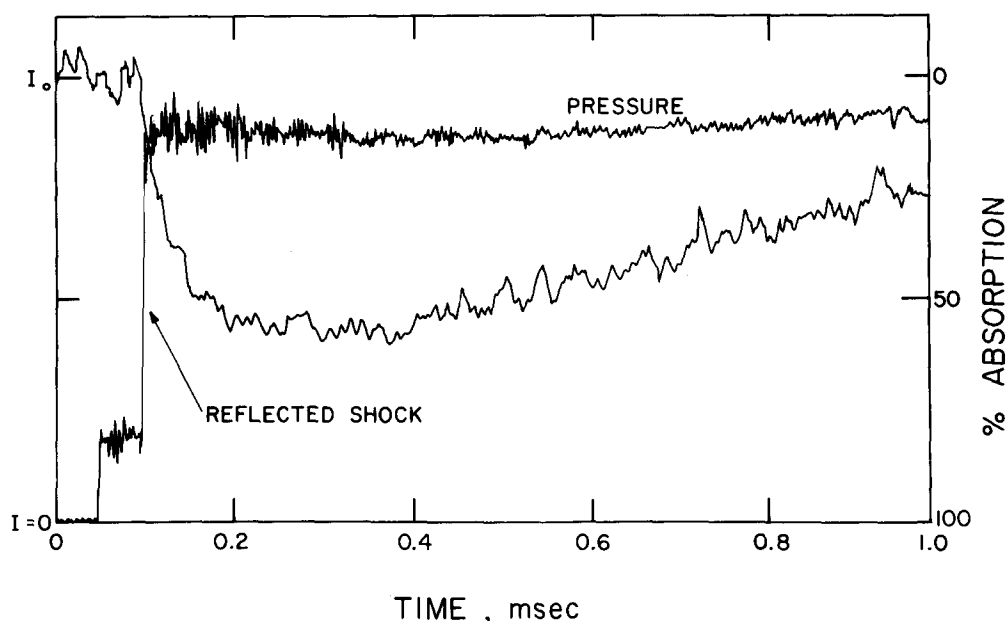


FIG. 1. Transmitted intensity of the lamp as attenuated by O atoms at 2157 K, 1.61 atm for 100 ppm  $\text{H}_2$ , 20 ppm  $\text{N}_2\text{O}$  in Ar mixture.

the same position along the tube, time is taken to be zero when the sudden pressure rise due to the reflected shock wave occurs. From Fig. 1 it can be seen that the light intensity begins to fall at the same time, due to formation of O atoms. The concentration of O atoms obtained from the oscillogram was plotted against time and is

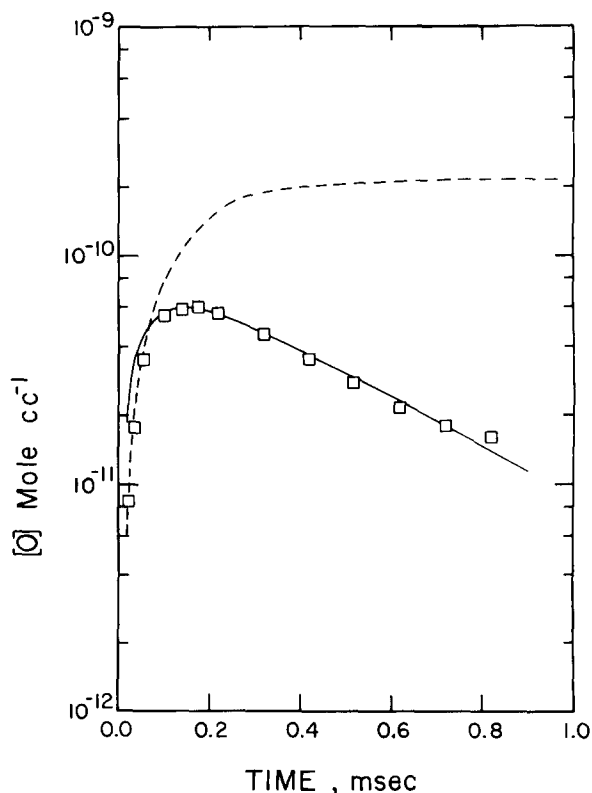


FIG. 2. A representative plot of [O] vs time. Time is taken as zero when the reflected shock first enters the field of view of the detector. □, observed [O] for mixture 1 at 2157 K; ---, observed [O] at 2157 K, 1.29 atm for 20 ppm  $\text{N}_2\text{O}$  in Ar with no added  $\text{H}_2$ ; —, [O] calculated using rate constants of Tables II and III.

shown in Fig. 2. After the passage of the reflected shock [O] rises, then reaches a maximum after a period of time before it decays gradually. At higher temperatures both the rise and the decay were more rapid. As one would expect, the maximum concentration of O atoms and the time to reach the maximum depend on both composition and temperature. All experimental observations were characterized in terms of  $[\text{O}]_{\text{max}}$  and  $t_{\text{max}}$ . These are listed in Table I for each temperature. In low temperature experiments, the concentration of O atoms was observed to increase slowly, going through a broad maximum before it decayed gradually. The [O] vs time profiles in all experiments reported here display essentially the same features.

A kinetic mechanism consisting of Reactions (1)–(5) and the elementary reactions listed below adequately describes the post-shock chemistry of the oxidation of  $\text{H}_2$  and  $\text{D}_2$  by  $\text{N}_2\text{O}$  under our experimental conditions:



TABLE II. Rate coefficients<sup>a</sup> used for numerical computations for dissociation of  $\text{N}_2\text{O}$ .

Reaction	A	E, kT	Reference
1. $\text{N}_2\text{O} + \text{Ar} \rightarrow \text{N}_2 + \text{O} + \text{Ar}$	$5.00 \times 10^{14}$	57.6	5, 6
2. $\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$	$1.00 \times 10^{14}$	28.0	6
3. $\text{N}_2\text{O} + \text{O} \rightarrow 2\text{NO}$	$1.00 \times 10^{14}$	28.0	6
4. $\text{O} + \text{O} + \text{Ar} \rightarrow \text{O}_2 + \text{Ar}$	$1.90 \times 10^{13}$	-1.8	6

<sup>a</sup>Expressed in the Arrhenius form  $k = A \exp(-E/RT)$  where A is in units of  $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$  or  $\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$  and E in  $\text{kJ mol}^{-1}$ .

TABLE III. Rate coefficients<sup>a</sup> used for calculating [O] in the oxidation of  $H_2$  by  $N_2O$ .

Reaction	A	E, kJ	Reference
Reactions 1-4 (Table II)			5, 6
5. $O + H_2 \rightarrow OH + H$	$2.3E14$	57.5	This work
6. $H + N_2O \rightarrow N_2 + OH$	$1.8E15$	113.0	6, 8
7. $OH + H_2 \rightarrow H_2O + H$	$5.2E13$	27.2	9
8. $H + O_2 \rightarrow OH + O$	$1.2E14$	67.4	10
9. $OH + OH \rightarrow H_2O + O$	$6.3E12$	4.6	11
10. $H + O_2 + Ar \rightarrow HO_2 + Ar$	$4.4E14$	-4.2	10
11. $H + H + Ar \rightarrow H_2 + Ar$	$2.4E14$	-9.6	b

<sup>a</sup>Expressed in Arrhenius form  $k = A \exp(-E/RT)$  where A is in units of  $cm^3 mol^{-1} s^{-1}$  or  $cm^6 mol^{-2} s^{-1}$  and E in  $kJ mol^{-1}$ .

<sup>b</sup>Based on Ref. 11 but converted to Arrhenius form for use in our temperature range.

Rate coefficients for reactions other than Reaction (5) were taken from several sources as indicated in Tables II-IV. We have carried out numerical integration of all 11 forward and reverse reactions and calculated [O] as a function of time over our entire test period. These calculations revealed that only a few of these reactions exerted any appreciable influence on the rise and decay of O atoms. Primary sensitivity under all conditions was to the rate coefficients of elementary Reactions (1) and (5), which are directly responsible for the formation and removal of oxygen atoms in the ignition stage, although Reactions (8) and (-5), the reverse of Reaction (5), become of some importance in reproducing the measured values of [O] toward the end of the reaction. The observed and calculated values of [O] toward the end of the reaction and the corresponding times are listed in Table I.

The rate coefficients of Reactions (1) and (5) were adjusted so as to obtain the best fit of observed [O]. Results of these calculations are given in Table I as "Ratio." This is the average of the ratios  $[O]_{obsd}/[O]_{cal}$  taken over 16 points along the curve.

## DISCUSSION

Numerical matching of the data in Table I established a direct sensitivity of [O] to a few rate coefficients while it is comparatively uninfluenced by the others. To il-

TABLE IV. Rate coefficients<sup>a</sup> used for calculating [O] in the oxidation of  $D_2$  by  $N_2O$ .

Reaction	A	E, kJ	Reference
Reactions 1-4 (Table II)			5, 6
5D $O + D_2 \rightarrow OD + D$	$1.6E14$	59.6	This work
6D $D + N_2O \rightarrow N_2 + OD$	$7.6E13$	63.2	6
7D $OD + D_2 \rightarrow D_2O + D$	$4.7E13$	29.3	10
8D $D + O_2 \rightarrow OD + O$	$5.8E14$	62.8	10
9D $OD + OD \rightarrow D_2O + O$	$3.9E12$	4.6	b
10D $D + O_2 + Ar \rightarrow DO_2 + Ar$	$2.2E14$	-4.2	10
11D $D + D + Ar \rightarrow D_2 + Ar$	$1.5E14$	-9.6	b

<sup>a</sup>Expressed in Arrhenius form  $k = A \exp(-E/RT)$  where A is in units of  $cm^3 mol^{-1} s^{-1}$  or  $cm^6 mol^{-2} s^{-1}$  and E in  $kJ mol^{-1}$ .

<sup>b</sup>Using kinetic isotope effect of 1.6 over entire temperature range. See Ref. 11.

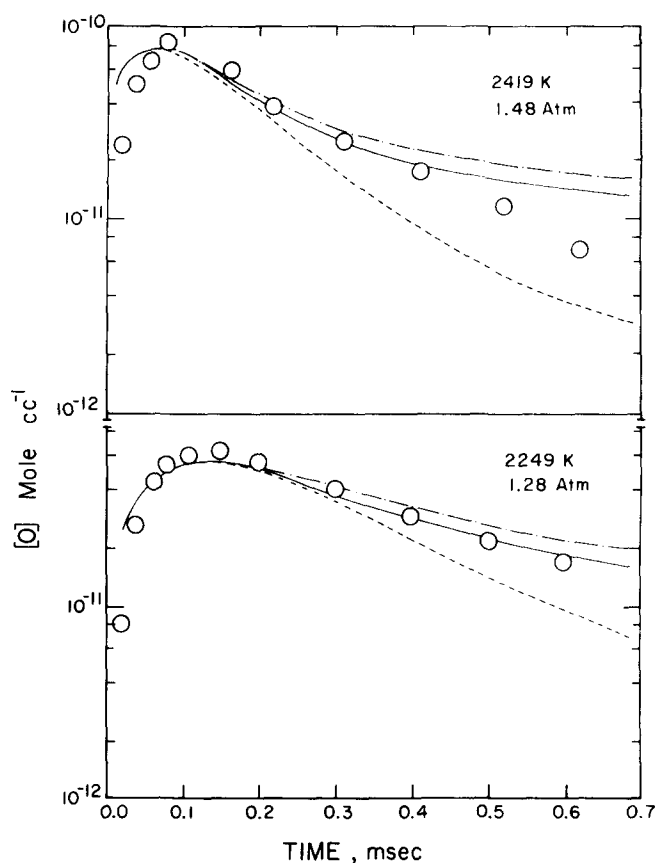


FIG. 3. Influence of  $k_{-5}$  and  $k_{-8}$  on formation and removal of O atoms in the oxidation of  $H_2$  by  $N_2O$ . Graphs of O atom concentrations vs time. —, numerical integration including all reactions; ---, omitting  $k_{-5}$ ; - · -, omitting  $k_{-8}$ ; O, observed [O].

lustrate how this sensitivity arises in the reaction mechanism for the conditions of the present experiments, we examine the steady state kinetics governing O atom concentrations. Initially, O atoms are produced by the dissociation of  $N_2O$  and are also consumed, but more slowly, primarily by Reaction (5). Since, at first, the O atoms are formed at a faster rate than they are consumed, we observed a buildup of O atoms at the beginning of the reaction. As the  $N_2O$  concentration decreases due to dissociation, the rate of formation of O atoms decreases. Since, in all of our experiments, the concentration of hydrogen exceeded that of  $N_2O$ , Reaction (5) continues to remove O atoms at a substantial rate, so that the O atom concentration levels off and finally decreases.

Dean,<sup>2</sup> working at higher concentrations than ours,

TABLE V. Equilibrium constants.<sup>a</sup>

Reaction	C	D, kJ	Reference
5 $O + H_2 \rightleftharpoons OH + H$	2.31	8.7	11
8 $H + O_2 \rightleftharpoons OH + O$	11.39	65.4	11
5D $O + D_2 \rightleftharpoons OD + D$	2.39	9.65	12, 13, 14
8D $D + O_2 \rightleftharpoons OD + O$	10.42	61.2	12, 13, 14

<sup>a</sup>Equilibrium constants expressed in the form  $k_{eq} = C \exp(-D/RT)$  where C is dimensionless and D has units of  $kJ mol^{-1}$ .

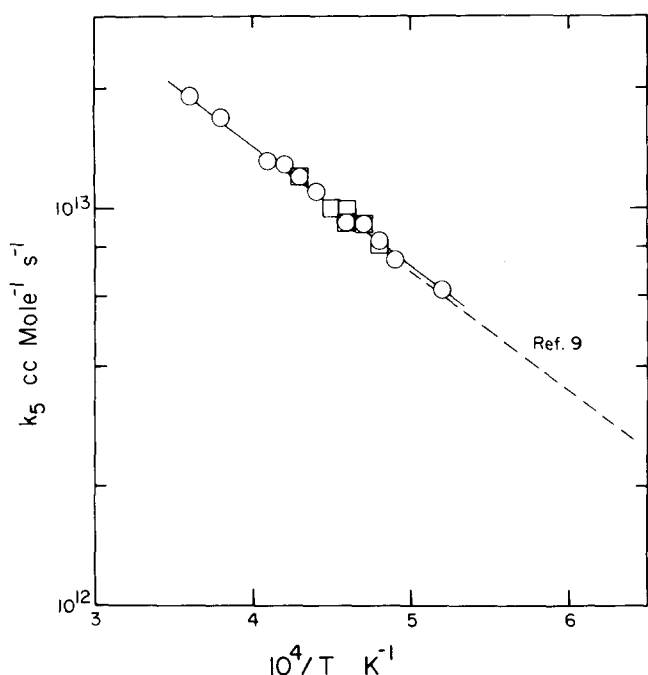
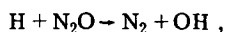


FIG. 4. Plot of second order rate constant,  $k_5$ , against  $10^4/T$ .  $\circ$ , mixture 1;  $\square$ , mixture 2; —, plot obtained using the equation of Table III; ---, plot obtained using the equation of Ref. 9.

found that  $\text{N}_2\text{O}$  dissociates more rapidly in the presence of  $\text{H}_2$  than otherwise. Our measurements show that at our low concentrations the initial rate of formation of O atoms is not affected by the presence of the hydrogen, and our calculations indicated that Reaction (6)



which presumably causes  $\text{N}_2\text{O}$  to disappear faster in the presence of  $\text{H}_2$ , is not significant here. The rate coefficients recommended by Baulch *et al.*,<sup>6</sup> and subsequently confirmed by us<sup>4</sup> for  $\text{N}_2\text{O}$  dissociation were used in our computations. The kinetic parameters for this reaction are listed in Table II.

From a sensitivity analysis, it was found that the only significant reactions, in decreasing order of importance, are (1), (5), (-5), (8), and (-8), the remaining reactions being substantially less important. Accordingly, one could write

$$\frac{d[\text{O}]}{dt} = k_1[\text{N}_2\text{O}][\text{Ar}] - k_5[\text{O}][\text{H}_2] + k_{-5}[\text{OH}][\text{H}] + k_8[\text{H}][\text{O}_2] - k_{-8}[\text{OH}][\text{O}] + \dots \quad (\text{I})$$

Reactions (1) and (5) are substantially more important than the next three until after the maximum in  $[\text{O}]$ , this maximum concentration being reached as a result of competition between these two reactions. Figure 3 shows the effects of omitting two of the secondary Reactions (-5) and (-8) from the total reaction scheme. Since  $k_1$  is known from the earlier work of ourselves and others, as is  $k_8$ , while the reverse rate constants are

related to the forward ones by well-known equilibrium constants (listed in Table V), it was possible to deduce  $k_5$  from the experimental results with little ambiguity. The rate coefficients are

$$k_5 = 2.3 \times 10^{14} \exp(-57.5 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

$$k_{5D} = 1.6 \times 10^{14} \exp(-59.6 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The kinetic isotope effect,  $k_5/k_{5D}$ , is 1.6 in the range 2000–2500 K. The rate coefficient obtained in the present study for the reaction  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$  is in excellent agreement with the value of Schott, Getzinger, and Seitz<sup>9</sup> and is shown in Fig. 4.

## CONCLUSIONS

These experiments on oxidation of  $\text{H}_2$  and  $\text{D}_2$  by  $\text{N}_2\text{O}$  provided a means of obtaining accurately the rate coefficients of the reactions  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$  and  $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$  at higher temperatures. Primarily, the  $[\text{O}]$  observed depend upon the reactions directly involved in formation and removal of O atoms although other reactions contribute slightly to the total O atom concentrations.

## ACKNOWLEDGMENT

This research was supported in part by the United States Department of Energy under contract DE-AC02-76ERO2944.

<sup>1</sup>D. Appel and J. P. Appleton, 15th (Int.) Symp. on Combustion (1974), p. 701.

<sup>2</sup>A. M. Dean, Int. J. Chem. Kinetics **8**, 459 (1976).

<sup>3</sup>P. Roth and T. Just, Ber. Bunsenges. Phys. Chem. **81**, 572 (1977).

<sup>4</sup>K. M. Pamidimukkala, A. Lifshitz, G. B. Skinner, and D. R. Wood, J. Chem. Phys. **75**, 1116 (1981).

<sup>5</sup>H. A. Olschewski, J. Troe, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **70**, 450 (1966).

<sup>6</sup>D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions* (Butterworths, London, 1972), Vol. 2.

<sup>7</sup>C.-C. Chiang, A. Lifshitz, G. B. Skinner, and D. R. Wood, J. Chem. Phys. **70**, 5614 (1979).

<sup>8</sup>A. M. Dean, D. C. Steiner, and E. E. Wang, Combust. Flame. **32**, 73 (1978).

<sup>9</sup>G. L. Schott, R. W. Getzinger, and W. A. Weitz, Int. J. Chem. Kinet. **6**, 921 (1974).

<sup>10</sup>K. M. Pamidimukkala and G. B. Skinner, Proc. 13th (Int.) Symp. on Shock Tubes and Waves, Niagara Falls, New York, July (1981) (to be published).

<sup>11</sup>D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions* (Butterworths, London, 1972), Vol. 1.

<sup>12</sup>D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed., Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. **37** (U.S. GPO, Washington, D.C., 1971).

<sup>13</sup>D. D. Wagman, W. M. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Natl. Bur. Stand. U.S. Tech. Note **270-3** (U.S. GPO, Washington, D.C., 1968).

<sup>14</sup>K. K. Kelley, U. S. Bur. Mines Bull. **584** (U. S. GPO, Washington, D.C., 1960).